Universitat de Girona

SINGLE AND MULTIPLE ADDITION TO C60. A COMPUTATIONAL CHEMISTRY STUDY

Montserrat CASES AMAT

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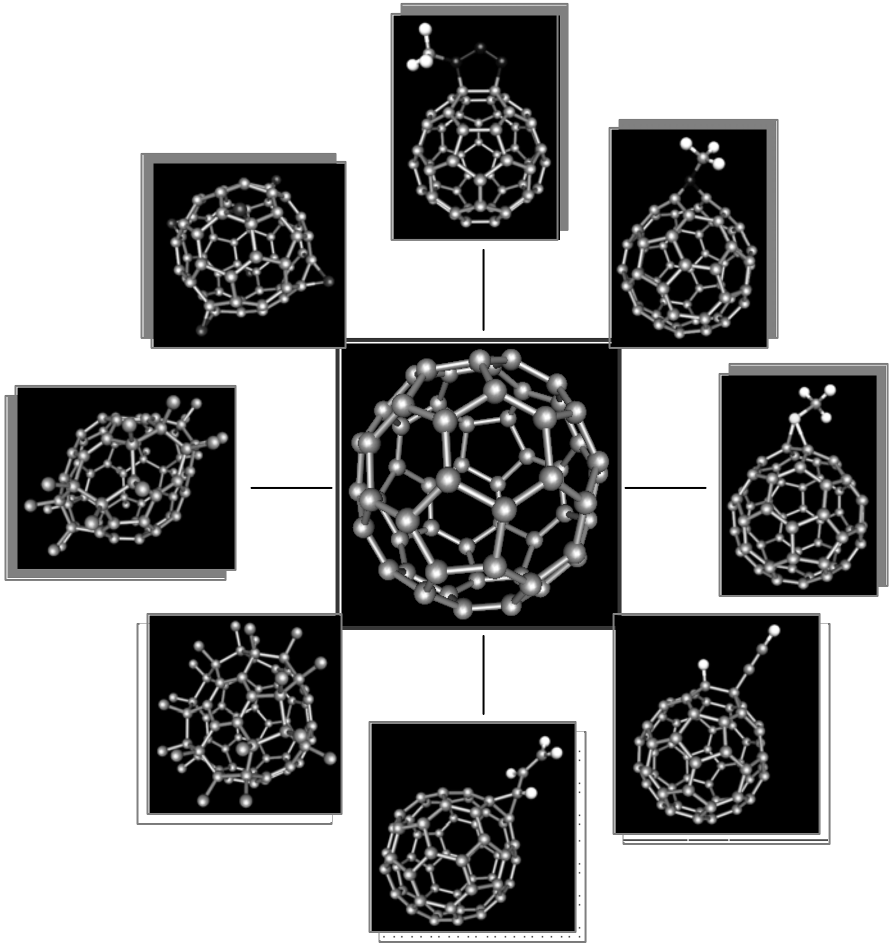

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SINGLE AND MULTIPLE ADDITION TO C_{60} . A COMPUTATIONAL CHEMISTRY STUDY

M. Cases

2003

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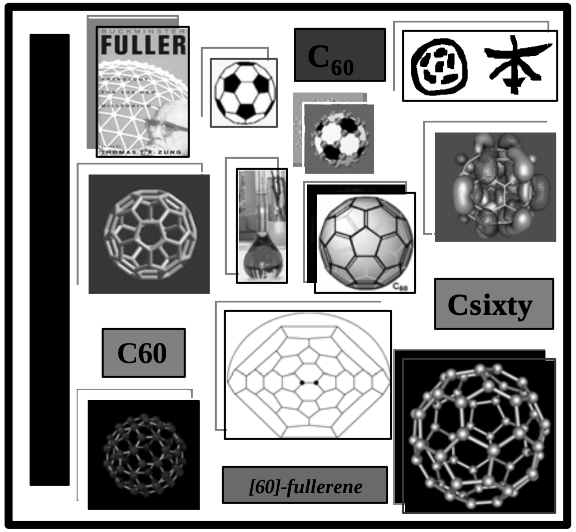

Modelatge Molecular i Metodologia Mecanoquàntica

Institut de Química Computacional

Departament de Química

Universitat de Girona

2003

Institut de Química Computacional
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Miquel Solà i Puig	Miquel Duran i Portas
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Catedràtic de la UdG	Catedràtic de la UdG
	Director Departament de Química

Girona, 7 de juliol de 2003

A l´Elvira, la meva mare,
amb el record del seu dolç somriure
visc el dia a dia…

A en Josep, el meu pare,
i a l'Àngels, la meva germaneta,
per donar sentit a la meva vida,
recolzar-me en tot moment,
per ser com sou, uns bons lluitadors…

A la Quimeta, la meva àvia,
perquè amb poc em dones molt…

A tota la tropa dels "carboners",
pels que erem, som i serem…

… us estimo molt a tots

SINGLE AND MULTIPLE ADDITION TO C_{60}
A COMPUTATIONAL CHEMISTRY STUDY

Montserrat Cases Amat

Single and Multiple Addition to C_{60}.

A Computational Chemistry Study.

This present Thesis project memory has been organized with the following order of sections with the purpose to firstly introduce the reader to the *chemistry of fullerenes* with a brief overview of C_{60} reactivity, especially extended in case of the derivatives of C_{60} molecule under study (azafullerenes, methanofullerenes, fullerene oxides, substituted hydrofullerenes and fluorofullerenes) (*Sec. 1*), and then show which are the *computational chemistry* concepts actually used to carry out the global project, how they are defined and which kind of results and conclusions can be obtained from their use (*Sec. 2*). Secondly, the objectives (*Sec. 3*) proposed for each study included in the thesis project are told to give a general idea of the work planned and then follows the discussion of the main results obtained for each of C_{60} derivatives studied (*Sec. 4*), which are deeply explained in the publications section (*Sec. 5*). Finally, the conclusions and a global evaluation of all results for each study are given (*Sec. 6)* and the references list *(Sec. 7)*. An annex section (*Sec. 8*) is also present where are listed other publications which have been carried out in parallel with this thesis project as the list of contributions to international and non-international conferences or symposia.

C O N T E N T S

1. FULLERENES CHEMISTRY

The discovery of fullerenes by Kroto and co-workers[1] initiated a new era in carbon chemistry. A large number of stable carbon structures were synthesized, using either variations of the original method (laser evaporation of graphite[1]), or the arc discharge technique of Krätschmer and Huffman[2]. Most of the processes in use today produce a soot consisting of a mixture of amorphous carbon and a variety of "interesting" materials in the first stage. The typical end products include the reactive C_{36},[3] a range of stable fullerenes (C_{60}, C_{70} and up),[4] multilayered carbon onions,[5] single[6] and multiwalled[7] nanotubes, and nanotubes bundles.

The fullerenes form a new class of carbon,[8] they are formed entirely of carbon in the sp^2-hybridized state, and consisting the third form of carbon (after diamond and graphite). Fullerenes are discrete molecules, they seem to be nets of carbon atoms as in case of diamond and graphite, but they include pentagons in their structures a part from the hexagons, and its presence lead to the characteristic curvature and sphericity of fullerenes. Based on a theorem of the mathematician Leonard Euler, one can show that a spherical surface entirely built up from pentagons and hexagons must have exactly 12 pentagons. Depending on the number of hexagons, molecules of different sizes are obtained and depending on the distribution of these 12 pentagons, one can talk about the "perfect fullerenes", which satisfy two rules: a) the isolated pentagon rule (IPR) and b) the hollow pentagon rule (HPR). The IRP rule means that there are no adjacent pentagon, and HPR means that all the pentagons are "holes", i.e. that every pentagon could have only external double bonds. The first 5/6 fullerene satisfying IPR is C_{60}, and it also satisfies HPR. The IPR is well known as the stability criterion: all fullerenes of lower order (less than C_{60}) are unstable, because they do not satisfy IPR. On the other hand, C_{70} satisfies IPR, but can not satisfy HPR.

C_{60} and C_{70} are the most accessible members of the family of closed-cage molecules known as fullerenes, they are a new family of compounds which have attracted considerable attention in many scientific disciplines. Since these molecular allotropes become available in macroscopic quantities in 1990[2] a large number of chemical transformations have been developed allowing for the synthesis of many different types of derivatives. The fullerenes are now established as versatile building blocks in organic chemistry introducing new chemical, electronic and photophysical properties. The interest in these molecules can be ganged from all the papers that have already appeared. Most of these have described chemical physics aspects of the fullerenes, but the proportion devoted to their chemistry is growing and likely to become dominant. As the cages consist entirely of sp^2-hybridized carbon, which have electron-withdrawing –I inductive effects[9] the fullerenes are strongly electron-attracting. This affects their chemical behaviour, for example they react readily with nucleophiles. In summary, the molecules appear to undergo all the reactions associated with poorly-conjugated and electron-deficient alkenes.

1.1. C_{60} molecule: properties and reactivity

The vast majority of research on the fullerene-based solids has been done on C_{60}. This allotropic carbon form can be purified with a good yield, and it is readily available on the market at a reasonable price. It is stable at temperatures well above room temperature.

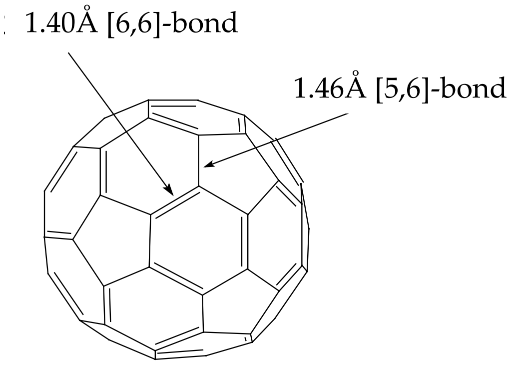


Figure 1. C_{60} molecule.

In C_{60} molecule (see Fig. 1), the carbon nuclei reside on a sphere of about 7 Å diameter, with the electronic wave functions extending inside and outside by about 1.5 Å. The diameter of the molecule is approximately 10 Å, and there is a 4 Å diameter cavity inside. The atoms are actually positioned at the 60 vertices of a truncated icosahedron structure (a structure analogous to a soccerball and reminiscent of the geodesic domes of Buckminster Fuller), with 90 edges, composed for 32 faces (12 pentagons and 20 hexagons).

The two different C-C bond lengths in C_{60} (1.40 and 1.46 Å),[10] indicate that the π electrons are not delocalized evenly over all bonds[11] (For comparison, the sp^3-bond in diamond is 1.54 Å and the C-C distance and in graphite is 1.42 Å).The shorter bond length belongs to a [6,6]-ring junction (C-C bond between two hexagons) and the larger to a [5,6]-ring junction (C-C bond between one pentagon and one hexagon).

The chemical behaviour of C_{60} molecule depends mainly on these structural properties:[12]

i) The 30 bonds at the junctions of two hexagons ([6,6]-bonds) are shorter than the 60 bonds at the junctions of a hexagon and a pentagon ([5,6]-bonds).

ii) The highly pyramidalized sp^2 C-atoms in C_{60} cause a large amount of strain energy within the molecule. The pyramidalization angle, defined by Haddon and Raghavachari, of carbon atom orbitals in C_{60} structure is 11.6°,[13, 14] an angle between sp^2 and sp^3 hybridization, which are 0 and 19.47° respectively (see Figure 2).

Due to the high symmetry of fullerenes, in these compounds the charge on

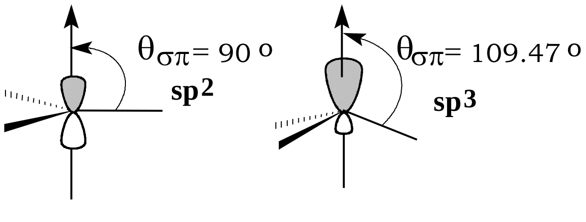


Figure 2.
Angle of pyramidalization, $\chi = \theta_{\sigma\pi} - 90°$.

carbon atoms and the molecular dipole moments are zero or close to zero. For this reason, it is expected that the reactivity of fullerenes can be understood and predicted mainly from the analysis of their frontier orbitals, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In particular, because of the high electron affinity of fullerenes,[15, 16] the LUMO plays a key role in the specific reactivity of fullerenes.

Pyramidalization has been commonly accepted as the main reason to justify the existence of a low-lying LUMO orbital in fullerenes.[14, 16, 17] In addition, pyramidalization plays an important role on the definition of the HOMO energy and shape, and therefore it has a large influence in the HOMO-LUMO energy gap that is of enormous importance to understand the properties of fullerenes as semiconductors.[18]

From simple molecular orbital considerations, the HOMO and LUMO orbitals are stabilized by pyramidalization due to the contribution of the carbon 2s atomic orbitals in these two molecular orbitals, as shows Figure 3. In this process the HOMO is slightly stabilized, meanwhile the energy reduction in the LUMO is larger.

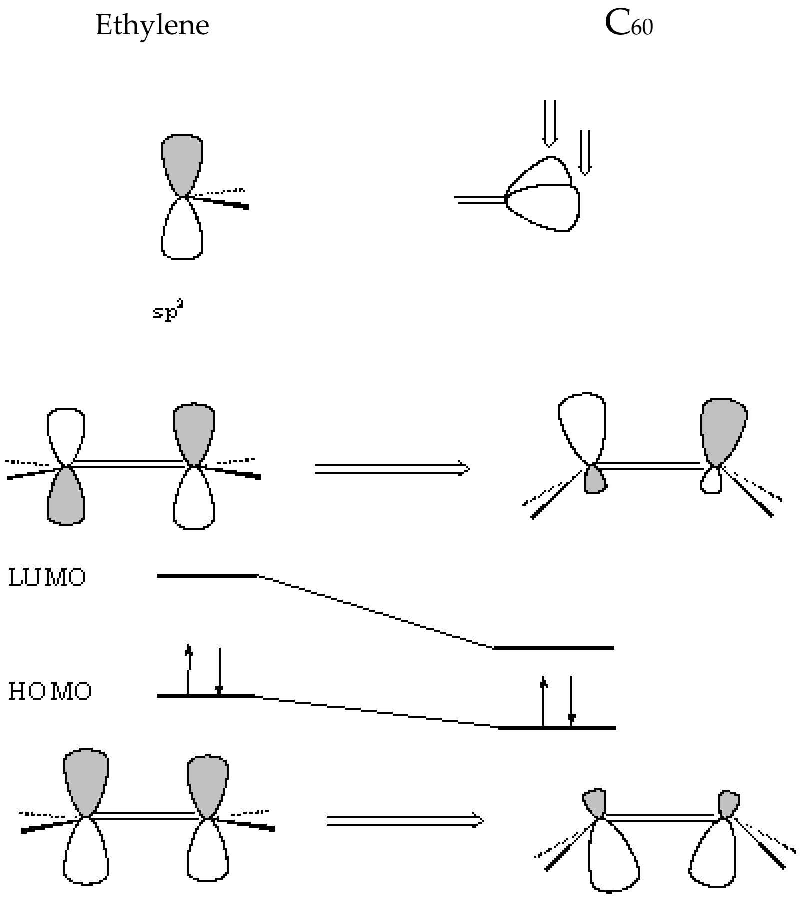


Figure 3. Schematic picture of the change in energy and shape of the frontier orbitals with increasing pyramidalization.

In base on these properties, some rules of reactivity can be deduced from the multitude of chemical transformations that have been carried out with C_{60}:[19, 20]

i) The reactivity of C_{60} is that of a fairly localized electron deficient polyolefin. The main type of chemical transformation is addition to the [6,6]-bonds, especially nucleophilic and radical attacks and cycloadditions.

ii) The regiochemistry of the addition reaction is governed by the minimization of the number of double bonds in [5,6]-ring junctions, because double bonds in five-membered rings are unfavourable. They would increase the strain in the cage. The addition to [5,6]-bonds or [6,6]-bonds can provide two different type of adducts depending on whether the addition means the breaking of C-C bond of C_{60} which is attacked, then one can distinguish between open and closed structures as Figure 4 shows. The nummerization of double bonds in 5-membered rings explains the larger stability of the [6,6]-closed and [5,6]-open isomers.

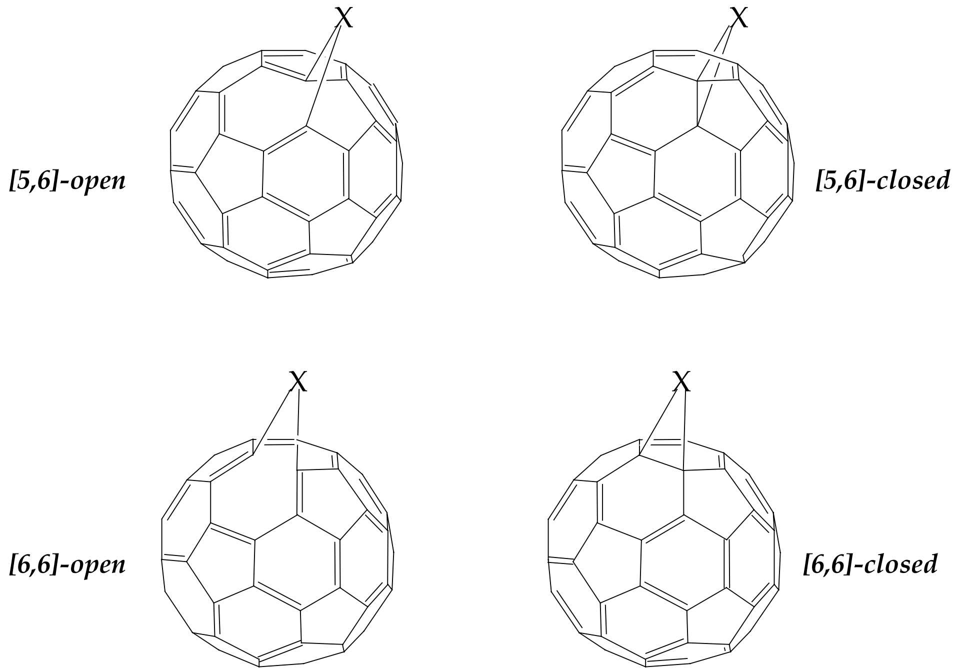


Figure 4. [5,6]-open and closed, and [6,6]-open and closed isomers.

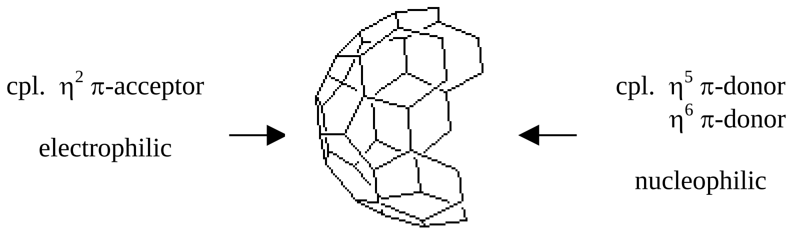


Figure 5. Different character of reactivity of C_{60}, inside and outside its surface.

iii) The driving force for addition reaction is the relief of strain in the fullerene cage. The rich exohedral addition chemistry of fullerenes can be considered to a great extend as the consequence of repyramidalization to sp^3 C-atoms. Also the reduction of C_{60} can be regarded as a strain-relief process, many carbanions are known to prefer pyramidal geometries. The curvature of C_{60} implies that the π-orbitals of the systems result hybridized orbitals between the typical π orbitals in case of sp^2 and sp^3 hybridization. The combination of these hybridized orbitals gives less symmetric orbitals in case of C_{60}, and that explains the different reactivity between inside (nucleophilic character) and outside (electrophilic character) surface[21] see Figure 5).

The two main types of primary chemical transformations, addition reactions[22] and redox reactions, lead to five groups of chemically modified cage molecules: *covalent exohedral adducts* and *salts*, *heterofullerenes* (in which one or several carbon atoms are replaced by a heteroatom), *endohedral fullerenes* (cluster open compounds) and *complexes* (defined degradation products). The largest group of fullerene derivatives are the exohedral adducts with one or several addends covalently bond to the carbon framework.

1.2. Functionalization of C_{60}

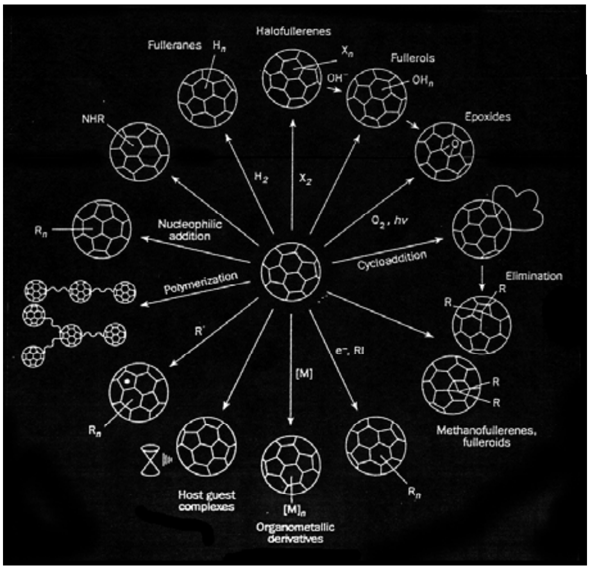


Figure 6. C_{60} reactivity.[22]

Most of the chemical reactivity and functionalization studies have been centered on C_{60} because of its relative abundance in the fullerene extracts compared to other higher fullerenes which are only available in minor quantities upon synthesis. The large number of derivatives of the C_{60} cluster synthesized[23] thus far testifies the rich chemistry of fullerenes (see Fig. 6). The key to the development of C_{60} chemistry is to form selectively single structural isomers in high yield.

Addition to fullerenes presents unusual problems. The rigidity of the cage means that eclipsing interactions can hardly be avoided, except, by introducing C-C bond strain.[24,25]

It is therefore difficult to obtain stable derivatives in which bulky groups lie adjacent, and the addition patterns changes according to the size of the added groups. Additions can be categorized into cycloadditions, additions involving bridging and additions of separate groups, examples of them are below explained, but firstly before discussing the chemistry of the fullerenes, the various addition patterns that occur and the possible reasons for them, must be considered.

1.2.1. Addition patterns

Whilst the factors governing the addition of several groups to fullerene are reasonably well understood, for higher addition levels much more work is needed both to ascertain the regiochemistry of addition (defined so far in only a few cases) and the underlying reasons for it. As said before in Sec. 1.1., C_{60} structure have two different type of C-C bonds, [6,6]-(bond shared by two hexagons) and [5,6]-(bond shared by one pentagon and one hexagon)junction.

i) Generally addition takes place across a [6,6]-junction and the main factors governing the [6,6]-bond addition because of its high double bond character and a better orbital interaction.

ii) Additions that place double bonds in pentagons will be unfavourable unless the strain in the pentagons is reduced through the presence of sp^3-hybridized carbons, or there are other stabilizing features.

iii) In some cases the steric effects also govern the choice between addition across a [6,6]-bond or insertion into a [5,6]-bond.

iv) The cages are relatively non-aromatic, and so any addition pattern that increases their aromaticity will increase stability and will therefore be favourable. Because the molecules have some aromaticity and hence electron delocalisation, addition across the [6,6]-bond between a pair of adjacent hexagons increases the electron localization in each of these rings.

v) When steric effects favour other than a 1,2;3,4-addition (cis1) pattern as a second addition, seven other possibilities (cis2, cis3, equatorial, trans1, trans2, trans3, trans4) are possible for 60-fullerene. (see Fig. 7)

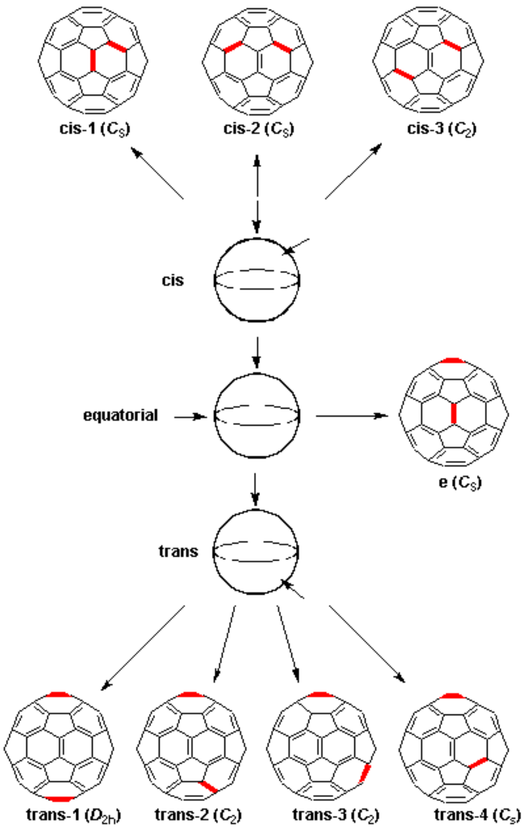


Figure 7. Regiochemistry of the second addition to C_{60}, the 1,2;3,4-addition and the other seven positions depending on the symmetry of [6,6]-bond in C_{60}.

vi) Therefore, steric consideration permitting, further addition will tend to take place across one of the other double bonds in either of these hexagonal rings (there are four such bonds in total and in [60]-fullerene they are all equivalent). One hexagon will therefore have addition across two of its double bonds, which should increase localization further for the remaining double bond. This is observed for example in hydrogenation, and the additions of oxygens. Thereafter steric interactions intervene so that further addition takes place preferentially in the other hexagon, in which there is a choice of two positions. This gives rise to either a 'T' or 'S' addition pattern as show in Figure 8.

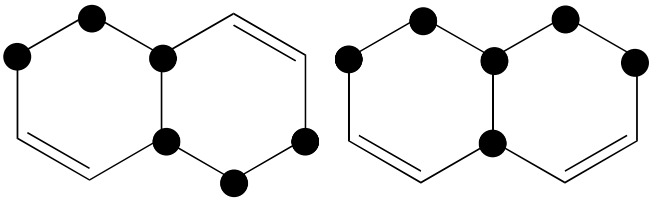


Figure 8. 'S' and 'T' addition patterns.

These patterns are commonly observed in e. g. hydrogenation, fluorination, epoxide formation, etc... There are greater eclipsing interactions in the 'T' structure compared to 'S' structure, consequently, the latter is predicted by *ab initio* calculations to be the more stable.

Because C_{60} is a spherical molecule and sometimes it becomes difficult with 3-D pictures to show all the positions where addends are bond, Schlegel diagrams are used. They are the equivalent 2-D pictures of fullerenes.

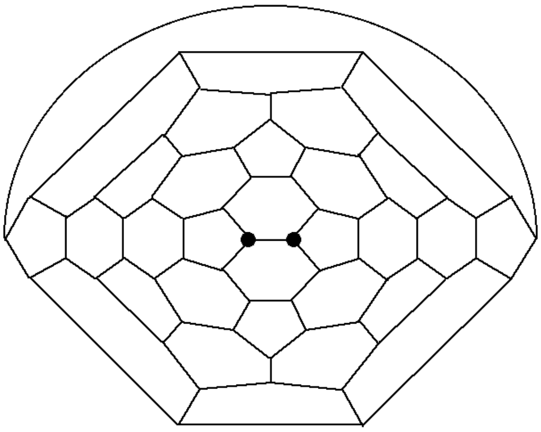
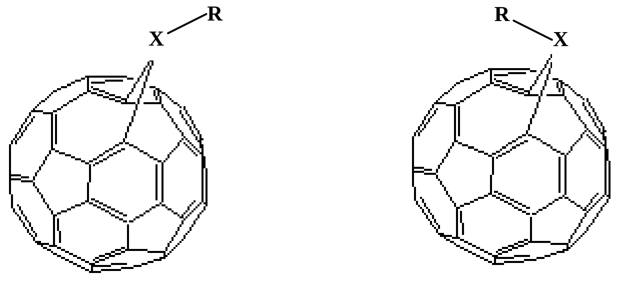


Figure 9. C_{60} Schlegel diagram.

1.2.2. Cycloadditions to C_{60}

Of all fullerene reactions, cycloadditions have received by far the most study. This popularity stems from the ability to control the reaction so that only one addend becomes attached to the cage, marking analysis of the produces relatively easy. The object of many of these synthesis is to produce intermediates for further reaction, although some of the functional groups do not undergo their normal reactions either readily or at all, when attached to fullerenes. This is due to both the strong electron withdrawal by the cage, and steric constraints.[26]

Six types of reaction are known: [1+2], [2+2], [3+2], [4+2], [6+2], and [8+2] cycloadditions. The number of compounds that have been made by cycloaddition is already too vast to be described in detail here, consequently as said previously, the reactions shown next are the reactions which have had a special interest in this Thesis project. Concretely the studies carried out are centred with the [1+2] cycloaddition which involve either nitrogen (azafullerenes), carbon (methanofullerenes), oxygen (fullerene oxides), numerous cyclopropanated derivatives based upon these additions being now know. Addition of carbon has been the most studied to date, but addition of nitrogen, and of oxygen (which can occur spontaneously) are rapidly gaining in importance. Two possible products are obtainable, arising from insertion into a [5,6]-bond or addition to a [6,6]-bond, giving the structures of Fig. 4, respectively, and the reason for these preferences have been given in Sec. 1.2.1.



[5,6]/5 [5,6]/6

Figure 10. [5,6]/5 or [5,6]/6 products.

For a single atom like oxygen, only one product is obtained in each case, [5,6]-open and [6,6]-closed. Closed [6,6]-bridged adducts and open [5,6]-bridged adducts are the most stable isomers. This fact is consistent with the rule of minimization of double bonds in 5-membered rings, (see Sec. 1.2.1). In case of [5,6] structure, the addition of either N-addend (NR) or C-addend (CRR’) can provide two products of the structure, depending upon the conformation of the addend faces up to the 5- or 6-membered ring, the called [5,6]/5 or [5,6]/6 products are possible (see Fig. 10). The addition of C and N addends to C_{60} leads to obtain the [6,6]-closed and [5,6]/5- and the [5,6]/6-open cycloadducts, the methano- and iminoderivatives respectively.

1.2.2.1. *Addition of Nitrogen to C_{60}*

Nitrogen may be either added across a [6,6]-bond or inserted into a [5,6]-bond, (see Fig. 11). With [60]fullerenes, the former gives [5,6]-open adducts or 1,2-epimino-[60]fullerenes, otherwise known as *aziridinofullerenes*, whilst the latter gives [6,6]-closed adducts or 1a-aza-1(6)a-homo[60]fullerenes (where if R=H are known as *azafulleroids*).

The insertion reaction allows greater bond angles at nitrogen which therefore tends to be sp^2-hybridized in azahomofullerenes (and sp^3-hybridized in epiminofullerenes).

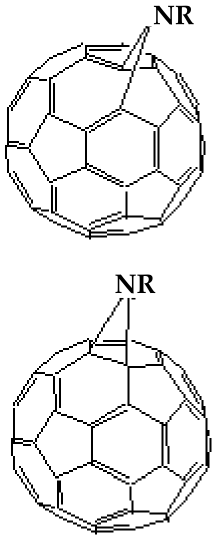


Figure 11. [5,6]-open adduct (aziridinofullerene) and [6,6]-closed adduct (azafulleroid).

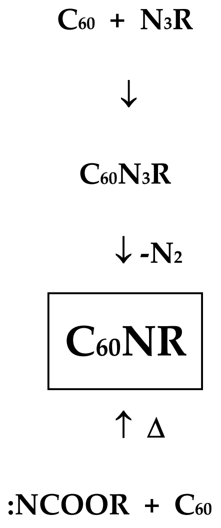


Figure 12. The usual vias of introducing nitrogen.

Two main methods are used for introducing nitrogen to the cage and provide monoiminofullerenes:

-reaction with azides (which proceeds via an initial [3+2] cycloaddition to afford the triazoline followed by nitrogen extrusion) gives mainly azahomofullerenes.[27-33]

-reaction with nitrenes (formed by either thermal[34-36] or photochemical[37] decomposition of azidoformates, by lead tetra-acetate oxidation of N-aminophthalimi-de[38] or by α-elimination of O-4-nitrophenyl-sulphonylalkylhydroxamic acids[39]), gives mainly the epiminofullerenes

A second nitrogen addition to the cage provides the formation of *bis azahomo-* or *bis epiminofullerenes* (see Fig. 13, one of the few examples of fullerene compound with open [6,6]-bonds is when R = COOR),[20] which are considered of interest as cage-opened derivatives of C_{60} they are and because they can provide easily access to heterofullerenes, which one or several carbon atoms are replaced by an heteroatom[40] (see Fig. 14) Hummelen and Wudl[41] published the first synthesis of $C_{59}N$ in the dimeric form in macroscopic amounts.

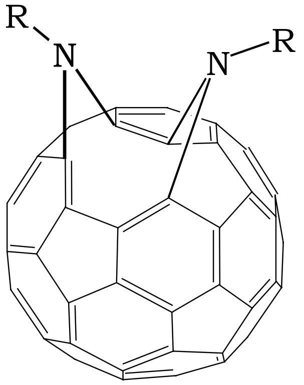


Figure 13.
Example of a bis-epiminofullerene.

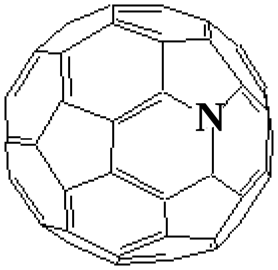


Figure 14.
Example of an heterofullerene of N, $(C_{59}N)^{\cdot}$.

1.2.2.2. *Addition of Carbon to C_{60}*

Carbon may be added to C_{60} molecule basically in form of carbene specie across a [6,6]-bond by a one step mechanism. The product of carbene addition to fullerenes at [6,6]-bonds are known as *methanofullerenes* meanwhile they are called *fulleroids* when the addition takes place in a [5,6]-bond. The fulleroids obtained from C_{60} have been originally speculated to possess open-bridge structures ensuing from the 1,2-addition,[42] but further experimental studies have demostrated that the reaction products are mixtures of the 1,2-adducts with rings composed of three carbon atoms and the 1,6-adducts with open bridges the latter believed to be less stable.[43] In fact, the fulleroid is the kinetic product that rearranges[44,45] into a methanofullerene (the thermodynamic product) under a variety of conditions (it can be done by light/thermal, pure light, or electrochemically).[46, 47] The reason why these two are the only observed isomers has been attributed to the preservation of the [5] radialene substructure within C_{60}.[48, 49] Formation of methanofullerenes results in a partial loss of conjugation of the C_{60} sphere, from the 60 π-electron to a 58 π-electron configuration. In contrast, formation of fulleroids ([5,6]open) does not result in a reduction of the parent C_{60} π-electron configuration. They are only derivatives that retain the 60 π-electron configuration of C_{60}.[50]

Apart from carbene addition, controlled addition of methylene and substituted methylene is achieved very efficiently through the use of diazo compounds. These may either eliminate nitrogen to give a carbene (which the participates in [1+2] cycloaddition to the cage), or they can carry out [3+2] cycloaddition to give an intermediate pyrazoline. On heating this loses nitrogen to give almost exclusively the homo[60]fullerene [5,6]-insertion product, whilst on irradiation it gives both this and the methano[60]fullerene [6,6]-addition product.[42, 44, 47, 50]

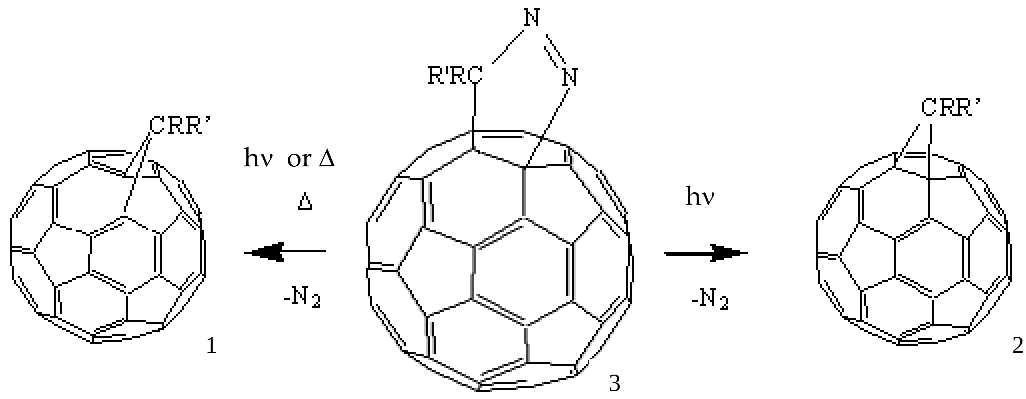


Figure 15. Fulleroid(1), methanofullerene(2), and adducts(3) from diazo addition to C_{60}.

Other vias of methanofullerenes formation are through the use of ylides or by α-halocarbonion addition, and with a low yield the reaction of Fischer carbene complexes $Me(OMe)C{=}Cr(CO)_5$ with [60]fullerene which produces the 1,2-methano[60]fullerene with methyl and methoxy groups substituted at the methylene group.[51]

Multiple addition levels are possible proceeds all the way up to the hexa-adduct, which should have an octahedral addition pattern. Investigations of mono- to hexa-adducts are under study in order to better known how control the sites of polyaddition in base of the steric hindrance of carbon atom substituents and their chemical features.

1.2.2.3. *Addition of Oxygen to C_{60}*

Formation of epoxides is an area of fullerene chemistry that is rapidly growing in importance, and is likely to continue to do so, given that fullerenes readily form epoxides, even on standing in air. Fullerene oxides are among the first derivatized fullerenes found to exist. The fullerene soot produced by Krätschmer-Huffman method[2] can contain fullerenes with up to 5 oxygen atoms attached.[52-55]

There are a wide range of methods of formation of fullerene epoxides. These comprise photoxidation of fullerene in the presence of photosensitizers, or by using chemically-generated singlet oxygen, oxidation by either dimethyl,…, ozonolysis,...).

Like most other fullerene reactions, oxidation does not go to completion (but also gives polyaddition) and so separation from unreacted fullerene (and higher oxides) is necessary to have isolated potential precursors of new C_{60} derivatives.

Reactions of C_{60} generally give complex mixture of products. Thus far, only a few well-defined monofunctionalized products have been isolated. Wood *et al.*[52] detected $C_{60}O$ in a similar mixture by mass spectrometry and Kalsberg and Thorp reported[56] generating $C_{60}O_n$ (n=1-4) by electrochemical oxidation of C_{60}. Cox, Smith *et al.*[57] obtained well-characterized monoxide $C_{60}O$ [6,6]-closed as the sole isolable product (7% yield) upon phothochemical oxidation of C_{60} in benzene. Recently, in 2001, Weisman *et al.* synthesized and characterized [5,6]-open $C_{60}O$ (oxohomo-[60]fullerene),[58] its synthesis confirmed long-standing computational predictions that the epoxide and ether isomers of $C_{60}O$ are both stable species.[59]

Epoxides are also formed spontaneously when reaction are perfomed with halogenofullerenes. They arise from nucleophilic substitution of halogen by OH and subsequent elimination of HX:

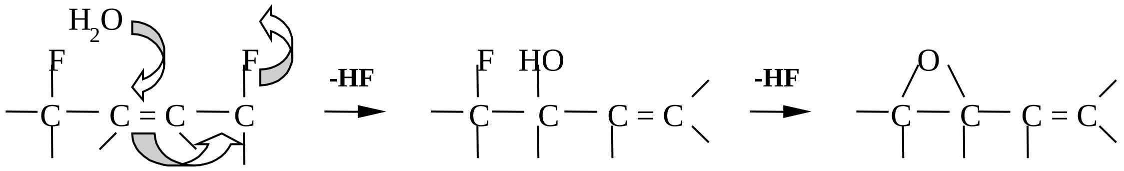


Figure 16. Mechanism of nucleophilic substitution of F by OH and subsequent elimination of HF.[26]

This is particularly evident with fluorofullerenes which are the most reactive halogenofullerenes towards nucleophilic substitution, and the subsequent elimination of HF is evident as etching of containers if the materials are not stored under anhydrous conditions.

In the formation of epoxides from fluoro[60]fullerenes, up to 18 oxygen are present, and also in case of gas-phase reaction between [60]fullerene anions and ozone.[60]The structure of $C_{60}O_2$ was determined as 1,2;3,4-diepoxy[60]fullerene (Fig. 17a), this being the expected isomer for the same underlying reason (see Sec. 1.2.1.) that gives rise to 1,2;3,4-tetrahydro[60]fullerene.

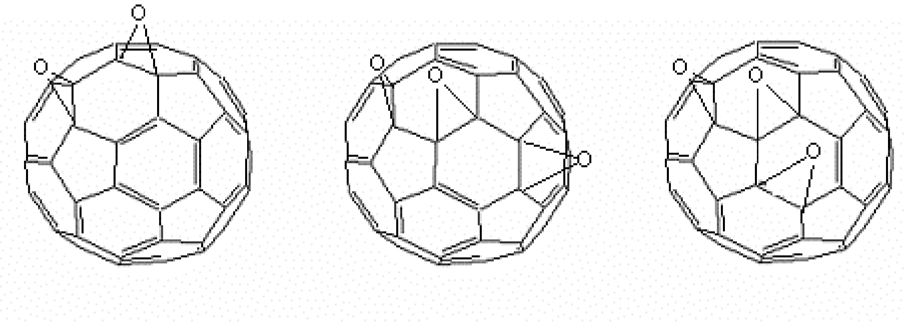


Figure 17. a) $C_{60}O_2$ more stable isomer, b) $C_{60}O_3$, isomer S and c) $C_{60}O_3$, isomer T.

Likewise $C_{60}O_3$ consists of a mixture of 1,2;3,4;9,10-triepoxy[60]fullerene (Fig. 17b), and 1,2;3,4;11,12-triepoxy[60]fullerene (Fig. 17c) in *ca.* 3:2 ratio.[53] Note that respectively, these have the 'S' and 'T' patterns expected as a result of bond localisation (see Sec. 1.2.1.) and which underlie the formation of $C_{60}H_{18}$ and $C_{60}F_{18}$ (see Sec. 1.2.3.2.1.). The possibility exists therefore that $C_{60}O_9$ and $C_{60}O_{18}$ are each isostructural with the $C_{60}X_{18}$ and $C_{60}X_{36}$, respectively.

The patterns of the oxygen addition are distinct from those predicted and observed for hydrogens, halogens and alkyl groups.

Deeply studies in addition patterns of oxygen would be necessary to better control the selective formation of other C_{60} derivatives, for instance facile preparation of monoepoxide opens new doors for monofunctionalization of C_{60}. It has been suggested that the formation of the mono-oxide is controlled by kinetics rather than by thermodynamics.[61] The epoxide is one of the most versatile functionalities and provides easy access to further modifications. Moreover, fullerene oxides show a rich chemistry in reactions both with fullerene and with themselves. Fullerene oxides are thermally labile and readily liberate the attached oxygen upon heating.

The *methano-, aza-* and *oxo*-bridged fullerenes have already attracted wide attention,[62] basically because they can be good precursors for higher functionalized C_{60} derivatives.

Experimental and theoretical studies show that the preference for [6,6]-closed and [5,6]-open structures is not due to substituent effects. Rather, [6,6]-closed and [5,6]-open are preferred over [6,6]-open and [5,6]-closed structures, respectively, since they conserve the bonding seen in C_{60} with higher single-bond character at all [5,6]-ring junctions and higher double bond character at all [6,6]-ring junctions.

Additionally, π-homoaromatic bridging provides a better steric fit at the longer [5,6]-ring junction and, correspondly, σ-homoaromatic bridging fits better geometrically at the shorter [6,6]-ring junction. In base of this knowledge obtained after an important evolution in C_{60} functionalization, the regiochemistry of nitrogen, carbon or oxygen addition to get C_{60} derivatives seems to be quite easily carried out under control single addition, but further studies related with multiple additions should be more deeply analysed in this field of cycloadditions to C_{60}.

1.2.3. Singly bonded functionalized derivatives of C_{60}

Addition reactions are one of the most important way of chemical modification in fullerene chemistry.[19] Apart from cycloadditions, there are other addition reactions that do not provide cycloadducts as products. Due to the electron deficient alkene-like character of C_{60}, chemical addition can be performed to yield a broad range of derivatives. The electron-withdrawing properties of fullerenes make them reactive towards radicals, but not necessarily a singly bonded functionalized derivative is obtained because a radical addition takes place.

1.2.3.1. *Addition of Hydrogen and Aryl groups directly to C_{60}*

Among a variety of addition reactions, the hydrogenation of the fullerene C_{60} has been performed by practically all current reducing methods (hydroboration,[63, 64] hydrozironation[65] and other chemical reductions with diimide, chromium (II) salts,[66] zinc-acid[67] and Birch reduction,[68,69] by hydrogen atom transfer,[70] hydrogen radical induced hydrogenation[71] and by catalytic and solid phase hydrogenation[66, 72, 73]…). Theory predicts an extremely high electron affinity for C_{60} molecule, so its reduction results facile.

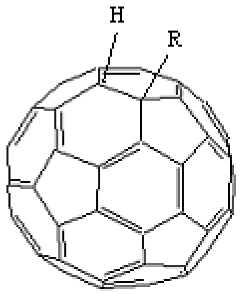


Figure 18.
Example of substituted hydrofullerene.

The special interest for hydrogenated derivatives forms of C_{60} (called *hydrofullerenes*), is because of their important acidic properties as well as for their possibilities in synthetic strategies. The substitution of one or more hydrogen atoms from the structure of hydrofullerenes by a number of alkyl-, oxygen-, chlorine- and fluorine containing functional groups, neighboring the remaining H atom on the resulting fullerene on a [6,6]-ring junction provides the formation of called *substituted hydrofullerenes*.[74]

As a general tendency for the different kind of C_{60} derivatives, the addition of hydrogen atoms takes place at [6,6]-bond of the C_{60} structure and concretely the 1,2-addition has been proved to be the most stable addition pattern for $C_{60}H_2$ and for some experimentally obtained $C_{60}HR$ systems.[75] 1,2-$C_{60}HR$ structures are important because of the fact that, via a careful choice of the R group, the properties of the system could be modified and adjusted in a desired way.

Moreover, each substituted hydrofullerene could be the starting product for further synthetic steps, resulting in a whole new series of modified fullerenes, each one with its specific properties.

1.2.3.2. *Halogenation of C_{60}*

In spite of its high electrochemical oxidation potential,[69] C_{60} easily undergoes oxidative halogenation with elemental fluorine, chlorine, and bromine, often the products are mixtures of polyhalogenated compounds, which probably consist of several compositions and their isomers.

The reaction of C_{60} with fluorine, chlorine, and bromine are important because the resulting halide products can be useful precursors to a variety of substituted derivatives. These reactions also involve addition to the C-C double bonds ([6,6]-ring junctions are preferred) and, initially, similar problems were encountered as with the radical addition reactions.

The halogens would tend to add to C_{60} in an uncontrolled manner, producing a range of products that were hard to separate and characterize.

Halogenation is especially interesting because of the different additions patterns produced by the different sizes of the halogens. This facilitates understanding of the mechanisms that govern addition to fullerenes. This bromation and chlorination will add a maximum of 24 halogens, whereas fluorination will readily add 48 fluorines, and more under forcing conditions.[76]

1.2.3.2.1. *Fluorination*

The first halogenation carried out on C_{60} was fluorination. Smith *et al.*[77] fluorinated C_{60} with elemental fluorine and obtained a mixture of polyfluorinated products. The major component of the mixture was $C_{60}F_{36}$ analogous to the Birch reduction product $C_{60}H_{36}$.[69] Subsequently, Holloway and co-workers[78] claimed the formation of $C_{60}F_{60}$, when 10mg of C_{60} was exposed to fluorine gas over a period of 12 days.

The fluoro derivatives are very soluble and reactive, but their formation (necessarily under heterogeneous conditions) is difficult to control.[26]

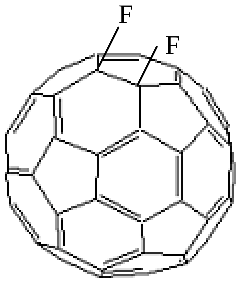


Figure 19.
Example of a fluorofullerene.

Two main conditions of fluorination have been used: fluorination with fluorine gas, and with metal fluorides. The former condition is difficult to control, and leads to a wide range of products, whereas the latter is easier to control, but is more expensive and ultimately unsuitable for large scale production. Fluorination with F_2 is strongly exothermic and may not occur, selectively. Because the C-F bond is strong and the F-F bond weak, it is unlikely that a kinetically controlled mixture of products could rearrange to an ordered thermodynamic product by a mechanism requiring dissociation and readdition of fluorine.

Of the halogenofullerenes, fluorofullerenes are the most reactive towards nucleophilic substitution, and they are also the most stable. The stability of the fluoro derivatives decreases beyond about $C_{60}F_{40}$[77] making subsequent addition of fluorine very slow.[78] The fluorocompounds are more stable than the chloro and bromo derivatives but decompose rapidly on heating above 80ºC. The more highly fluorinated species are less stable, so that peaks for $C_{60}F_{50}$-$C_{60}F_{60}$ in mass spectrum disappear after sublimation.

The utility of halogenated fullerenes in general as intermediates in the production of other fullerene derivatives has been demonstrated by several groups. Fluorofullerenes react readily with water to replace F by OH in a process which probably involves addition-elimination (see Sec. 1.2.2.3., Fig. 16).

Evidence for substitutions of fluoride in $C_{60}F_n$ by methoxide and a number of other nucleophilic species has been also presented.[79, 80]

1.3. Spherical Aromaticity

The magnetic properties of fullerenes clearly reflect delocalized character of the conjugated π-electrons can cause the establishment of diamagnetic or paramagnetic ring currents within the loops of the hexagons and pentagons. Neutral C_{60}, for example, exhibits no pronounced overall aromaticity since it contains diatropic hexagons and paratropic pentagons and was labeled ambiguously aromatic. Hirsch and Bühl,[81] have showed that the treatment of the π-electrons system as a spherical electron gas allows to determine the nature of three-dimensional aromaticity of fullerenes and other cage compounds.

The aromaticity of two-dimensional annulenes in singlet ground states follows the Hückel rule, i. e. annulenes with $4N+2$ π electrons are aromatic, those with $4N$ π electrons are antiaromatic. Due to their closed-shell structures, annulenes with $4N+2$ π electrons are not distorted (D_{nh}-symmetry) and show strong diamagnetic ring currents. The rule is reversed for triplet open-shell analogues.

The aromaticity of icosahedral fullerenes (C_{20}, C_{60} and C_{80}) and their cluster distortions depends on the number of delocalized electrons in the valence shell. The maximum of spherical aromaticity of a cluster can only achieved with $2(N+1)^2$ electrons filling the shell completely. The $2(N+1)^2$ rule[81] represents the spherical analogue of the Hückel rule for planar annulenes.

2. COMPUTATIONAL CHEMISTRY

Scientific Research can be classified into four main categories: Observational, Experimental, Theoretical, and Computational Science. Concretely, Computational Science uses everything that scientists already know about a problem and incorporates it into a mathematical problem which can be solved by special programs incorporated in computers. The mathematical model which then develops gives scientists more information about the problem. Computational Science is beneficial for two main reasons: it is a cheaper method of conducting experiments and it provides scientists with extra information which helps them to better plan and hypothesize about experiments.

Computational Chemistry is a branch of Computational Science like Chemistry is a branch of Science, and generates data, which complements experimental data on the structures, properties and reactions of substances. Computational Chemistry is particularly useful for determining molecular properties which are inaccessible experimentally and for interpreting experimental data. With Computational Chemistry, one can perform: electronic structure determinations, geometry optimizations, frequency calculations, transition structures location, electron and charge distributions analysis, potential energy surfaces (PES) construction, kinetics calculations (rate constants for chemical reactions) and thermodynamic calculations (heat of reactions).

Computational Chemistry applies high-performance computer (clusters of PCs, supercomputers and scientific workstations) and advanced mathematical techniques to the study of complex chemistry problems. Most computational chemistry studies are concerned with the area of quantum chemistry, which uses the classic Schrödinger equation to be able to describe the chemical properties and behavior of atoms and molecules.

There are three main types of calculations:

i) Ab Initio: (Latin expression for “from scratch”), which were defined for Atkins at 1991 as “a group of methods in which molecular structures can be calculated using nothing but the Schrodinger equation, the values of the fundamental constants and the atomic numbers of the atoms present”.
ii) Semi-empirical methods are techniques which use approximations from empirical (experimental) data to provide the input into the mathematical models.
iii) Molecular mechanics, which uses classical physics to explain and interpret the behavior of atoms and molecules.

The information given in this section is a brief overview of theoretical concepts, methodologies… used in Computational Chemistry.[82, 83] As done in previous section, here the aspects treated are the more related with the different studies carried out in this Thesis project, in order to give to the reader the information to go on the lecture and understanding of next sections, especially for non-computational chemistry users.

Computational Chemistry let us to calculate the electronic structure of a molecule and know its properties from the application of theoretical definitions to represent chemical concepts related with molecular features.

2.1. Theoretical methods

Chemists working with large and small molecules are accustomed to using computer codes and software modules that are based on quantum mechanical methods. But most properties of macroscopic materials depend on microscopic phenomena to one degree or another and also require for their correct description the application of quantum mechanics. Quantum mechanical methods can be divided into two categories: semi-empirical models and *ab initio*.

Semi-empirical quantum chemical methods lie between *ab initio* and molecular mechanics (MM). Like MM, they use experimentally derived parameters to strive for accuracy; like *ab initio* methods, they are quantum-mechanical in nature. Semi-empirical methods are computationally fast because many of the difficult integrals are neglected. The error introduced is compensated through the use of parameters. Thus, semi-empirical procedures can often produce greater accuracy than *ab initio* calculations at a similar level.

Ab initio methods refer to quantum chemical methods in which all the integrals are exactly evaluated in the course of a calculation. *Ab initio* methods include Hartree-Fock (HF) or molecular orbital (MO) theory, configuration interaction (CI) theory, perturbation theory (PT), and density functional theory (DFT). *Ab initio* methods that include correlation can have an accuracy comparable with experiment in structure and energy predictions. However, a drawback is that *ab initio* calculations are extremely demanding in computer resources, especially for large molecular systems.

1.1.1. Semi-empirical methods

Semi-empirical quantum mechanical methods allow in principle the evaluation of the same properties as first-principles methods, i.e. structures, energies, electronic states, charge distributions, spin distributions, and related quantities. AM1 (Austin Model 1)[84] as other semi-empirical methods as MNDO[85] or PM3,[86,87] are capable of reproducing a wide variety of geometric and electronic molecular properties for a wide variety of molcules, to give good agreement with experiment in the majority of cases.

Semi-empirical usefulness comes from the balance between several characteristics, namely theoretical rigor and pragmatism, speed and accuracy, specific parameterization and generality. These methods capture the essential aspects of a quantum mechanical approach including electronic levels, charge transfer, and spin polarization; it allows the making and breaking of chemical bonds; it provides geometric structures, heats of formation, infrared spectra, normal modes, as well as electronic charges, electrostatic potentials, dipole and multipole moments, polarizabilities, hyperpolarizabilities and, with the proper parameterization, also optical spectra. The heavy computational effort of first-principles calculations is avoided by a number of algorithmic simplifications such as the use of minimal basis sets (see Sec. 2.1.4.) and the elimination of difficult integrals, which are either made small by proper mathematical transformations and then ignored or by using them as parameters to fit experimental data such as geometries, heats of formation, and ionization potentials.

Their implementation in the programs like AMPAC[88] allows them to be easily used for a variety of property computations, simply by specifying appropriate choices of keywords in the programs. Geometric energy minimization (optimization with or without constraint of some structural parameters), reaction coordinate following (IRC), transition state location, vibration mode prediction, population analysis, optimization and/or energy comparison of various CI corrected states, dipole and polarizability predictions.

2.1.2. Hartree-Fock Approximation

Hartree-Fock theory is fundamental for the electronic structure theory. It is based on the molecular orbital (MO) theory, which posits that each electron's motion can be described by a single-particle function (orbital) which does not depend explicitly on the instantaneous motions of the other electrons. The ubiquity of orbital concepts in chemistry is a testimony to the predictive power and intuitive appeal of Hartree-Fock MO theory. However, it is important to remember that these orbitals are mathematical constructs which only approximate reality. Only for the hydrogen atom (or other one-electron systems, like He^+) are orbitals exact eigenfunctions of the full electronic Hamiltonian. As long as one is content to consider molecules near their equilibrium geometry, Hartree-Fock theory often provides a good starting point for more elaborate theoretical methods which are better approximations to the electronic Schrödinger equation (e.g., many-body perturbation theory, configuration interaction methods, etc…).

The starting point is to write down the many-electron wavefunction as a product of one-electron wavefunctions:

$$\psi = \psi_{a,\alpha}(1)\psi_{a,\beta}(2)...\psi_{z,\beta}(N) \qquad \text{(eq. 1)}$$

This is the wavefunction for an N-electron closed-shell molecule in which electron 1 occupies molecular orbital ψ_a with spin α, electron 2 occupies molecular orbital ψ_a with spin β, and so on... However, the wavefunction must satisfy the Pauli principle and change sign under the permutation of any pair of electrons. To achieve this behaviour, one writes the wavefunction as a sum of all possible permutations with the appropriate sign:

$$\psi = \psi_{a,\alpha}(1)\psi_{a,\beta}(2)\ldots\psi_{z,\beta}(N) - \psi_{a,\alpha}(2)\psi_{a,\beta}(1)\ldots\psi_{z,\beta}(N) + \ldots \qquad \text{(eq. 2)}$$

There are N! terms in this sum, and the entire sum can be written as a determinant, the Slater determinant:

$$\psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{a\alpha}(1) & \psi_{a\beta}(1) & \ldots\;\ldots & \psi_{z\beta}(1) \\ \psi_{a\beta}(2) & \psi_{a\beta}(2) & \ldots\;\ldots & \psi_{z\beta}(2) \\ \ldots & \ldots & & \ldots \\ \psi_{a\alpha}(N) & \psi_{a\beta}(N) & \ldots\;\ldots & \psi_{z\beta}(N) \end{vmatrix} \qquad \text{(eq. 3)}$$

The initial factor ensures that the wavefunction is normalized if the component molecular orbitals are normalized. When the determinantal wavefunction is combined with the variation principle, it turns out that the optimum wavefunctions, in the sense of corresponding to the lowest total energy, must satisfy the Hartree-Fock equations, which in general can be considered as follows:

$$\hat{F}\varphi_i = \sum_k \lambda_{ki}\varphi_k \qquad \text{(eq. 4)}$$

where $\hat{F}$ is the Fock Operator: $\hat{F}_1 = \hat{h}_1 + \sum_j \left\{ 2\hat{J}_j(1) - \hat{K}_j(1) \right\}$ (eq. 5)

$\hat{h}$, $\hat{J}$ and $\hat{K}$ are the core hamiltonian, the Coulomb and the exchange operators, respectively:

$$\hat{h}_1 = -\frac{\eta^2}{2m_e}\nabla_1^2 - \sum_n \frac{Z_n e^2}{4\pi\varepsilon_0 r_{n1}}$$

$$\hat{J}_j(1)\psi_a(1) = \left[\int \psi_j^*(2)\psi_j(2)\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)d\tau_2\right]\psi_a(1)$$

$$\hat{K}_j(1)\psi_a(1) = \left[\int \psi_j^*(2)\psi_a(2)\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)d\tau_2\right]\psi_j(1)$$

φ_i occupied MOs and unoccupied MOs(virtual), complete set and *k* runs over occupied MOs. The λ_{ji} form a hermitian matrix since $\hat{F}$ is an hermitian operator:

$$\left\langle \varphi_i \middle| \hat{F} \middle| \varphi_i \right\rangle = \lambda_{ji} = \lambda_{ij}^* \qquad \text{(eq. 6)}$$

The most popular form of the HF equations is:

$$\hat{F}\,\tilde{\varphi}_j = \varepsilon_j \tilde{\varphi}_j \qquad \text{(eq. 7)}$$

where the new form of MOs is defined as $\tilde{\varphi}_j = \sum_i \varphi_i V_{ij}$ (eq. 8)

in which *V* denotes the matrix which diagonalizes $\lambda, (\lambda V = V\varepsilon, \varepsilon$ diagonal).

The equation 7 is reminiscent of the Schrödinger equation and can therefore be interpreted as a set of effective one-electron Schrödinger equations for the orbitals. They are often referred to as the *canonical Hartree-Fock equations*. The corresponding orbitals are the canonical Hartree-Fock orbitals, and the eigenvalues ε_i are referred to as *orbital energies*. Some observations should be mentioned:

i) The particularly simple form of eq. 7 can be obtained because all orbitals are equivalent, and the energy therefore remains invariant to transformations among the orbitals.

ii) The orbital energies are given by

$$\varepsilon_i = \left\langle \varphi_i \middle| \hat{F} \middle| \varphi_i \right\rangle \qquad \text{(eq. 9)}$$

iii) Finally, one should note that $E \neq \sum_i \varepsilon_i$. Actually,

$$E = \sum_i \varepsilon_i - \frac{1}{2} \sum_i \left\langle \varphi_i \middle| 2\hat{J} - \hat{K} \middle| \varphi_i \right\rangle \qquad \text{(eq. 10)}$$

In semi-empirical theories it is often assumed that the total electronic energy equals to sum of one-electron energies, but clearly that is not this case.

The *Hartree-Fock Approximation* is what is known as a *Self-Consistent Field Metho* (SCF). It represents an immense simplification compared to the original Schrödinger equation; the resulting equations are still too complicated to be solved exactly for most systems of chemical interest. The method begins with a set of approximate orbitals for all the electrons in the system; then one electron is selected, and the potential in which it moves is calculated by freezing the distribution of all the other electrons and treating their averaged distribution as the centrosymmetric source of potential. The Schrodinger equation is solved for this potential, which gives a new orbital for it. This procedure is repeated for all the other electrons in the system, using the electrons in the frozen orbitals as the source of the potential. At the end of one cycle, there are new orbitals from the original set and the process is repeated until there is little or no change in the orbitals.

2.1.3. DFT methods

Density Functional Theory (DFT) is a general approach to the *ab initio* description of quantum many-particle systems, in which the original many-body problem is rigorously recast in the form of an auxiliary single-particle problem. For the most simple case of (nondegenerate) stationary problems, DFT is based on the fact that any ground state observable is uniquely determined by the corresponding ground state density n, i.e. can be understood as a functional of n. This statement applies in particular to the ground state energy, which allows to (indirectly) represent the effects of the particle-particle interaction as a density-dependent single-particle potential.

In addition to the Hartree-Fock definition this potential contains an exchange-correlation (xc) part, which is obtained from the so-called xc-energy functional. The exact density functional representation of this crucial quantity of DFT is not known, the derivation of suitable approximations being the major task in DFT. Extensions of this scheme to spin-dependent, relativistic or time-dependent systems, utilizing the spin-densities, the four current or the time-dependent density as basic variables, are also available.

The central focus of DFT is the electron density, ρ, rather than the wavefunction ψ. If N is the number of electrons then density function, ρ(r), is defined by

$$\rho(r) = N\int ... \int |\psi|^2 dx_1 dx_2 ... dx_N \qquad \text{(eq. 11)}$$

where $\psi(x_1 x_2 ... x_N)$ is the electronic wavefunction for the molecule. Then one observes that

$$\int \rho(r)dr = N \qquad \text{(eq. 12)}$$

Density Functional Theory is based in two main theorems, the first and the second Hohenberg-Kohn theorems:

Theorem 1. The external potential $V_{ext}(\vec{r})$ is (to within a constant) a unique functional of the $\rho(r)$; since, in turn $V_{ext}(\vec{r})$ fixes $\hat{H}$, then the full particle ground state is a unique functional of $\rho(r)$. In other words, there is unique relation of the external $V_{ext}(\vec{r})$ (arising from the positive charges of the nuclei) within a N electron system and its (ground state) electron density ρ(r).

$$V_{ext}(\vec{r}) \rightarrow \rho(r).$$

The density $\rho(r)$ contains all the information of the system, meaning every property, could be calculated with the help of $\rho(r)$.

The proof of this first theorem is based on reduction *ad absurdum* and runs as follows:

- Suppose there are two different external potentials $V_{ext}(\vec{r})$ and $V_{ext}(\vec{r})'$ which differ by more than a constant and give rise to the same density $\rho(r)$ associated with the (non degenerated) ground state ψ_0.

$$V_{ext}(\vec{r}) \neq V_{ext}(\vec{r})' \qquad \text{(eq. 13)}$$

- Since both external potentials differ, they lead to two different Hamiltonians $\hat{H}$, with two different ground state wavefunctions ψ.

$$H = H_0 + V_{ext} \qquad H\psi = E\psi \qquad \text{(eq. 14)}$$

$$H' = H_0 + V_{ext}' \qquad H'\psi' = E'\psi' \qquad \text{(eq. 15)}$$

- Therefore ψ and ψ' are different N particle wavefunctions, and using the variational principle one can write the inequality:

$$E = \langle \psi | \hat{H} | \psi \rangle < \langle \psi' | \hat{H} | \psi' \rangle = \langle \psi' | \hat{H}' | \psi' \rangle + \langle \psi' | \hat{H} - \hat{H}' | \psi' \rangle \qquad \text{(eq. 16)}$$

  or, because the two Hamiltonian differ only by the external potential,

$$E < E' + \langle \psi' | V_{ext} - V_{ext}' | \psi' \rangle \qquad \text{(eq. 17)}$$

  which yields

$$E < E' + \int \rho(\vec{r}) \{ V_{ext} - V_{ext}' \} d\vec{r} \qquad \text{(eq. 18)}$$

- The last transformation is based on the fact that the external field interacts only via a classical electrostatic interaction between the negatively charged electrons and the positive charges of the nuclei. Interchanging the primed and the unprimed quantities and repeating the steps above leads two the corresponding equation,

$$E' < E + \int \rho(\vec{r}) \{ V_{ext}' - V_{ext} \} d\vec{r} \qquad \text{(eq. 19)}$$

- Adding eq. 18 and 19 leaves the clear contradiction E'+E<E+E', from which one can conclude that there can not be two different external potentials $V_{ext}(\vec{r})$ and $V_{ext}(\vec{r})'$ that yield the same density $\rho(r)$.

- Since the complete ground state energy E_0 is a unique functional of the density *ρ(r)*, so must be its individual parts. One can write:

$$E_0[\rho] = T[\rho] + V_{int}[\rho] + V_{ext}[\rho] \qquad \text{(eq. 20)}$$

- This expression can be classified by parts dependend on the actual system (determined by the external potential) and parts which are universal in the sense that the form of the functional is independent of N, R_A and Z_A.

$$E_0[\rho] = \underbrace{V_{ext}[\rho]}_{\text{System dependent}} + \underbrace{T[\rho] + V_{int}[\rho]}_{\text{System independent}} \qquad \text{(eq. 21)}$$

Where the system independent part defines the *Hohenberg-Kohn functional*:

$$F_{HK}[\rho] = T[\rho] + V_{int}[\rho] \qquad \text{(eq. 22)}$$

Theorem 2. For a trial density $\tilde{\rho}(r)$, *such that* $\tilde{\rho}(r) \geq 0$ *and* $\int \tilde{\rho}(r)dr = N$,
$E_0 \leq E_v[\tilde{\rho}]$.

Given any density $\tilde{\rho}$ associated to a N electron system with external potential V_{ext}, one can state that:

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + V_{int}[\tilde{\rho}] + V_{ext}[\tilde{\rho}]$$
or
$$E_0 \leq E_v[\tilde{\rho}] = T[\tilde{\rho}] + V_{ne}[\tilde{\rho}] + V_{ee}[\tilde{\rho}] \qquad \text{(eq. 23)}$$

with the equal sign only valid if $\tilde{\rho} = \rho$.

Taking a closer look at the Hohenberg-Kohn functional, both known and unknown parts can be identified. One can write:

$$F_{HK} = T + V_{ee} \qquad \text{(eq. 24)}$$

with potential energy term:

$$V_{ee} = \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{NCL}(\rho) = J(\rho) + E_{NCL}(\rho) \qquad \text{(eq. 25)}$$

where J(*ρ*) is the classical interaction of two charge densities and $E_{NCL}(\rho)$ contains all non-classical parts. Thus, the complete energy functional can be written as

$$E[\rho] = \underbrace{T[\rho]}_{\text{unknown}} + \underbrace{J[\rho]}_{\text{known}} + \underbrace{E_{NCL}[\rho]}_{\text{unknown}} + \underbrace{\int V_{ext}\,\rho(\vec{r})\,d\vec{r}}_{\text{known}} \qquad \text{(eq. 26)}$$

The basic problem is the unknown functional for the kinetic energy. A solution to this problem was given by Kohn and Sham, they suggested to formally splitting this functional into two parts:

$$T[\rho] = T_S[\rho] + T_C[\rho] \qquad \text{(eq. 27)}$$

where the first part $T_S[\rho]$ is expressed in a one particle approach similar to Hartree-Fock, thus being well known, and the second, still unknown part contains the difference between the real functional $T[\rho]$ and the one particle term $T_S[\rho]$, and is treated, as well as the other, remaining parts of the total energy functional, which are still unknown, in an approximative way. Thus one can write:

$$\begin{aligned} E[\rho] &= T_S[\rho] + J[\rho] + V_{ext}[\rho] + E_{NCL}[\rho] + T_C[\rho] \\ &= T_S[\rho] + J[\rho] + V_{ext}[\rho] + E_{XC}[\rho] \qquad \text{(eq. 28)} \end{aligned}$$

With the so-called *exchange-correlation functional* $E_{XC}[\rho]$, which remains unknown, and the rest being well defined terms. T_S is defined as

$$T_S[\rho] = -\frac{1}{2}\sum_i \langle \phi_i | \nabla^2 | \phi_i \rangle \qquad \text{(eq. 29)}$$

where the ϕ_i are one particle wavefunctions which are determined, similar as in Hartree-Fock theory, by applying the variation principle, which leads finally to the *Kohn-Sham* equations,

$$\hat{f}^{KS}\phi_i = e_i \phi_i \qquad \text{(eq. 30)}$$

with the *Kohn-Sham operator*

$$\begin{aligned} \hat{f}^{KS} &= -\frac{1}{2}\nabla^2 + \int \frac{\rho(\vec{r}_2)}{r_{12}}\,d\vec{r}_2 + V_{XC}(\vec{r}_1) + \sum_A \frac{Z_A}{r_{1A}} \\ &= -\frac{1}{2}\nabla^2 + V_S(\vec{r}_1) \qquad \text{(eq. 31)} \end{aligned}$$

Due to the similarity between Fock operator and Kohn-Sham operator, one can solve the Kohn-Sham equations using the same algorithms as in Hartree-Fock theory, including the usage of Basis Functions and the SCF approach. Kohn-Sham orbitals are not the same as the Hartree-Fock orbitals, which implies that they also lack the physical interpretation of the Hartree-Fock one electron molecular orbitals.

In contrast to the Hartree-Fock picture, which begins conceptually with a description of individual electrons interacting with the nuclei and all other electrons in the system, density functional theory starts with a consideration of the entire electron system. In density functional theory, the total energy is decomposed into three contributions, a *kinetic energy*, a *Coulomb energy* due to classical electrostatic interactions among all charged particles in the system, and a term called the *exchange-correlation energy* that captures all many-body interactions. This decomposition is formally exact, but the actual expressions for the many-body exchange and correlation interactions are unknown. The local density approximation (LDA) turned out to be computationally convenient and surprisingly accurate. In this approximation, the exchange-correlation energy is taken from the known results of the many-electron interactions in an electron system of constant density ("homogeneous electron gas").

Within the LDA one assumes that the density functional of a N particle system can be expressed in the following form:

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r})\varepsilon_{XC}(\rho(\vec{r}))d\vec{r} \qquad \text{(eq. 32)}$$

where $\varepsilon_{XC}(\rho(\vec{r}))$ is the exchange-correlation energy per particle of a uniform gas. This quantity can be further split into two parts:

$$\varepsilon_{XC}(\rho(\vec{r})) = \varepsilon_X(\rho(\vec{r})) + \varepsilon_C(\rho(\vec{r})) \qquad \text{(eq. 33)}$$

The exchange part $\varepsilon_{XC}(\rho(\vec{r}))$ can be derived analytically and read as

$$\varepsilon_{XC}(\rho(\vec{r})) = -\frac{3}{4}\sqrt[3]{\frac{3\rho(\vec{r})}{\pi}} \qquad \text{(eq. 34)}$$

The LDA amounts to the following picture: at each point in a molecule or solid there exists a well defined electron density; it is assumed that an electron at such a point experiences the same many-body response by the surrounding electrons as if the density of these surrounding electrons had the same value throughout the entire space as at the point of the reference electron. The exchange-correlation energy of the total molecule or solid is then the integral over the contributions from each volume element. The contributions are different from each volume element depending on the local electron density. The LDA is exact for a perfect metal (which has a constant electron density) and becomes less accurate for systems with varying electron density. Remarkably, the LDA is also quite well suited for systems with a high electron density such as transition metals.

In DFT, the total electron density is decomposed into one-electron densities, which are constructed from one-electron wave functions. These one-electron wave functions are similar to those of Hartree-Fock theory. For molecular systems, DFT leads to a molecular orbital (MO) picture in analogy to the Hartree-Fock approach.

Like Hartree-Fock methods, density functional calculations provide structural, energetic, and vibrational properties. More than Hartree-Fock calculations, density functional calculations enable also the prediction of electronic, optical, and magnetic properties of condensed phases.

In general, the density functional approach is applicable to all atoms of the periodic table, provided relativistic effects are taken into account for heavier elements such as third-row transition metals, rare-earths, and actinides. Calculations at DFT level are possible for systems of the order of 100 atoms at maximum and they tend to be computationally more efficient than Hartree-Fock calculations. Its accuracy is quite consistent. Thus, the numerical precision of Hartree-Fock calculations is limited by the machine precision (typically 14 decimal figures) whereas the precision of density functional calculations is governed by the grid resolution. One could argue that if a theory has a certain intrinsic error compared with experiment, any computational approach that gives results within that error range is acceptable and any improvement in numerical precision has no physical meaning.

Density functional theory is an extremely successful approach for the description of ground state properties of metals, semiconductors, and insulators. The success of density functional theory (DFT) not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes.

In computational chemistry world several programs exist that they can afford DFT calculations (GAUSSIAN,[89] ADF,[90-92]...) the use of one instead of other depends mainly on the functionals and basis sets that they include and how the different calculations that can run are defined.

2.1.3.1. Functionals

Various approaches exist to calculate the exchange and correlation energy terms in DFT methods. These approaches differ in using either:

i) only the electron density, which are known as *local methods*: Local Density Approximation (LDA), Local Spin Density Approximation (LSDA) or Slater exchange and Vosko-Wilk-Nusair (SVWN) functionals.[89]

ii) the electron density as well as its gradients, which are known as *gradient corrected methods* or generalized gradient approximation (GGA): a) exchange: Becke88 (B), Perdew-Wang (PW91), Modified Perdew-Wang by Barone and Adamo (MPW), Gill96 (G96), b) correlation: LYP by Lee, Yang, and Parr (LYP), Perdew 86 (P86) or Becke96 (B96).[89]

In all cases, the names of these functionals refer to their respective authors and the year of publication. All combinations of exchange and correlation functionals are possible, the keywords being composed of the acronyms for the two functionals. The frequently used *BLYP method*, for example, combines Becke's 1988 exchange functional with the correlation functional by Lee, Yang, and Parr and another frequently used GGA functional is *BP86* composed of the Becke 1988 exchange functional and the Perdew 86 correlation functional. The *PW91* functional combines exchange and correlation functionals developed by the same authors in 1991.

Aside from these "pure" DFT methods, another group of *hybrid functionals* exists. The basic concept behind the hybrid functionals is to mix exchange energies calculated in an exact (Hartree-Fock-like) manner with those obtained from DFT methods in order to improve performance. Two frequently used methods are based on mixtures of the BLYP method with exact exchange energies: BHandHLYP and B3LYP. This latter is widely used in DFT calculations, and it corresponds to:

$$E_{XC} = A^*E_X(\text{Slater}) + (1\text{-}A)B^*E_X(\text{HF}) + B^*\Delta E_X(\text{Becke}) + C^*E_C(\text{LYP}) + (1\text{-}C)^*E_C(\text{VWN})^{[89]} \qquad \text{(eq. 35)}$$

It is important to note that these functionals are implemented in several programs (GAUSSIAN, ADF, TURBOMOLE,...), but they can vary somewhat.

2.1.4. Basis sets

Basis sets are defined as a group of numerical constants used in the wavefunctions. They are named by number and type of wavefunction in order to represent an atom. There are two general categories of basis sets: *minimal basis sets* (which describe only the most basic aspects of the orbitals) and *extended basis sets* (which gives a much more detailed description of the orbitals).

Basis sets were first developed by J. C. Slater, he fit linear least-squares to data that could be easily calculated. The general expression for a basis function is given as:

$$\text{Basis Function} = N\,e^{-\alpha(\vec{r}-\vec{r}_A)} \qquad \text{(eq. 36)}$$

where N = normalization constant, α = orbital exponent, r = radius in angstroms, and r_A is the reference position of the center. This expression given as a Slater Type Orbital (STO) equation is :

$$\text{STO} = \chi^{\text{STO}}(r) = P(r)e^{-\zeta r}\,Y_{lm}(\theta,\phi) \qquad \text{(eq. 37)}$$

where P(r) is a polynomial in the radial coordinate which can take on several different forms, and $Y_{lm}(\theta,\phi)$ are the harmonic spherics functions.

It is important to remember that STO applied to Hartree-Fock calculations yields tedious calculations. S. F. Boys came up with an alternative when he developed the Gaussian Type Orbital (GTO) equation:

$$\text{GTO} = \chi^{\text{GTO}}(r) = P(r)\,e^{-\alpha r^2}\,Y_{lm}(\theta,\phi) \qquad \text{(eq. 38)}$$

All basis set equations in the form STO-NG (where N represents the number of GTOs combined to approximate the STO) are considered to be "minimal basis sets". Otherwise, the "extended basis set", are the ones that consider the higher orbitals of the molecule and account for size and shape of molecular charge distributions.

There are several types of extended basis set: *double-, triple- and quadruple-zeta; split-valence, polarized sets and diffuse sets*.

Use of minimal basis sets, means that one has a single basis function corresponding to each of the occupied atomic orbitals in the atom and it is the smallest set that one can reasonable use in any calculation, and one should not expect any quantitative accuracy with such a basis. In order to have a more accurate representation, each atomic orbital is expressed as the sum of two Slater Type Orbitals (STOs). The two equations are the same except for the value of ζ (zeta). The value accounts for how diffuse (large) the orbital is. The two STOs are then added in some proportion. The constant 'd' determines how much each STO will count towards the final orbital. Thus, the size of the atomic orbital can range anywhere between the value of either of the two STOs. For example, if one takes the 2s orbital definition:

$$\Phi_{2s}(r) = \Phi_{2s}^{STO}(r,\zeta_1) + d\Phi_{2s}^{STO}(r,\zeta_2) \qquad \text{(eq. 39)}$$

where $\Phi_{2s}^{STO}(r,\zeta_1)$ is the Slater Orbital 1, $\Phi_{2s}^{STO}(r,\zeta_2)$ is the Slater Orbital 2 and 'd' is a constant. In this case, each STO represents a different sized orbital because the zetas are different. The 'd' accounts for the percentage of the second STO to add in. The linear combination then gives us the atomic orbital. Since each of the two functions are the same, the symmetry remains constant.

The triple- and quadruple-zeta basis sets work the same way, except use three or four Slater equations instead of two. The typical trade-off applies here as well, better accuracy and more time to get the results. Often it takes too much effort to calculate a double-zeta (or triple or quadruple) for every orbital. Instead, many scientists simplify matters by calculations a double-zeta only for the valence-orbital. Since the inner-shell electrons are not as vital to the calculations, they are described with a single Slater Orbital. This method is called a split-valence. A few examples of common split-valence basis sets are 3-21G,[93-98] or 6-31G.[99-104]

Sometimes orbitals share qualities 's' and 'p' orbitals or 'p' and 'd', etc... And not necessarily have characteristics of only one or the other. As atoms are brought close together, charge distribution causes a polarization effect (the positive charge is drawn to one side while the negative charge is drawn to the other) which distorts the shape of the atomic orbitals. In this case, 's' orbitals begin to have a little of the 'p' flavour, and 'p' orbitals begin to have little 'd' flavour. One asterisk (*) at the end of the basis set denotes that polarization has been taken into account in heavy atoms and two asterisks (**) means that polarization has taken into account the hydrogen atoms.

Finally, in order to consider the increase the flexibility of the basis set, the basis sets can add diffuse functions with very small exponents to have present this consideration, which are represented by the '+' signs. One '+' for the diffuse functions for heavy atoms, while '++' signals when heavy atoms and H atoms are considered.

In case of semi-empirical methods basis sets are defined as an integral part of the methods and in *ab initio* methods the user chooses the basis set. The important point of basis sets choosing is the fact that one should consider how much time it will take to run the molecule and use the basis set that will run the fastest without compromising its desired level of accuracy.

2.2. What can we do/know with theoretical calculations?

As said before, Computational Chemistry can provide a wide range of molecular properties, here are detailed a several number of them which have been used to carry out this Thesis project.

2.2.1. Geometries

The experimentalists can know the geometry of the molecules that they have synthesized if they can characterize them using several experimental techniques after a correctly purification of the sample. In the world of computational scientists, the technique applied is the well-known "geometry optimization" technique which is a method of taking rough geometric approximations and making them as exact as possible. It is a series of iterations performed on the molecule until the energy of the molecule has reached a minimum.

How does one finds the geometries corresponding to reactants, products, and transition states? Reactants and products correspond to *minima* on the potential energy surface, whereas transition-states correspond to saddle-points. These two kinds of points are illustrated on Figure 20. On a potential energy surface depending only on a few nuclear coordinates, *i.e.* for systems containing few atoms, finding these points is easy - all one needs to do is calculate the energy at *all* geometries, and pick out the special geometries.

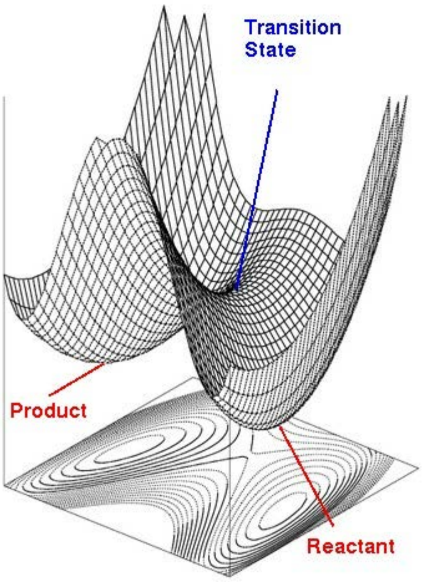


Figure 20. Potencial Energy Surface.

For larger systems such as the ones we will study, it is essential to use more powerful methods. These rely on calculating *derivatives* of the PES with respect to the nuclear positions. The way this is done relies on the fact that once one has solved the semi-empirical or Hartree-Fock or other version of the Schrödinger equation, one has a *wavefunction,* which together with the Hamiltonian, gives an *analytic* (but very complicated) expression for the energy:

$$V = \int dr_1 dr_2 ... dr_N \psi(r_1 r_2 ... r_N) \hat{H} \psi(r_1 r_2 ... r_N) \qquad \text{(eq. 40)}$$

This multiple integral over all the electronic coordinates is usually written in the following, more compact, form:

$$V = \langle \psi | \hat{H} | \psi \rangle \qquad \text{(eq. 41)}$$

This function can be differentiated with respect to the Cartesian coordinates of all the nuclei, so that one can compute *e.g.* the *gradient* of the potential with respect to all the Cartesian coordinates X_I:

$$\nabla V(X_1, X_2, ... X_{3N,nuclei}) = \left\{ \frac{\partial \langle \psi | \hat{H} | \psi \rangle}{\partial X_1} \right\} \qquad \text{(eq. 42)}$$

One can consider of the gradient of a multi-dimensional function such as the potential as being the equivalent of the *slope* for the two-dimensional function of *height* as a function of map coordinate. If one follows the slope downhill, one will eventually find a point where the slope is zero - a minimum of the potential energy, or the bottom of the nearest valley. This is the principle behind the *ab initio* (or semi-empirical) quantum-mechanical optimization of molecular geometry: Starting with a guessed geometry, one first computes the potential energy, then the gradient of the potential energy, then changes the geometry by moving "downhill" by a reasonable amount. At the new geometry, the cycle is repeated until the geometry stops changing.

Geometry optimization of Transition States also uses the gradient of the energy. However, finding transition states is harder than finding minima because they are *maxima* along one direction, and minima along all the others. Finding the transition state relies on having available the matrix of *second* derivatives of the potential energy with respect to the nuclear coordinates, also called the Hessian matrix:

$$\frac{\partial^2 V}{\partial X_I \partial X_J} = \begin{bmatrix} \frac{\partial^2 V}{\partial^2 X_1} & \frac{\partial^2 V}{\partial X_1 \partial X_2} & \cdots & \frac{\partial^2 V}{\partial X_1 \partial X_N} \\ \frac{\partial^2 V}{\partial X_2 \partial X_1} & \frac{\partial^2 V}{\partial^2 X_2} & \cdots & \frac{\partial^2 V}{\partial X_2 \partial X_N} \\ \cdots & \cdots & & \cdots \\ \frac{\partial^2 V}{\partial X_N \partial X_1} & \frac{\partial^2 V}{\partial X_N \partial X_2} & \cdots & \frac{\partial^2 V}{\partial^2 X_N} \end{bmatrix} \qquad \text{(eq. 43)}$$

This can be computed by explicit differentiation of the function given above. This is however rather computationally expensive, so in many cases, geometry optimization of transition states uses an *approximate* form of the Hessian matrix, constructed from the value of the gradient at successive points along the geometry optimization. (In fact, to speed up the optimization, even optimization of minima usually uses the approximate Hessian generated in this way, too). The geometry optimization process consists in the scheme showed in next figure :

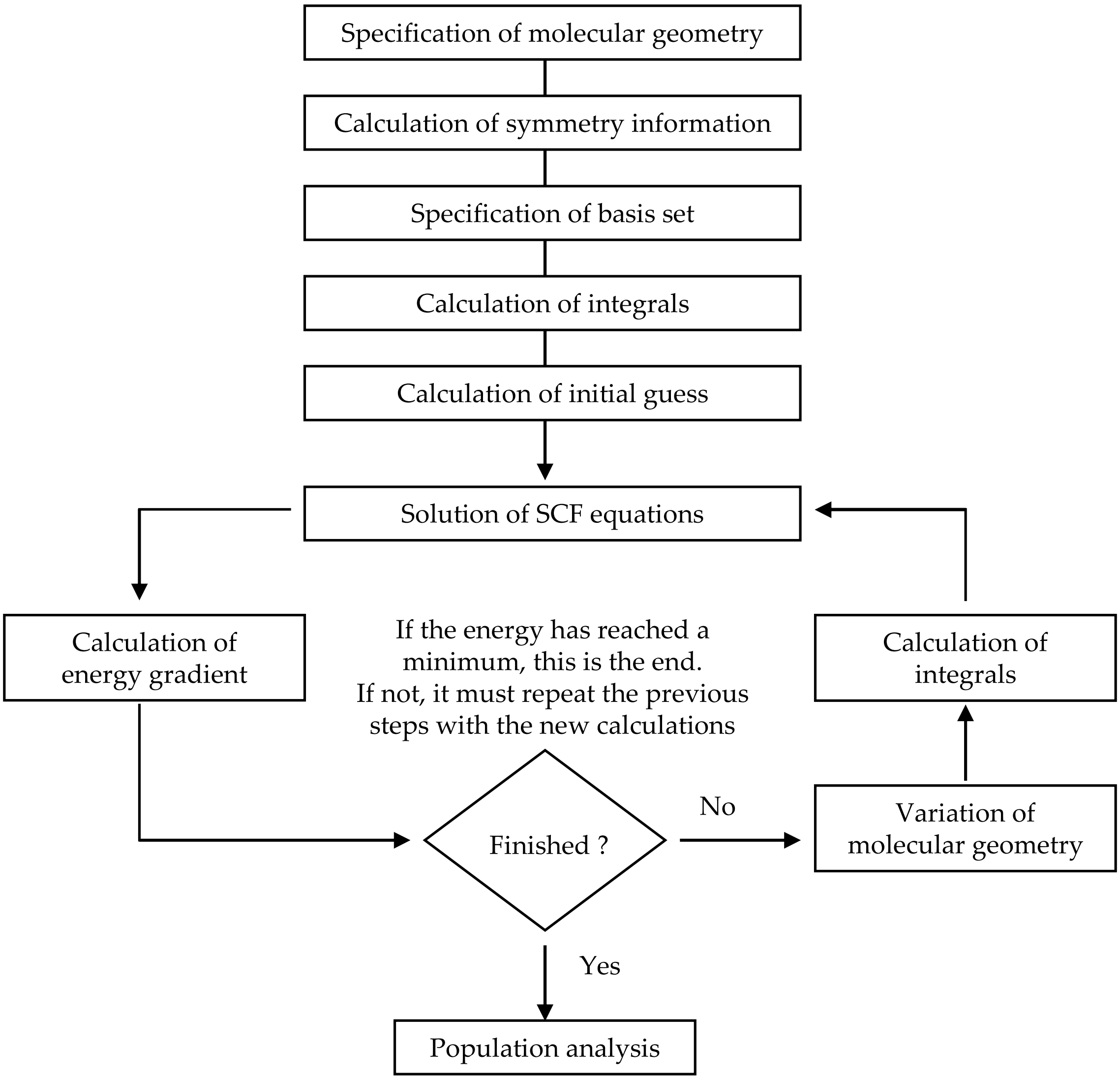


Figure 21. Geometry optimization process.

2.2.2. Energies

For each method and basis set chosen to run geometry optimization, one can know the energy value corresponding to an specific structure (reactants, transition states, intermediates or products). Sometimes SP (Single Point) energy calculations are done. They give the corresponding energy at determinate level for an specific geometry which has been optimized at other level of theory. For example, full optimization at AM1 (semi-empirical calculations gives quite accurate geometries for organic molecules) and then SP calculation at HF or DFT level are carried out.

In case of study the kinetics and thermodynamics of a reaction one can extract the reaction energy and the activation energy values in base of the energies corresponding to reactants, transition states, and products structures as next equations show:

$$\Delta E_{reaction} = E_{products} - E_{reactants} \qquad \text{(eq. 44)}$$

$$\Delta E^{\neq}_{activation} = E_{transition\ state} - E_{reactants} \qquad \text{(eq. 45)}$$

From chemical knowledge, one knows that negative reaction energy values and lower activation energy values means that the procedure of a reaction would be favourable. From Computational Chemistry one can explain why the energies have one or other values from the different contributions of several aspects to the global energy values.

Firstly, one can divide the total bond energy in terms of deformation energy (ΔE_{def}) and interaction energy (ΔE_{int})(see eq. 46), the former is the energy needed to modify the geometry of the free molecules to attain the geometry that they have in the final structure and the latter corresponds to the energy released when the two free deformed molecules are brought to the position that they have in the final structure.

$$\Delta E_{total} = \Delta E_{def} + \Delta E_{int} \qquad \text{(eq. 46)}$$

The interaction energy term can be explained as a summation of several contributions as next equation shows:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} \qquad \text{(eq. 47)}$$

The term ΔE_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments and is usually attractive. The Pauli repulsion ΔE_{Pauli} comprises the destabilizing interactions between occupied orbitals and is responsible for the steric repulsion. The orbital interaction ΔE_{oi} accounts for charge transfer (interaction between occupied orbitals on one moiety with unoccupied orbitals of the other, including the HOMO-LUMO interactions (see next section, Sec. 2.2.3.)) and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment). ΔE_{oi} can be decomposed according to the extended transition state method (ETS)[105-107] into the contributions from each irreducible representation Γ of the interacting system.[105-108] In systems with a clear σ/π separation this symmetry partitioning proves to be quite informative.

ADF program gives the possibility to analyse the bonding interactions between two fragments of a molecule with the energy decomposition scheme of the program package which is based on the Energy Decomposition Analysis method of

Morokuma[109,110] and the Extended Transition State partitioning of Ziegler and Rauk.[107] The bond dissociation energy ΔE between the two fragments is partitioned into several contributions which can be identified as physically meaningful quantitites.

From all the contributions energy terms one have more details in reference of the molecules which participate in a concrete reaction and then taking these values in consideration is possible to better understand the reasons why one isomer is more stable and feasible than other one.

The change that one reactant molecule experiences from its reactant structure until its final structure when it takes part of a product structure is possible thanks to the structure distribution of its molecular orbitals, especially of its frontier orbitals.

2.2.3. Frontier Orbitals

One characteristic of a molecule that explains a great deal about these properties is their molecular orbitals. A better or worst definition of molecular orbitals will depend on the basis set used to carry out the calculations and also on the theoretical method chosen.

All the orbitals of the molecule are important to describe the molecular structure, but the frontier orbitals HOMO (High Occupied Molecular Orbitals) and LUMO (Low Unoccupied Molecular Orbitals) have more importance because they can help to explain the reactivity and physicochemical properties of the molecule. They both play a predominant role in chemical reactions; they are the responsible of new bond formation. In Fig. 3 (see Sec. 1.1.) HOMO and LUMO shape orbitals were shown in case of C_{60} in comparison with HOMO and LUMO ethylene orbitals.

The HOMO-LUMO energy separation has been used as an index of kinetic stability for fullerenes,[111] as for other type of molecules. However, its utility is rather limited, in that a larger fullerene molecule in general has a smaller HOMO-LUMO energy separation even if is kinetically stable.

It is well-known that a small HOMO-LUMO gap implies low kinetic stability, because it is energetically favourable to add electrons to a low lying LUMO and to receive electrons from a high lying HOMO. In the case of C_{60} molecule the HOMO-LUMO gap is quite large because the HOMOs and the LUMOs are highly degenerated (5 and 3, respectively). A low LUMO energy orbital explains its electrophilic character.

In reference to frontier orbitals, different concepts have been defined. For example, Aihara reported[112-115] that the T value which corresponds to the HOMO-LUMO energy separation value multiplied by the number of carbon atoms in the system in study, seems to be preferred as an index of kinetic stability. In case of fullerenes molecules, all the fullerene isomers that have been isolated so far have a T value > 13.0. Fullerenes with a large T value have a large minimum bond resonance energy[115] meanwhile fullerenes with a very small or zero T value are also reactive. Those with T value < 11.0 are then presumed to be kinetically unstable or chemically reactive.

There are other two concepts which are defined from the HOMO-LUMO energy values, the hardness and softness, which are considered in the framework conceptual DFT.

2.2.3.1. *Hardness and Softness*

The global or absolute hardness of a chemical species is:[116]

$$\eta = ((\partial^2E/\partial N^2)_\upsilon)/2 \qquad \text{(eq. 48)}$$

where E is the electronic energy, N is the number of electrons and υ is the external potential due to the nuclei plus any other external potential. Absolute hardness is an important property which measures both the stability and reactivity of a molecule.[117-119]

A finite approximation to equation 48 yields:[116]

$$\eta = (I-A)/2 \qquad \text{(eq. 49)}$$

where I and A are the ionization potential and electron affinity, respectively. It is important to remark that this formula is independent of any molecular model, it does not depend on a quantum mechanical model for molecules, because ideally one could simply use experimental ionization potential and electron affinity values. Using the Koopmans' theorem,[120] one can determine hardness values from equation 50:[121]

$$\eta = (\varepsilon_{LUMO}-\varepsilon_{HOMO})/2 \qquad \text{(eq. 50)}$$

Large band gaps have been associated with stable structures, and according to *the maximum hardness principle*: "molecules will arrange themselves to be as hard as possible",[118] what means that high hardness values correspond to stable and less reactive molecules.

At the same time global softness has been defined as the inverse of the global hardness:[122, 123]

$$S = 1/\eta \qquad \text{(eq. 51)}$$

In consequence large band gaps will be associated with lower softness values. This conceptual DFT molecular property was empirically shown to be proportional to the polarizability of a system.[124, 125]

One then has another possible stability criteria when classify a molecule in base of its hardness or softness.

2.2.4. Aromaticity Analysis

Aromaticity is a key concept in physical organic chemistry. It has been shown to be a useful quantity in the rationalization of structure, stability and reactivity of many molecules. The structure and reactivity of aromatic compounds are areas where theory and experiment meet closely and symbiotically to provide new insights.

This property is associated with the cyclic delocalization of electrons, resulting in extra stabilization in the case of aromatic compounds and destabilization in case of antiaromatic compounds.

Several criteria have been put forward in attempts to rationalize and quantify this property. The most important requirements that a criterion of aromaticity should meet are as follow:[126]

i) it must be directly related with some known physicochemical effect regarded as a manifestation of aromaticity and this effect must be experimentally quantifiable.

ii) it is essential that fulfillment of the chosen criterion should indicate the presence of such properties in a given compound as are commonly regarded to be the main attributes of aromaticity.

Of many criteria for aromaticity proposed until these days, the most characteristic measures of aromaticity have proven to be: geometric, energetic, electronic and magnetic criterias. There is no necessary relationship between them. Bond lengths usually alternate between single and double for non-aromatic or antiaromatic systems, while aromatic systems have nearly equal bond lengths. Kinetic stability is a function of the energies of transition states for reactions, and thermodynamic stability depends upon the reference molecules. Magnetic properties arise from the diamagnetic ring currents of aromatic systems.[127]

For quantification of the three common aromaticity criteria, the following measures are used:

i) Geometric: bond length alternation can be quantified in base of the number of delocalized C-C bonds in the system (for instance the harmonic oscillator model of aromaticity (HOMA) index, defined for Kruszewski and Krygowski,[128, 129] can be used).

ii) Energetic: aromatic stabilization energy is used to access the degree of stabilization (an usual energy-based index is the aromatic stabilization energy (ASE) index).[130-132]

iii) Electronic: based on the delocalization/localization indices lastly defined, the *para* delocatization index (PDI).[133, 134]

iv) Magnetic: the nucleus independent chemical shift (NICS) is a simple aromaticity probe when the chemical shift at the center of the ring is calculated (see next section, Sec. 2.2.4.1.)

In this Thesis, magnetic criterias have been used basically to analyse the aromaticity of different derivatives of C_{60}, for this reason here they will be more extendly explained.

Aromaticity can be defined as the ability of a compound to sustain an induced ring current; these compounds are then called diatropic, otherwise antiaromatic compounds are called paratropic. Although ring currents are not directly observable, their existence has been inferred from magnetic measurements such as ^{1}H NMR chemical shifts [$\delta(^1H)$], magnetic anisotropy ($\Delta\xi$) and exaltation of isotropic magnetic susceptibility (Λ). These properties, which are determined by integration of the induced current density, are of considerable practical and theoretical interest.[135]

As said before, several methods can be use to measure it. The most important ones are based on NMR chemical shifts and diamagnetic susceptibilities. GAUSSIAN program lets to predict NMR shielding tensors and magnetic susceptibilities using the Hartree-Fock method, all DFT methods (it is important to remark that not all current functionals include magnetic field dependence, and so the DFT methods usually do not provide systematically better NMR results than Hartree-Fock) and the MP2 method.[89]

The main problem in magnetic properties calculation using finite basis sets is the gauge-invariance problem. This simply means that the results of such a calculation depend on the chosen gauge-origin and are not invariant with respect to gauge transformations as required by exact theory. A trivial solution to the gauge-invariance problem would be the use of very large basis sets in order to minimize the gauge error, but this approach, due to large computational costs, is limited to small molecules. GIAO (Gauge-Independent Atomic Orbital)[136-140] and CSGT (Continuous Set of Gauge Transformations)[141-143] methods were defined to solve this problem, and they are usual applied to carry out magnetic properties calculations, not only for small molecules. The GIAO method transforms the gauge of the basis set functions to the position of their nuclei, whereas the CSGT method defines a gauge which depends on the position where the induced current is to be calculated.

Depending on if one looks for a global or a local aromaticity analysis, different kind of calculations should be done. Diamagnetic susceptibilities to analyse the global aromaticity of the systems and NICS, HOMA or PDI values calculation to deep analyse the local aromaticity.

It is important to remark that analysis of aromaticity considering the several possible criterias can provide difference in the prediction of the more or less aromatic character of a molecule, ring,… The aromaticity has a multidimensional character and for that, one can compare between systems on base on a same criteria and if several criterias are used, try to understand the reasons for discrepancies between results, depending on the systems studied.[144]

2.2.4.1. *Global Aromaticity analysis: Diamagnetic susceptibilities*

The diamagnetic susceptibility is the dimensionless quantity describing the contribution made by a substance to the total magnetic flux density present when it is subjected to a magnetic field.

In 1996, Jiao and Schleyer said: "compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic electron delocalization also may result in bond lenght equalization, abnormal chemical shifts, and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilization. Those compounds with exalted paramagnetic susceptibility may be called antiaromatic".

Concerning the diamagnetic susceptibilities, two factors are important when measuring a compound's aromaticity: the anisotropy and the exaltation. Aromatic molecules were found to possess high diamagnetic susceptibility anisotropies $\Delta\chi$, i.e., large differences between the perpendicular and average in plane component of the diamagnetic susceptibility:

$$\Delta\chi = \chi_{zz} - (\chi_{xx} + \chi_{yy}) \qquad \text{(eq. 52)}$$

where χ_{xx}, χ_{yy} and χ_{zz} are the three principal components of the diamagnetic susceptibility.[145-147]

Diamagnetic susceptibilities values become useful to predict a higher o lower aromatic character of a structure.

2.2.4.2. *Local Aromaticity analysis: NICS*

The magnetic behavior of cyclic conjugated π-electron systems is increasingly employed to access aromaticity and antiaromaticity.[126, 147-149]

The diamagnetic and paramagnetic effects of the ring currents associated with aromatic and antiaromatic compounds (i. e., shielding and deshielding of nuclei) are measured by simple and efficient criterion vis. nucleus-independent chemical shift (NICS).[150]

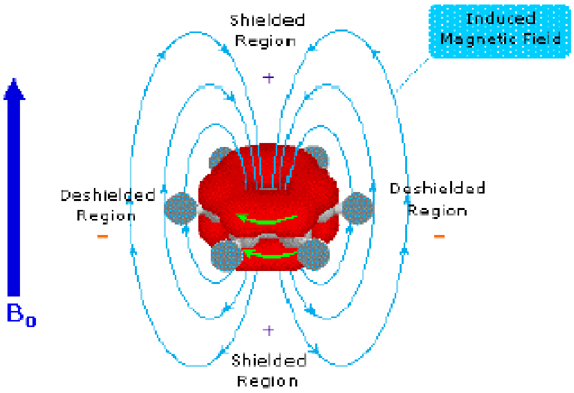


Figure 23. Shielding and deshielding regions.

Since its introduction in 1996,[150] the "NICS" index has been widely used to characterize aromaticity and antiaromaticity of rings,[151-155] clusters,[81,156-159] transition states,[160-165] transition metal complexes,[166] etc... with cyclically delocalized or localized electrons.

Based on computed magnetic shielding, the NICS data are reported[81,146,150-158,160-165] with reversed signs in order to conform to the NMR chemical shift sign conventions (negative upfield and positive downfield). NICS are computed at selected points inside or around molecules, typically at ring centers and above. Significantly negative (i.e., magnetically shielded) NICS values in interior positions of rings or cages indicate the presence of induced diatropic ring currents or "aromaticity" whereas positive values (i.e., deshielded) at each position denote paratropic ring currents and "antiaromaticity".

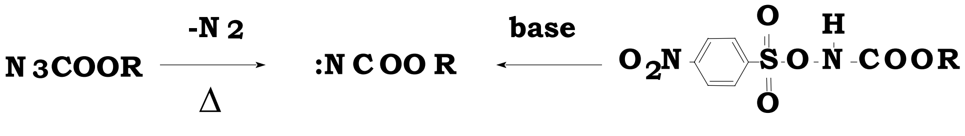
3. OBJECTIVES

The study of Fullerenes Chemistry at experimental and theoretical level has become an important field in chemistry research. Experimental processes have provided a large number of derivatives of C_{60} molecule, as it has been showed briefly in Sec. 1, with the purpose to have new molecules with specific properties and consequently with large application possibilities. Theoretical calculations should be in consideration as usual tool for chemists, they can help to better explain preferences in reactivity and reaction mechanism, in base of the electronic structure of the molecules. For this reason, this Thesis project studies some single and multiple additions to C_{60}, in order to better clarify, using computational techniques, several points which are not understandable or not enough clear from the results that experimental chemists get when they synthesize some of the C_{60} derivatives, paying an especial attention to understand the preferential addition pattern in case of the additions to C_{60} studied.

3.1. Single addition

Addition of N to C_{60} can take place mainly by two possible vias of synthesis, as said in Sec. 1.2.2.1, reaction with oxycarbonylnitrenes directly ([2+1] cycloaddition) or with azides firstly (1,3-dipolar addition ([3+2] cycloaddition)) and consequently N_2 extrusion. Both vias of synthesis provide the monoimino-[60]fullerenes which are considered as intermediates precursors of a kind of heterofullerenes: the nitrogenfullerenes (which one or several carbon atoms are replaced by nitrogen atoms), compounds of characteristic properties, and with remarkable applications.

In case of *directly oxycarbonylnitrene addition*, this addend molecule can be generated *in situ:* a) from thermally decomposition of an azide compound or b) from α-elimination, catalyzed by base, of some derivative of O-4-nitrophenil-sulfonylhydroxamic acid, as Figure 24 shows.



Decomposition of azidoformates

α-elimination of O-4-nitrophenylsulphonylalkyl-hydroxamic acid

Figure 24. Two possible vias of *in situ* generation of oxycarbonylnitrene.

The experimental results have showed that the main product of addition is the adduct [6,6]-closed independently of which process of oxycarbonylnitrene generation is considered, likewise approximately a 10% of the product corresponds to [5,6] regioisomer adduct. As said in Sec. 1.2.1., mainly the addition reactions take place in the [6,6]-bond, and the formation of adducts resulting from the addition to [5,6]-bonds of C_{60} is unusual, for that reason it is necessary to find a justification for its formation in a non negligible quantity. To explain this mixture of isomers, experimentally two different mechanisms have been proposed that takes into account the two possible states (the singlet or triplet state) of oxycarbonylnitrene molecule added to C_{60}. In the first mechanism proposed, the product [5,6] is formed thanks of the direct attack of singlet oxycarbonylnitrene to a [5,6]-bond of C_{60}, meanwhile the second mechanism explains the formation of [5,6]-adducts, with a previous intermediate formation after triplet oxycarbonylnitrene addition, and then both the addition to [6,6]- or to [5,6]-bond can be possible.

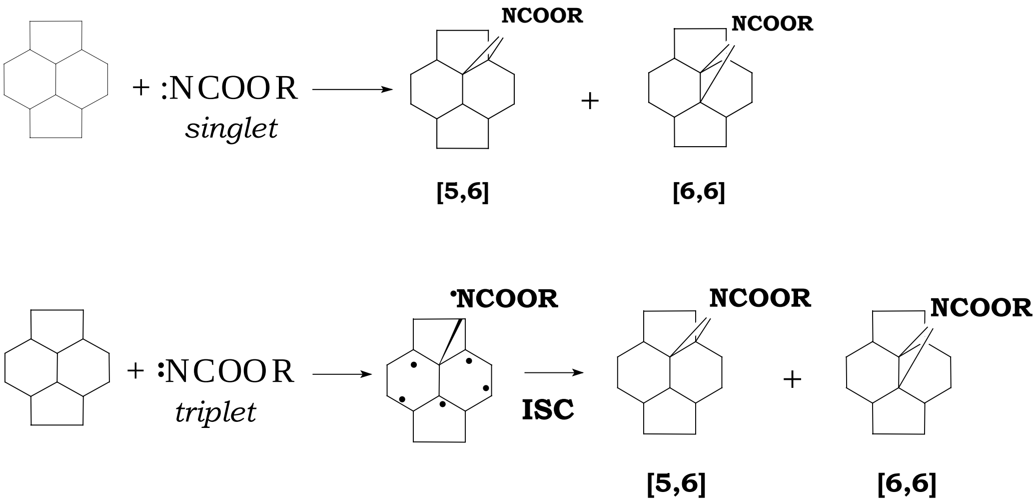


Figure 25. Proposed mechanisms to explain the formation of [5,6]- and [6,6]-monoimino-[60]fullerenes.

In case of *firstly azide addition and consequent N_2 extrusion*, the first products of reaction are the resulting from the 1,3-dipolar cycloaddition of an azide to the C_{60}, triazolinic adducts, and then the elimination of N_2 molecule from the triazolinic structure provides the final formation of monoimino-[60]fullerenes. This first part of the reaction has been considered as a one step process because of the low polarity of the transition state structure[167, 168] and with one only type of product formation, [6,6]-triazolinic adduct.[27, 33, 37, 41, 169-180] Otherwise, the subsequent elimination of N_2, thanks to a thermal decomposition (100°C),[181] provides mainly [5,6]-aziridinicadduct. As in case of direct oxycarbonylnitrene addition to C_{60}, the formation of [5,6]-adduct is few understandable, if one consider the major tendency found in additions reactions to C_{60}.

On base of this knowledge from the experimental point of view, the purpose is to describe the mechanism of the two main possible vias of monoimino-[60]fullerene formation, considering as a model of nitrene addend molecule the simple $NCOOCH_3$ (in case of direct oxycarbonylnitrene addition reaction study) and $N_3CH_3 \rightarrow NCH_3$ (in case of first 1,3-dipolar addition and subsequent N_2 elimination reaction study) species.

The full optimization of all reactants, transition states, intermediates and products should be useful to understand the kinetics and thermodynamics of the reaction, and a further analysis of the geometries of the structures (bond distances, angles…) and the orbital distribution of the atoms which participate more directly in the cycloaddition, as well as a decomposition of the energy will provide different ways of justification of a one or other mechanism in base of geometric, electronic and energetic point of view, and give explanation to the experimental results.

Comparison of the stabilities of the different [5,6]- and [6,6]-adducts for a series of $C_{60}X$ systems (where X= CH_2, NH, NCH_3, NCOOH, PCH_3 and O), would be useful to know if the preference for a [5,6]- or [6,6]-addition depends on the susbstituent or on the heteroatom bridged between the two C atoms attacked in C_{60} structure.

Addition of C to C_{60} via direct carbene addition is the most extended process of methanofullerenes synthesis, as said in Sec. 1.2.2.2., and provides [6,6]-adducts as a result of the carbene attacks preferently to [6,6]-bonds of C_{60}. The reactivity of carbene species is widely well-known in the field of organometallic chemistry as they are intermediates in many chemical reactions. They are potencial ligands of a low valent group VI to VIII transition metal, in this case they form the so-called Fischer or Schrock carbene complexes, where the central carbene carbon atom is linked through a formal metal-carbon double bond.

The interest in this kind of C_{60} derivatives was not related with mechanism explanations in this case. The purpose of studying a series of $C_{60}CHR$ (where R= H, CH_3, $CH{=}CH_2$, Ph, $C{\equiv}CH$, OH, OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$) would be on one hand, try to know the possible influence of a different donor or acceptor R substituent of the carbene fragment in the stability of the systems (the selected series of carbenes would be firstly well studied at theoretical level in order to analyse their geometric, energetic and electronic characteristics when they form part of a Fischer carbene complex of Chromium, for which a large knowlegde at experimental level exists, so theoretical and experimental results can be contrasted). And on the other hand, how acidic is each structure in comparison with the series of substituted hydrofullerenes, $C_{60}HR$, with the same R substituents. As it is well-know from experimental results, $C_{60}HR$ systems are more acidic than $C_{60}CHR$ systems, but our aim was to find reasons to explain this behaviour, trying to know what happens with the negative charge after deprotonation, if it remains more located in the same C atom where H atom was bonded or it is delocalized along the C_{60} structure. For this reason, aromaticity analysis would be useful apart from geometric, electronic and energetic analysis.

Full optimization of all the acid and corresponding basic structures ($C_{60}CHR$, $C_{60}HR$ and $C_{60}CR^-$, $C_{60}R^-$) will provide the relative stability between systems of the same series and between different series, and from the energy analysis we will be able to classify the acidic character of these series of systems. Calculations of diamagnetizabilities and NICS (for each 5- and 6-membered ring center of C_{60}), will be necessary to evaluate global and local aromaticity, respectively.

3.2. Multiple addition

Addition of F to C_{60} takes place in two main conditions, fluorination with fluorine gas, or with metal fluorides as said in Sec. 1.2.3.2.1. At experimental level, the control of a multiple addition of F radicals to C_{60} becomes difficult for both processes of synthesis of fluorofullerenes because they lead to a wide range of products. It is well-know from the experimental results that always addition of F takes place preferentially at [6,6]-bonds of C_{60} molecule and from the products which have been able to be experimentally characterized, two possible addition pattern of F addition to C_{60} have been defined. It is possible to consider that some products follows the ‘S’ and other ones the ‘T’ addition pattern (see Sec. 1.2.1.) to finally provide $C_{60}F_{20}$ and $C_{60}F_{18}$ fluorofullerenes, respectively.

There should be a reason to explain this difficult kinetic control, and aromaticity could play an important role in this addition process. The addition of F takes place at [6,6]-bonds of C_{60}, which have a more double character behaviour in comparison with the other C-C bond in C_{60}, the [5,6]-bonds. Moreover, continuous addition of F to C_{60} takes place in adjacent [6,6]-bonds, that means that the F addition takes place in bonds where the electrons are more localized, because when one [6,6]-bond in one hexagon of C_{60} molecule is attacked, then the other two [6,6]-bonds of the same hexagon show a higher localization of its π electrons. The continuous addition of F radicals to the [6,6]-bonds of C_{60} would increase the localization of the π electron system of C_{60} on the neighbourhood of addition site, and the increasing in the number of F atoms added leads that the resulting products become more aromatic and the difficulty of the kinetic control would be explained for the reason that the chemistry of fullerenes is suggested to proceed in such a manner that the reaction products become as aromatic as possible.

Calculations of NICS values for each of the 5- and 6-membered rings of the series of $C_{60}F_n$ fluorofullerenes (series S (n= 2, 4, 6,…, 20) and series T (n= 2, 4, 6,… , 18)) could help to understand the pattern of the attacks that had these two possible series of fluoroderivatives of C_{60}. We expect that from the knowledge of local aromaticity values, one could predict the best route (series S or T) for fluorination. At the same time, diamagnetic susceptibility calculations will give us a reference of global aromaticity of the systems, and confirm that the uncontrolled multiple addition of F has some relation with the aromatic character of the different fluorofullerenes.

Addition of O to C_{60} can be possible with a range of methods, as was indicated in Sec. 1.2.2.3., and like fluorofullerenes the resulting derivatives of addition of O to C_{60} shows multiple addition that difficults the control of number of O atoms added and the low functionalized systems isolation. In contrast with fluoro- or hydrofullerenes derivatives, the addition pattern of the series of epoxide fullerenes seems to be not much clear, mainly because of its difficulty in isolation, one can not know nowadays from the experimental results which is the addition pattern describing the multiple addition of O to C_{60}.

From the global and local aromaticity analysis in case of $C_{60}F_n$ series studied previously, one could get more information related with the behaviour of C_{60} cage when it is subjected to a multiple addition and in this case one has some experimental results that support and confirm the theoretical results. Following the same analysis of NICS values and diamagnetic susceptibilities calculation, it seems to be possible to predict which could be the addition pattern for O addition to C_{60}.

In summary, these Thesis projects studies the next points in relation with the C_{60} functionalization:

1) Direct cycloaddition of oxycarbonylnitrene ($NCOOCH_3$) to [5,6]- or [6,6]-bond to C_{60} to give monoimino-[60]fullerenes. Understand why mainly [6,6]-adduct is formed but also a 10% of product corresponds to [5,6]-adduct, contrary to what is expected. Kinetic and Thermodynamic analysis.

2) 1,3-dipolar cycloaddition of an azide (N_3CH_3) to C_{60} to [5,6]- and [6,6]-bond to give triazolinic adducts, and subsequent N_2 elimination which provides monoimino-[60]fullerenes, mainly [5,6]-adduct. Kinetic and Thermodynamic analysis and try to explain the mechanism of reaction.

3) Comparison of [5,6]- and [6,6]-adducts relative stabilities for $C_{60}X$ systems (X= CH_2, NH, NCH_3, NCOOH, PCH_3 and O) in order to find if there is some dependence with the heteroatom or size in addend molecule.

4) Study a series of twenty five different Fischer carbenes, $(CO)_5Cr{=}C(R)X$ (R= H, CH_3, $CH{=}CH_2$, CCH, Ph and X= H, OH, OCH_3, NH_2, $NHCH_3$), to analyze the influence of different heteroatoms and several π-donor substituents on the electronic structure of the complex. A comparison of their different structural and electronic characteristics (bond distances and angles, frequencies and components of the interaction energy). Carry out a charge decomposition analysis (CDA) to quantify the relative importance of donation and back-donation between the carbene and Chromium fragments.

5) Comparison between $C_{60}CHR$ and $C_{60}HR$ systems (R= H, CH_3, $CH{=}CH_2$, Ph, $C{\equiv}CH$, OH, OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$) based on their geometric, electronic and energetic characteristics. Analysis of their acidic character (deprotonation process) and their aromatic character. Following the previous geometric, energetic and electronic carbene analysis, understand the influence of the substituent.

6) Global and local aromaticity analysis for the series of fluorofullerenes $C_{60}F_n$, S and T addition patterns considered, in order to find a possible explanation in terms of aromaticity for the addition patterns in this kind of C_{60} derivatives.

7) From the results obtained in case of addition patterns of fluorofullerenes, try to predict possible addition patterns for the O addition to C_{60}.

These different studies have provided a number of results which are summarized in the next section. Then Sec. 5 gathers the articles which have been written about these studies. Finally in Sec. 6 the most remarkable conclusions that one can extract from all the results obtained of these studies proposed are collected.

4. RESULTS AND DISCUSSION

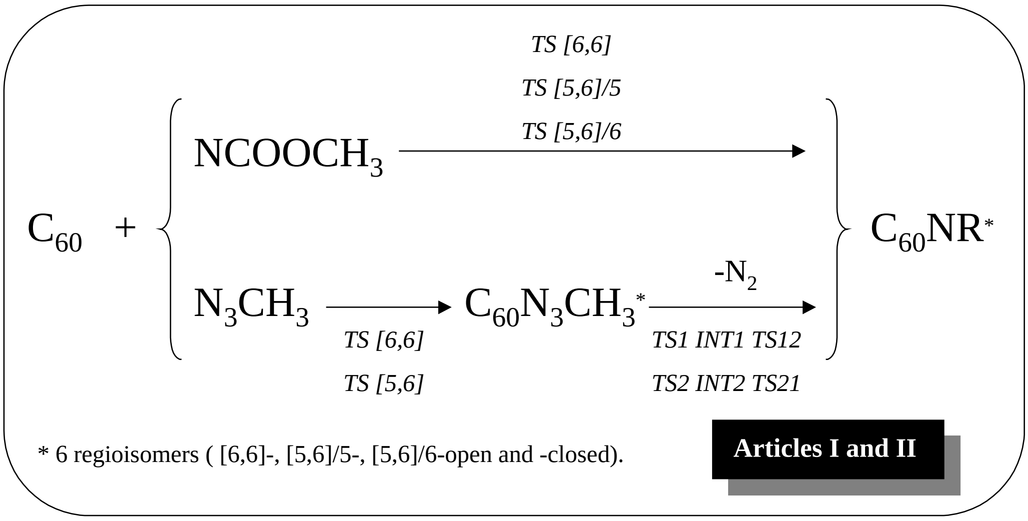
This section has been written in order to give to the reader a general idea of all the results obtained for this Thesis from the different projects considered to carry on described in previous section. An accurate reading of each article, see next section, is necessary to known more details about them, especially respect to Computational Methodology used for each case. The size of the systems studied prevents to use *ab initio* molecular quantum mechanical methods to perform geometry optimizations. Therefore, full geometry optimizations without symmetry constraints have been carried out with the AM1 semi-empirical method for all reactants, intermediates, TSs and products structures). Also, the molecule pictures and tables are not reproduced again in this section.

With this summary of results one pretends to remark the most interesting aspects for each C_{60} derivatives studied and emphasizes the importance of this kind of Computational Chemistry studies for better understanding the experimental results.

Firstly the discussion of results related with the C_{60} derivatives provided by just a single addition to C_{60} is given, and secondly, the analysis about the multiple addition type of functionalization of C_{60} is presented.

4.1. Single additions to C_{60} studies

4.1.1. [5,6]- and [6,6]-Monoimino-[60]fullerenes formation, $C_{60}NR$



* 6 regioisomers ([6,6]-, [5,6]/5-, [5,6]/6-open and -closed).

The addition of N to C_{60} was studied considering the two possible synthetic routes to monoimino-[60]fullerenes formation. As said in Sec. 1.2.1.1., they can be obtained through a 1,3-dipolar cycloaddition of organic azides to C_{60} followed by the thermal N_2 extrusion or by direct [2+1] cycloaddition to C_{60} of oxycarbonylnitrenes generated *in situ* either by thermal elimination of N_2 from organic azides or by base-catalyzed α-elimination of O-4-nitrophenylsulfonyl-hydroxamic acid derivatives.

Firstly, the [2+1] cycloaddition of the oxycalbonylnitrene $NCOOCH_3$ to the cage (see the article in Sec. 5.1.) was studied and then the mechanism of the addition reaction of the alkyl azide N_3CH_3 to C_{60} with the subsequent N_2 extrusion (see the article in Sec. 5.2.).

The six possible regioisomers ([6,6]-open or closed and [5,6]/5-, [5,6]/6-open or closed) where fully optimized at AM1 for both vias of synthesis, $C_{60}NR$ (R= $COOCH_3$ and CH_3). The so-called open structures present a C-C bond breaking when the addend molecule attacks this C-C bond, and its length bond changes from 1.385 or 1.458 Å in case of [6,6]-bond or [5,6]-bond respectively, to over 2.20 Å. Meanwhile the so called closed structures keep the C-C bond although it becomes somewhat elongated to 1.62 or 1.56 Å in the case of [6,6]-bond or [5,6]-bond attacked, respectively.

From the enthalpies of formation of reactants (C_{60}, NR), TSs ([6,6]-attack or [5,6]-attack (/5 and /6 considered), and adducts (6 regioisomers of $C_{60}NR$), it is found that the [6,6]-closed and [5,6]-open isomers for both NR addends studied have a similar stability, although the [5,6]/5 isomer is more stable. The [6,6]-open and [5,6]-closed structures are clearly destabilized with respect to the [6,6]-closed and [5,6]-open isomers, the reason being that they require the introduction of unfavourable double bonds in 5-membered rings (see Fig. in Sec. 5). At the B3LYP/6-31G**//AM1 level of theory , the [6,6]-, [5,6]/5-, and [5,6]/6-attacks have similar energy barriers, the [5,6]/5-attack being somewhat favoured. For all these three TSs, the bond lengths of the two N-C forming bonds are rather large (3.32 and 3.74 Å) and the deformation enthalpies of C_{60} and $NCOOCH_3$ are close to zero. Thus their geometry corresponds clearly to TSs with reactant-like character and concerted and asynchronous nature.

In case of direct addition of an oxycarbonylnitrene like $NCOOCH_3$, two mechanisms of addition where considered depending on the state of the addend molecule, singlet or triplet. The $NCOOCH_3$ species has a triplet ground state that is 13.1 kcal/mol more stable than the lowest-lying singlet state at the B3LYP/6-31G** level. Nonetheless, triplet $NCOOCH_3$ species generated under thermal conditions from N_3COOCH_3 are probably inaccessible, since one can expect that the crossover from the singlet to the triplet surface through spin-orbit coupling must be difficult for systems of such small size. This, together with the low barrier for the direct attack of singlet $NCOOCH_3$ to the [5,6]-bond of C_{60} prompt us to conclude that the direct singlet nitrene addition to a [5,6]-bond is most likely responsible for the obtention of the *ca.* 10% of closed [5,6]-aza-bridged regioisomer obtained in the cycloaddition of oxycarbonylnitrenes to C_{60}.

The present results show that the reactivity of [5,6]- and [6,6]-ring junctions of C_{60} are similar, at least as far as the nitrene addition is concerned. In fact, our results slightly favour the [5,6]-attack both kinetically and thermodynamically. This conclusion is surprising since it is commonly said that the [6,6]-bonds in fullerenes are more reactive than the [5,6]-ring junctions.

In case of the two steps process to get the monoimino-[60]fullerene, the 1,3-dipolar addition of N_3CH_3 azide with the subsequent N_2 elimination, a more detailed study was done. Firstly 1,3-dipolar addition of N_3CH_3 to C_{60} was analysed, and secondly the N_2 elimination from the triazolinic products to the monoimino-[60]fullerene formation.

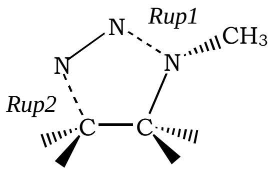
The most thermodynamically and kinetically stable product of the 1,3-dipolar addition was found to be the [6,6]-closed regioisomer confirming that the [6,6]-bond is more reactive than [5,6]-bond. The 1,3-dipolar species such N_3CH_3 have two possible resonance structures depending on if the first and the third N atoms have the positive or the negative charge located. For this reason, four possible TSs structures were studied (considering: 1) attack at [6,6]-bond or [5,6]-bond, and 2) different distribution of the positive and the negative charge on the 1,3-dipolar azide). The attack at a [6,6]-bond showed a lower barrier and concretely the addition of N_3CH_3 molecule was predicted to follow an addition more favourable when the negative charge of the 1,3-dipolar species is located on the N atom substituted by a methyl group, the so called attack II type. A further analysis of the TSs structures showed that the deformation energy necessary to lead the interaction between N_3CH_3 and the C_{60} molecule is larger when the attack takes place at a [6,6]-bond, specially for the higher energy needed to close the NNN angle of N_3CH_3 azide, but this contrast with the fact that the interaction energy is higher too.

Indeed, the main difference comes from the interaction energy that favours the [6,6]-attacks by more than 20 kcal/mol. This interaction energy has two main components, namely, the steric repulsion (Pauli repulsion + electrostatic interactions) and the orbital relaxation (polarization + charge-transfer effects). The results of this energy decomposition showed that the steric repulsion was more smaller for the [5,6]-attack by only 3.5 kcal/mol, whereas the orbital relaxation term favours the [6,6]-addition by 21.1 kcal /mol because of better overlaps between the frontier orbitals in the [6,6]-attack, especially between those involved in the charge transfer from C_{60} to N_3CH_3. The main reason then for the preference of the [6,6]- over the [5,6]-attack is the more favourable orbital interactions through better overlaps between frontier orbitals in the [6,6]-addition. Therefore, for the study of the next reaction step (the N_2 extrusion from the triazoline intermediate), only the closed [6,6]-triazoline intermediate was considered.

Experimentally at slightly higher temperatures (100°C), thermal elimination of N_2 takes place, leading almost exclusively to the [5,6]-open product. In contrast, photolysis of the triazoline intermediate produces an isomeric mixture of open [5,6]- and [6,6]-monoimino-[60]fullerene.

As done in previous step, all possible TSs structures were considered in base on the breaking bond order.

A total of four different TSs were described corresponding two of them to the so called via1 TSs (TS1 and TS12) and two other two to the called via 2 TSs (with vice versa breaking bond order, TS2 and TS21), see Fig. 26.



via 1 : Rup 1 , Rup 2
via 2 : Rup 2 , Rup 1

Figure 26. Breaking bond order nomenclature.

The localization of these TSs structures was possible, and then using the IRP procedure we confirmed the existence of one intermediate between each pair of TSs structures of each via, 1 or 2. The intermediate structures between TS1 and TS12 and between TS2 and TS21 were located at the AM1 level, too. Both of second TSs were connected to the open [5,6]-aziridine adduct. The geometry of these TSs already suggest that the thermal N_2 loss occurs simultaneously with the formation of the new C-N bond. One should expect that delocalization of spin density within the 6-membered ring as the loss of N_2 proceeds may result in the synthesis of both [6,6]- and [5,6]-adducts. However, the evolution of TS12 or TS21 along the IRP shows that the N_2 molecule sterically prevents the nitrene substituent form adding to the originally attacked [6,6]-bond and forces the nitrene substituent to attack either of the two adjacent [5,6]-ring junctions. This is in agreement with experimental findings and in line with previous mechanistic suggestions.

These two studies about mononimino-[60]fullerene formation show how both [6,6]-closed and [5,6]-open adducts are the more stable, and explain the preference for [5,6]-open aziridine formation. In order to know if different addends molecule (X= CH_2, NR, PCH_3, and O) or different substituents of the addend (R= NH, NCH_3, NCOOH and $NCOOCH_3$) could have an influence on the stability between the possible isomers the third study was carried out.

4.1.2. Stabilities of [5,6]- and [6,6]-$C_{60}X$ (X=CH_2, NH, NCH_3, NCOOH, PCH_3 and O)

$$C_{60} + X\ (= CH_2, NH, NCH_3, NCOOH, PCH_3 \text{ and } O) \longrightarrow C_{60}X^*$$

* 6 regioisomers ([6,6]-, [5,6]/5-, [5,6]/6-open and -closed).

Article III

In general all $C_{60}X$ systems studied show quite similar stabilities between [5,6]-open and [6,6]-closed, and in all cases studied, except for X= PCH_3, the [5,6]-open adducts are more stable than the corresponding [6,6]-closed. The position of the substituent, face up the hexagon ([5,6]/6) or the pentagon ([5,6]/5), does not have relevant influence on the stability of open or closed [5,6]-adducts studied, which means that it is not necessary to take in consideration, a simple "umbrella" movement can provide the two isomers.

A geometric analysis shows that the closed structures present a less significant elongation of the bond length of the C-C bond attacked from 1.55 to 1.64 Å depending on the substituent than in case of open structures which range from 2.06 to 2.27 Å.

The relative stability of the open [5,6]-isomer increases slightly in the order CH_2 < O < NR. Noteworthy, the energy decomposition values, the deformation and interaction energy terms, show that the increase in the deformation energy when going from [6,6]-closed to [5,6]-open isomers is more important in the order O > NR > CH_2, mainly because the decrease of deformation energy of the closed [6,6]-isomer in the same order. On the other hand, the interaction energy when going from closed [6,6]-isomer to open [5,6]-isomer becomes more favourable in the reverse order, O < NR < CH_2.

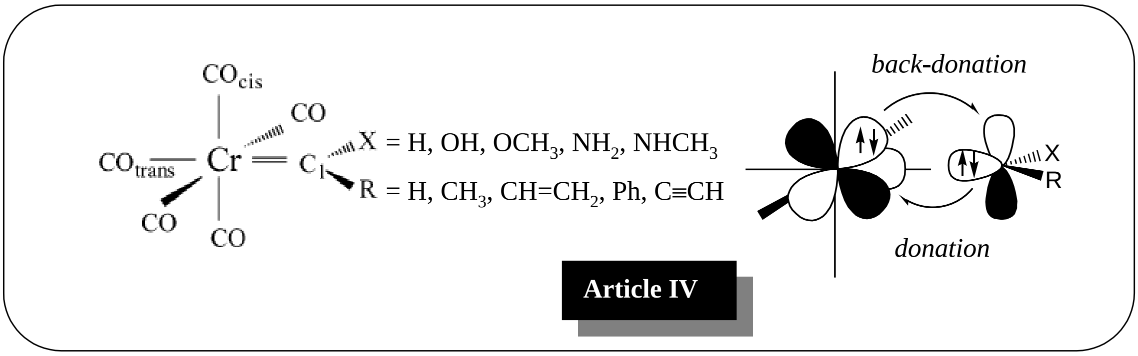
Comparison between the different R substituents of NR derivatives show that bulky substituents destabilize the [5,6]-open isomers. This is the result of somewhat smaller total deformation energies and more importantly of larger interaction energies as a consequence of smaller Pauli repulsion in the NH systems compared to NR systems with bulkier R substituents. Favourable interaction energy can be explained by the fact that the distance between the N atom and the centre of the C-C bond attacked in the open structures is shorter for NH systems compared to bulkier addends, and that favours better overlaps among the frontier orbitals and stabilizes the open structures as compared to the closed ones.

Moreover, it was observed that the main effect of increasing the electron-withdrawing character of the substituent is to increase the relative stability of the [6,6]-open isomer, and the relatives stabilities of the rest of the regioisomers remains almost constant.

4.1.3. Comparison between substituted hydrofullerenes and methanofullerenes. Deprotonation process of $C_{60}HR$ and $C_{60}CHR$

The aim of this fourth project was to compare the two series of systems, $C_{60}HR$ and $C_{60}CHR$ (R= H, OH, OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$, CH_3, $CH{=}CH_2$, Ph and C≡CH), in order to know in which way the direct addition of a different functional group to the C_{60} affects the cage, $C_{60}HR$, in comparison with the addition of a carbene having this functional group as a substituent of the carbene, *i. e.* the methanofullerenes, $C_{60}CHR$. One would like to check how influential could be the donor or acceptor character of this R substituent, and to know the influence of R with respect to the acidic character of the C_{60} derivatives when the other substituent of the carbene is an H atom. It is well-known that the substituted hydrofullerenes show a more important acidic character than the methanofullerenes. A study of geometric, electronic, energetic and magnetic analysis could allow making the comparison between a series of $C_{60}HR$ and $C_{60}CHR$ depending on R considered.

Before starting to study the two series of fullerenes derivatives, do a systematic comparative study of a series of Fischer carbene chromium complexes differing in the substituents of the carbene was considered interesting, because a part from provide answers to the changes in the nature of the chromium-carbene bond, could provide answers especially to the origin of different reactivity of some carbene complexes after modification of carbene substituents. In particular, the relative strength of σ donation and π back-donation as a function of the nature of the different substituents in the carbene was analyzed. A series of 25 different Fischer carbene chromium complexes were chosen ($(CO)_5Cr{=}C(X)R$).



Comparisons of their different structural, electronic and energetic characteristics (bond distances and angles, frequencies, and components of the interaction energy) were carried out and also a charge decomposition analysis (CDA, see Fig. 26 for an idea of the scheme for a CDA analysis) was done to quantify the relative importance of donation and back-donation. Different possible correlations between the properties of the complexes and the amount of donation and back-donation were analyzed.

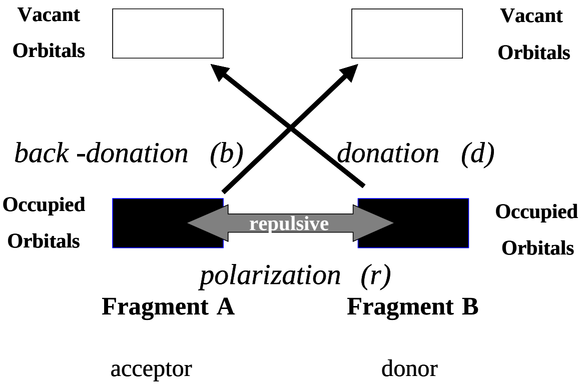


Figure 27. The three terms of the linear combination of the donor and acceptor fragments orbitals (LCFO) in a CDA analysis.[182]

From these analyses several trends between some properties vacant of the complex and the importance of back-donation were found, meanwhile the donation values were not clearly connected to any of the properties analyzed. The back-donation values decrease according to the following order: H > OH > OCH_3 > NH_2 > $NHCH_3$, which is related to the π-donor character of the X substituents, as it can be expected from the fact that NR_2 substituents are better π-donor than OR substituents and these are better than an H atom. Further, a smaller back-donation is found in Fischer carbene chromium complexes with bulky substituents. Interestingly, the effect of the R group (R= H, CH_3, $CH=CH_2$, Ph and $C\equiv CH$) in general is less important in comparison to the effect of the X substituents (X= H, OH, OCH_3, NH_2 and $NHCH_3$).

In particular, it was found that the $(CO)_5Cr=C(X)R$ complexes with X substituents having higher π-donor character show smaller back-donation values, larger $Cr\text{-}C_{carbene}$ and $C\text{-}O_{trans}$ bond lengths, and shorter $Cr\text{-}CO_{trans}$ bond distances. The greater influence of back-donation on the structural properties of the complexes may be attributed to the fact that donation values are almost uniform for all complexes analyzed, whereas charge back-donation numbers are more dispersed over a wide range of values.

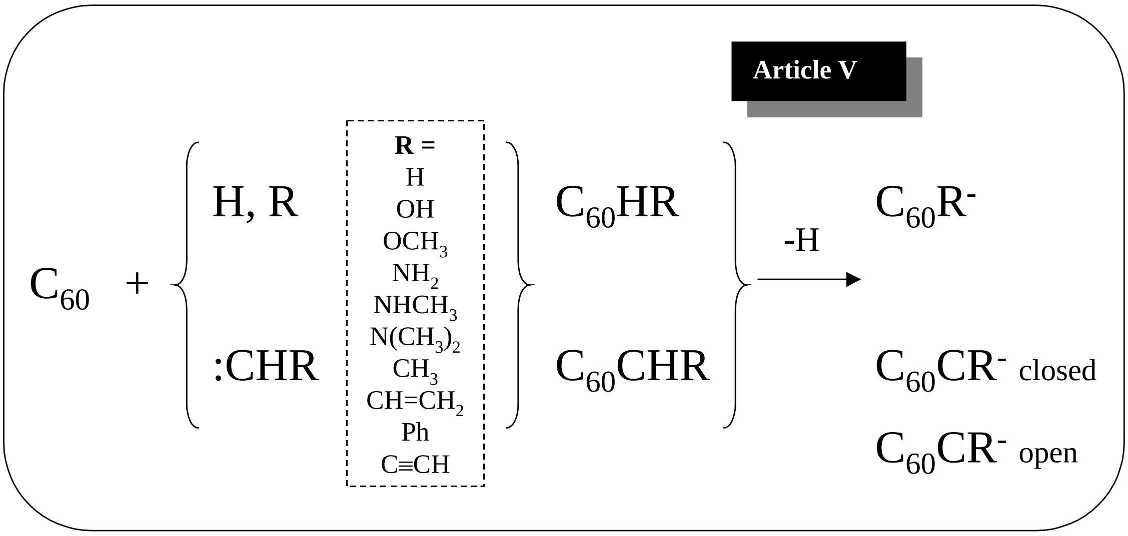
A good correlation could be expected between the energies of the HOMO and LUMO of the carbene and charge donation and back-donation, respectively. However, the correlations obtained in these cases are rather poor because other factors such as the $Cr\text{-}C_{carbene}$ bond length and the overlaps between frontier orbitals of the carbene and the $Cr(CO)_5$ fragment can have a great influence on charge transfer (donation and back-donation).

A direct relationship between the bond dissociation energies and the chromium-carbene bond length is not observed, although commonly a larger distance between the carbene and the pentacarbonyl chromium fragments is connected to a smaller bond energy dissociation value, as expected. To gain a deeper insight into the nature of the $Cr\text{-}C_{carbene}$ bond, an energy decomposition analysis of this dissociation energy was carried out.

The bond dissociation energy can be divided into the deformation energy term (ΔE_{def}) and the interaction energy term (ΔE_{int}). From the results obtained, it is clear that the key to understanding the differences between the Fischer carbene complexes must be found in the ΔE_{int} term, and not in the ΔE_{def} energy value. There is a relation with the $Cr\text{-}C_{carbene}$ bond length and the different components of the interaction energy. Thus in general, a larger $Cr\text{-}C_{carbene}$ bond distance goes with smaller (in absolute values) ΔE_{Pauli}, ΔE_{elstat} and ΔE_{oi} energy terms (which are the terms corresponding to the ΔE_{int} term partitioning). For a given R, the ΔE_{Pauli}, ΔE_{elstat} and ΔE_{oi} energy terms increase in absolute value following the order of decreasing π-donor character of the X substituent: H > OR′ > NHR′. Concretely, the Pauli repulsion and electrostatic terms more or less tend to cancel each other, for this reason the analysis of the bonding interactions can be performed by looking only at the orbital interaction energy term. Stronger orbital interactions and shorter bonds do not always translate into higher bond dissociation energies, because the electrostatic attraction and the Pauli repulsion also play a role when differences in ΔE_{oi} are small. To further analyze the orbital interaction energy term, a slightly modification of the geometry of optimized complexes was done in order to attain C_s symmetry and then make possible the separation of interaction energy into the σ and π orbital interaction components. From the results of this last analysis, first it was found that the component connected with donation (ΔE_σ) was more than two times as large as the term associated with back-donation (ΔE_π), and secondly that ΔE_π values were more scattered over a broad range of values, whereas

ΔE_σ values were more uniform. Correlations between these two terms of orbital interaction energy were done as in case of donation and back-donation values provided by the CDA analysis, and the same tends were found with other properties analyzed for each carbene considered.

Based on this previous knowledge about the series of Fischer carbene studied, we performed the study of carbene addition to C_{60}. The list of carbene chosen in this case was reduced from 25 to 10, because we were just interested in carbenes with an H atom as a substituent to study the acidity of the C_{60} derivatives.



The fifty different systems described were fully optimized at the AM1 level, and the resulting geometries were analyzed in several aspects: geometric (bond length and angles), electronic (Mulliken charge to calculate electronic delocalisation), energetic (deprotonation energy, HOMO-LUMO gap (hardness and softness), deformation energy o C_{60} fragment) and magnetic (NICS and magnetizabilities) characteristics. In general words, as it was expected, we could collect differences between the two series of systems studied, $C_{60}HR$ and $C_{60}CHR$.

In reference with geometric aspects it was found that the functionalization of C_{60} in case of substituted hydrofullerenes represented a more important perturbation for the fullerene cage than for the methanofullerenes studied which was quantified by the calculation of the deformation energy for C_{60} fragment, but after deprotonation the systems $C_{60}R^-$ recovered in higher percentage the original C_{60} geometry than the corresponding basic forms of methanofullerenes, especially the $C_{60}CR^-$ open species for which the breaking of the C-C bond attacked for the carbene implied a larger modification of the reaction site of the cage.

There was not found a clear relation between the character of the R substituents with the change in geometry due to deprotonation in case of substituted hydrofullerenes but a quite reasonable tendency in methanofullerenes systems studied depending on if the R substituent is a more π-donor or more acceptor substituent type. Apparently it was clear that also the nonbonding electrons of N or O atoms of the substituents can play an important role on the interaction between R substituents and C carbene atom and also between C carbene atom and the two C atoms of the C-C bond at C_{60} structure attacked.

It was interesting to confirm that the open basic forms of $C_{60}CHR$ systems were less stable than the corresponding closed structure as it was previously found in the project about the stabilities of [5,6]- and [6,6]-$C_{60}X$ species (see Sec. 4.1.2., or Sec. 5.3.), where the [6,6]-closed structure were always more stable than the [6,6]-open structures. We confirmed also that methanofullerenes presented a lower acidic character then the substituted hydrofullerenes species.

At the same time that open structures showed a higher modification of the C_{60} fragment geometry they were the species that delocalized more along the cage of C_{60} the negative charge existing upon deprotonation, and the amount of charge could be more comparable as in case of the basic forms of the substituted hydrofullerenes studied. A higher interaction between the carbene fragment and the C_{60} fragment π-systems as showed the NICS values of the ring centre of the two hexagons and two pentagons around the reaction site became more difficult when the C-C bond attacked for the carbene kept formed. In case of $C_{60}HR$ after deprotonation in general the NICS values of the rings around the C-C bond attacked varied slightly and they kept positive and quite close to 0, and in case of $C_{60}CHR$ the NICS values show a higher antiaromatic character of the rings around the reaction site after carbene addition, but after deprotonation they lost antiaromatic character and showed more remarkable differences as in $C_{60}HR/C_{60}R^-$ series.

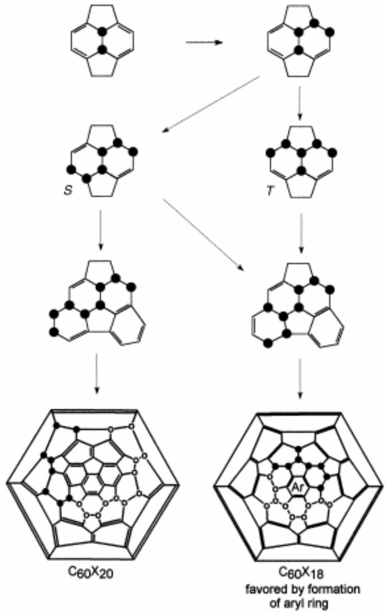
Analysis of the global aromaticity by HOMO-LUMO band gap energy values, and hardness or softness values showed that the methanofullerenes have a slightly higher band gap (consequently, higher hardness and lower softness values) as compared to the respective substituted hydrofullerenes. As a further prediction of global aromaticity, the magnetizabilities values showed that the carbene systems were more aromatic in almost all cases as compared with its substituted hydrofullerene counterpart with the same functional group.

4.2. Multiple additions to C_{60} studies

4.2.1. S and T addition patterns of fluorofullerenes, $C_{60}F_n$

The multiple addition of F to the C_{60} structure was studied considering the two addition patterns defined experimentally from the different possible $C_{60}F_n$ derivative isolated until nowadays, S and T addition patterns. This study based mainly on the NICS values calculations for each 5- and 6-membered ring centre of the C_{60} structure of each $C_{60}F_n$ derivatives, showed how based on the NICS values one can predict the preferential [6,6]-bond attacked in the fluorination of C_{60} process.

From the knowledge that this kind of addition takes place only at [6,6]-bond type, the different $C_{60}F_n$ structures were fully optimized at AM1 level of theory taking the NICS values in consideration to know for each new pair of F atoms added to the cage which is the preferential C-C bond to be attacked. When in some cases more than one possibility (not equivalents) was possible, they were considered and analysed to decide which was the more favourable.



$C_{60}F_n$ ADDITION PATTERNS

S (n = 2,4,6,8,…,20)

Article VI

T (n = 2,4,6,8,…,18)

$C_{60}F_2$ and $C_{60}F_4$ are the first and common $C_{60}F_n$ derivatives for both series studied. NICS values of the rings of $C_{60}F_2$ showed as it was expected that the second addition was more favourable to take place at an adjacent [6,6]-bond of the first [6,6]-bond attacked instead to take place far away of this [6,6]-bond where are added the two F atoms, like and octahedral position could be for instance.

Which [6,6]-bond is chosen for the addition of the third pair of F atoms to the cage is the key for starting a continuous fluorinating process following a S or T addition pattern of multiple addition. In agreement with experimental results it was found that $C_{60}F_6$-S isomer was more stable than $C_{60}F_6$-T isomer, and also the NICS values analysis of $C_{60}F_4$ structure predicted this structure as the most probable.

From $C_{60}F_6$-S to $C_{60}F_{20}$-S structure it was easy to follow the S addition pattern to define the distribution of F atoms along of the C_{60} surface because for each new pair of F atoms added the resulting fluorofullerene derivative had two equivalent hexagons with a negative value of NICS quite close to 0. These hexagons included yet a pair of F atoms added and the C atoms of one of the other two [6,6]-bonds corresponding to two pentagons with the negative value of NICS closer to 0 in comparison with the rest of 5-membered rings around the previous [6,6]-bond attacked. Following this criteria it was possible to achieve the same geometry of $C_{60}F_{20}$ experimentally proposed, the "Saturnene" structure, and for this it is reasonable to conclude that the intermediate structures found from $C_{60}F_6$-S to $C_{60}F_{20}$-S structure could be reliable, not necessarily isolable, perhaps the $C_{60}F_{10}$ could be one possibility because it showed a higher stability and also a higher increasing of magnetizability (global aromaticity calculation) value with respect to its precursor and in comparison with the other $C_{60}F_n$-S structures.

Experimentally $C_{60}F_n$ (n= 8, 16 and 18) with T addition pattern have been isolated. Considering the NICS values of $C_{60}F_6$-T structure, it was found a different $C_{60}F_8$-T isomer respect to the one experimentally proposed, and it was difficult to understand how they got such structure, because it was less stable and showed a minor increasing of magnetizability value respect to $C_{60}F_6$-T system. At this point our $C_{60}F_8$-T isomer was considered the one to continue our study, and following the NICS criteria established as said before in $C_{60}F_n$-S formation.

Applying the NICS criteria taken to predict the next preferential [6,6]-bond to be attacked, the fluoroderivatives structures that NICS predict are not in agreement with the experimentally structures known for $C_{60}F_{16}$ and $C_{60}F_{18}$. The main difference to obtain our proposed structures or the experimental ones was found in the fact that depending on which [6,6]-bond the new pair of F atoms are attached to the $C_{60}F_{10}$ structure, the new fluoroderivative includes one benzenoid central ring or two benzenoid central rings. Both $C_{60}F_{12}$ possible showed a quite similar stability and global aromatic character, but the structure with one benzenoid provides the $C_{60}F_{18}$ structure isolated, meanwhile the other one (proposed by NICS analysis criteria) probably would provide the $C_{60}F_{36}$ structure, because $C_{60}F_{18}$ proposed shows a new preferential [6,6]-bond to be attacked and a continuous more F atoms addition could provide the $C_{60}F_{36}$ structure as a very flatted molecule with the two benzenoid rings in the centre of the two faces.

An analysis of the different [6,6]-bonds length of C_{60} structure was done in order to localize bonds with a higher double bond character because they show a shorter length. Sometimes it has been said that between several aromaticity criteria should not have necessarily any relationship, but here we found that geometric and magnetic criteria had a reasonable agreement in terms of bonds with more double character detection.

At the same time, magnetizabilities, HOMO-LUMO gaps and T index values were considered in order to give an idea about the global properties of the systems studied. The increasing of F atoms addition to the surface of the C_{60} helps to increase the global aromaticity of the systems as magnetizabilities and HOMO-LUMO gaps reflected and T index showed that the structure which have been isolated have a higher kinetics stability in comparison with other.

4.2.2. Addition pattern of fullerene epoxides, $C_{60}O_n$

$C_{60}O_n$ n= 1, 2, 3, 4,…, 10

ADDITION PATTERNS

S, **T** and $\mathbf{O_h}$

Article VII

The addition pattern which describes the multiple addition of O atoms to the C_{60} cage was not well-known neither experimentally and theoretically as in case of fluorofullerene derivatives. For this reason and considering as a good technique the local aromaticity analysis by NICS calculation to elucidate the addition pattern of a multiple addition process, we decided to study the three more logic addition patterns for multiple addition of O atoms to C_{60}. T and S addition patterns were well defined in case of fluorofullerenes and apart from that it seemed quite interesting to check also the O_h addition pattern.

As it is the case of other type of addition to the C_{60}, we just considered the addition of O atoms to [6,6]-bond type and in the first place when we studied the low degree oxide fullerene derivatives we found that the closed [6,6]-bonds to the first C-C bond attacked were preferentially attacked than far away [6,6]-bonds, for instance octahedral positions. That seemed clear to reject the O_h addition pattern and give more importance to the other two possible addition patterns proposed to study. Nevertheless, we studied the O_h addition pattern and when one analyzed the local aromaticity values of NICS for $C_{60}O_2$-O_h, we can apply our NICS analysis criteria to describe the most stable $C_{60}O_3$-O_h isomer and continue this prediction until the $C_{60}O_6$-O_h.

After a second addition of an O atom to the cage next to the first addition site, the new pair of C-C bond chosen to be attacked was the key to have one or other isomer of $C_{60}O_3$, the $C_{60}O_3$-S and $C_{60}O_3$-T. As it happened for the isostructural fluorofullerenes structures, $C_{60}F_6$-S and $C_{60}F_6$-T, the S isomer was found to be a little more stable than the T isomer.

From $C_{60}O_3$ until $C_{60}O_{10}$ structures were studied considering the S addition pattern, and similarly as S-fluorofullerene derivatives it was possible to define the different structures of $C_{60}O_n$ n= 4, 5, 6, 7, 8 and 9, following the zigzag continuous addition taking in consideration that NICS values of two pentagons and two hexagons around a [6,6]- bond had more positive value (they represent antiaromatic character of the ring, so electrons are more localized).

We started to study the possible T addition pattern, but after the sixth addition of O atom to the cage the new C-C bond predicted by our NICS analysis criteria was one [6,6]-bond which respect to the previous ones attacked broke the T tendency addition pattern to follow a S addition pattern. In other words, S addition pattern should be the expected addition pattern to explain the multiple addition of O atoms to C_{60} molecule mainly, and as said before O_h addition pattern should be less probable but possible, which was demonstrated that it was not the case of T addition pattern.

As found in case of fluorofullerenes addition patterns study, here also the [6,6]-bond lengths analysis for the different $C_{60}O_n$ structures defined provided the same information, in general the C-C bond length of the [6,6]-bonds where O atoms were predicted to be attached was shorter which mean a double bond character, and again the geometric and magnetic aromaticity criteria were in agreement.

Besides the local aromaticity analysis; the magnetizabilities and HOMO-LUMO gaps values were considered to analyze the global aromaticity of the systems like also the kinetics of the process by means of T index values. $C_{60}O_n$-S derivatives showed a higher global aromaticity character and stability than the $C_{60}O_n$-T or $C_{60}O_n$-O_h corresponding isomers studied which explained in part the preference for a zigzag continuous addition.

In summary Figure 27 shows all the fullerene derivatives studied in this Thesis project:

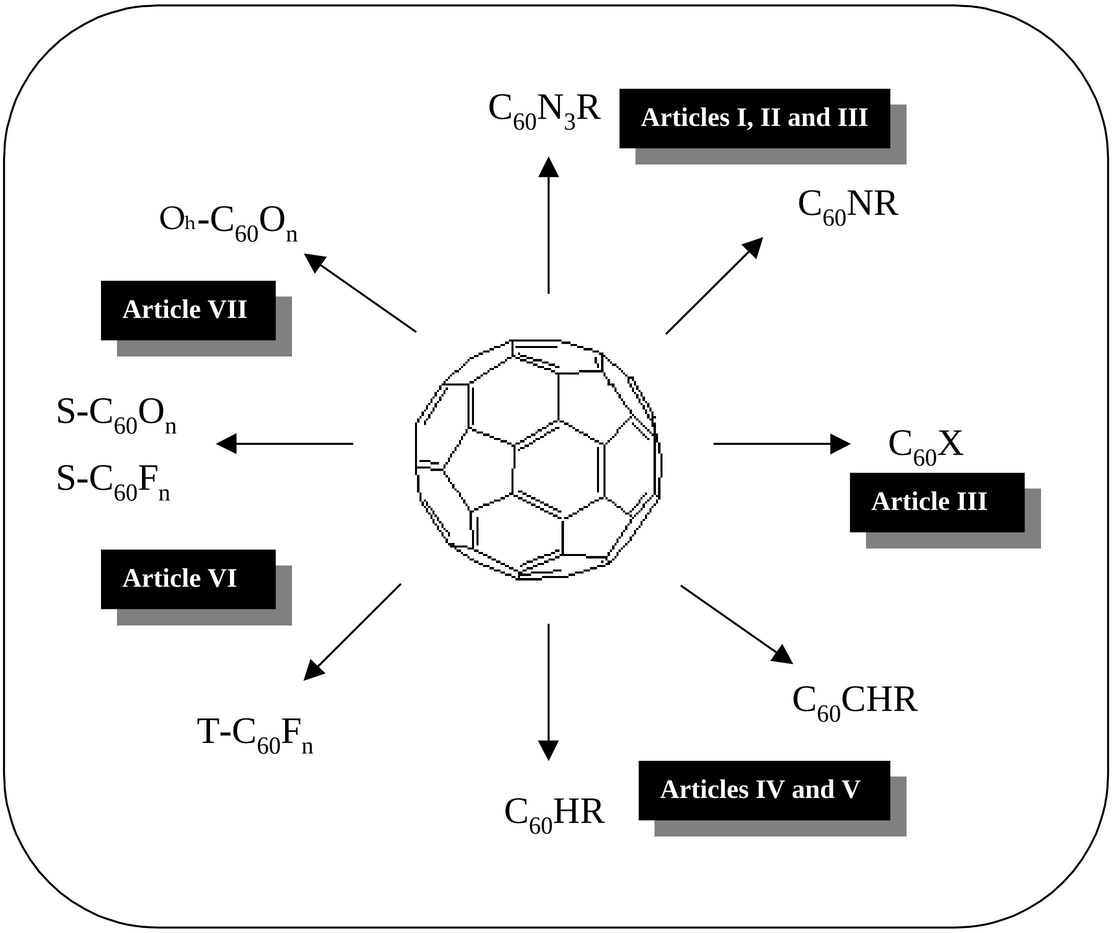


Figure 27. Scheme of all fullerenes derivatives studied in this Thesis project.

5. PUBLICATIONS

5.1. Article I:

The [2+1] Cycloaddition of Singlet Oxycarbonylnitrenes to C_{60}

M Cases, M. Duran and M. Solà

J. Mol. Model. 2000, 6, 205-212

5.2. Article II:

Mechanism of the Addition Reaction of Alkyl Azides to [60]Fullerene and the Subsequent N_2 Extrusion to Form Monoimino-[60]Fullerenes

M. Cases, M. Duran, J. Mestres, N. Martín and M. Solà

J. Org. Chem. 2001, 66, 433-442

5.3. Article III:

The Reactivity of the [5,6]-bond in Cycloadditions to Fullerenes

M. Cases, M. Duran, J. Mestres, N. Martín and M. Solà

Proceedings: Recent Advances In The Chemistry And Physics Of Fullerenes And Related Material, Kamat PV, Ed., Pennington: Electrochemical Society Inc., Vol 101, 2001, 245-269

5.4. Article IV:

Molecular Structure and Bond Characterization of the Fischer-Type Chromium-Carbene Complexes $(CO)_5Cr=C(X)R$ (X= H, OH, OCH_3, NH_2, $NHCH_3$, and R= H, CH_3, $CH=CH_2$, Ph, $C\equiv CH$)

M. Cases, G. Frenking, M. Duran and M. Solà

Organometallics 2002, 21, 4182-4191

5.5. Article V:

Ab initio Quantum Chemical Study of the Reactivity of $C_{60}HR$ and $C_{60}CHR$ Derivatives.

M Cases, G. Van Lier, M. Solà, M. Duran and P. Geerlings

Ab initio Quantum Chemical Study of the Reactivity of C_{60}HR and C_{60}CHR Derivatives.

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ABSTRACT.

In the present work an *ab initio* quantum chemical study is presented, analysing the properties of a series of substituted hydrofullerenes (C_{60}HR) and a series of methanofullerenes (C_{60}CHR), in order to compare their reactivity based on their geometrical, energetic and electronic properties, as well as on the influence of the substituent. As a probe of the reactivity, the acidic properties of these fullerene derivatives were predicted, based on the calculated deprotonation energies, with a previously set up scheme. The electronic delocalisation upon deprotonation was described, and the global (global hardness and softness and magnetisabilities) and local aromaticity (NICS) was analysed and compared with respect to the group properties for the series of functional groups. The geometries of both acidic and basic forms were fully optimized at AM1 level, and all property calculations were performed at HF/3-21G and B3LYP/6-31G* levels of theory.

Keywords:
Ab initio calculations, Fullerenes, Aromaticity.

I. INTRODUCTION.

In fullerene chemistry, addition reactions are the most important route to functionalisation, lending to a whole range of organic reactions.[1-5] In this study, two types of addition products are considered, in order to compare their reactivity based on geometrical, energetic and electronic properties, as well as on the influence of the substituent. A series of substituted hydrofullerenes, C_{60}HR (which are systems derived from 1,2-$C_{60}H_2$ by substituting one hydrogen atom by a functional group) and a series of methanofullerenes, C_{60}CHR (which are systems derived from the formal addition of a carbene fragment), with 10 distinct functional groups are analysed.

Substituted hydrofullerenes C_{60}HR are of special interest for their acidic properties, that can be tailored by the variation of the functional group R.[6] Furthermore, these systems can serve as precursors for further functionalisation of C_{60}, based on these acidic properties and the high thermodynamic stability of the conjugated bases.[7,8] While the methanofullerenes $C_{60}CHR$ are one of the most versatile and widely studied class of fullerene adducts,[4] the question remains if the acidity could also be used here as a tool for further functionalisation of these systems. Also the geometry is of importance for this type of [1+2] cycloadditions. For substituted hydrofullerenes, addition takes place preferentially at the more reactive [6,6]-ring junctions, rather than at the longer [5,6]-bonds,[1,9,10] but in case of carbene addition to C_{60}, four possible ways exist to add a one-carbon bridge across a carbon-carbon bond. Of these, only the [5,6]-open methanofulleroids (methanoannulenes)[11-15] and the [6,6]-closed methanofullerenes (cyclopropane derivatives)[16] have been experimentally observed. Addition of carbene transfer reagents such as diazo-compounds to C_{60} often generates the [5,6]-open fulleroid as the kinetically controlled product, while the thermodynamically controlled product is the [6,6]-closed methanofullerene. The [6,6]-closed and [5,6]-open forms are the two most stable isomers.[17] Upon heating, the mixture of [6,6]-closed and [5,6]-open isomers formed together in the course of the synthesis are converted exclusively to the most stable [6,6]-closed isomer. The rearrangement from [5,6]-open fulleroid to [6,6]-closed fullerene has been studied both experimentally[11,15,18] and theoretically.[4]

Since the discovery of fullerenes, special attention has also been paid to the possible aromaticity of these conjugated systems. First predicted to be aromatic,[19] buckminster-fullerene C_{60} soon appeared to be much less aromatic and hence more reactive, with important conjugation from the alternation of single and double bonds resulting in a conjugated-alkene-like behaviour.[20] The difference in bond type between the bonds located at the junctions of the hexagons ([6,6]-bonds) and the bonds of the pentagonal rings ([5,6]-bonds)[21,22] is very important for the analysis of the structural aspect of the aromaticity for C_{60}. The chemistry of the fullerenes is suggested to proceed in such a manner that the reaction products become as aromatic as possible, resonance energy methods indicating that C_{60} is moderately aromatic with some olefinic character.[20] For this, the analysis of the global and local aromaticity can give important information about the reactivity and the addition patterns for fullerenes.[23,24]

In the present study we will analyse the difference in geometry and electronic structure between a series of substituted hydrofullerenes and methanofullerenes, with different functional groups (R= H, OH, OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$, CH_3, $CH=CH_2$, C_6H_5 (further referred to as Ph), and C≡CH), in both their acidic ($C_{60}HR$ and $C_{60}CHR$) and basic ($C_{60}R^-$ and $C_{60}CR^-$) forms. For all the systems, only the thermodynamically preferred [6,6]-adduct is analysed. Differences in geometrical and energetic characteristics are presented between the series and the influence of the different functional groups is addressed. As a probe of the reactivity, their acidity is predicted using a previously set up scheme.[25] Also the global and local aromaticity is studied for the whole series under consideration, in order to further analyse the reactivity of these fullerene derivatives. We have performed NICS calculations at all geometrical ring centres for all systems ($C_{60}HR$, $C_{60}R^-$, $C_{60}CHR$ and $C_{60}CR^-$). Nucleus-independent chemical shifts (NICS)[26] can be computed reliably with modern quantum-chemical methods and afford a simple and efficient probe of the local aromatic properties.[27]

In the next section we present the theoretical and computational details. In section III, the results are presented and discussed. In Part A the geometrical characteristics are discussed and Part B describes the deprotonation. Part C and D account for the global and local aromaticities respectively. Conclusions are drawn in section IV.

II. COMPUTATIONAL DETAILS.

The geometries of acidic and basic forms in both series, $C_{60}HR$ and $C_{60}CHR$, were fully optimised at the semiempirical AM1 level of theory[28] using the AMPAC program.[29] Two deprotonated forms were optimised for the $C_{60}CR^-$ series, with the functionalised bond remaining closed or opening upon addition, the so-called [6,6]-closed and [6,6]-open isomers. Starting from different bond lengths for the functionalised bond, full AM1 optimisation yielded two structures in each case, with relative stabilities varying, and the bond length being significantly enlarged for one structure as compared to the other one. Single point calculations at the AM1 fully optimised geometries at HF/3-21G and B3LYP/6-31G* were performed using GAUSSIAN98.[30] The AM1 method has been preferred to other semiempirical methods because it yields reliable results for geometries of C_{60} derivatives, as for example for Diels-Alder adducts.[31,32]

For each substituted hydrofullerene and each methanofullerene we calculated the (gas-phase) deprotonation energy, ΔE. As considered in our previous studies,[33] the deprotonation energy is defined as:

$$\Delta E = E(A^-) - E(AH) \qquad (1)$$

where E(AH) and $E(A^-)$ are respectively the total energy for the acidic form of these compounds and that of its conjugated base form.

We also calculated the charges on the different atoms for all the molecules. These charges were evaluated by a Mulliken population analysis,[34] in order to be comparable with our previous studies.[35] From these Mulliken populations, the electronic delocalisation Δ is calculated, as introduced in previous work.[25] This electronic delocalisation is expressed in terms of the amount of electrons leaving the C atom carrying the acidic proton upon deprotonation of the acid. We define this quantity as

$$\Delta = [\, N_C(n) - N_H(n)] - N_C(n-1) \qquad (2)$$

where $N_C(n)$, $N_H(n)$ and $N_C(n-1)$ are the Mulliken populations at the C and H atoms of the acidic system and at the same, thus deprotonated, C atom of its conjugate base respectively.

To make a further interpretation of the reactivity, the global hardness and softness are calculated. The global hardness is obtained as:

$$\eta = (\, IE - EA\,)/2 \qquad (3)$$

where we consider the finite-difference approximation to its definition.[36] Approximating further the ionisation energy (IE) and electron affinity (EA) by the negative of the energy of highest occupied molecular orbital, ε_{HOMO}, and the negative of the energy of the lowest unoccupied molecular orbital, ε_{LUMO}, respectively, according to Koopmans' theorem,[37] we get the working equation:

$$\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2 \qquad (4)$$

The global softness is defined according to equation 5:[36]

$$S = 1/2\eta \qquad (5)$$

the working equation being obtained by combining eqs. (4) and (5). Finally we analysed the global aromaticity in terms of the HOMO-LUMO gap and the molecular magnetizability for each structure, using the CSGT method.[38] The local aromaticity of a ring is described by its ability to support diamagnetic ring (i.e. diatropic) currents, which can be described by the nucleus-independent chemical shift or NICS.[26] It is calculated at the geometrical centres of the ring, determined by the non-weighted mean of the ring atom coordinates, using the GIAO method.[39] Both were calculated at the *ab initio* HF/3-21G level of theory using the AM1 fully optimised geometries.

III. RESULTS AND DISCUSSION.

A. Geometrical characteristics

In Table 1, relevant bond lengths are given for the series of substituted hydrofullerenes and of methanofullerenes, as well as the value for the angle, resulting from the carbene addition. (The numbering of the carbon atoms, used in Table 1 and in the discussion below, refers to the depicted structures in Figure 1. For the sake of clarity we have chosen to use the acronym of the functional group for labelling the systems).

Comparing the distances for the bond where the addition occurred, d(C_1-C_2), between both series considered, we see a similar elongation upon addition to the [6,6]-bond (the experimental value for C_{60} is 1.401Å.[40] Upon deprotonation however, a clear shortening occurs in case of the substituted hydrofullerenes, the C_1-C_2 bond recovering some double bound character, whereas the same bond gets elongated upon deprotonation of the carbene. In general, this elongation forces an opening of the angle between the three C atoms of the three membered ring ($\alpha(C_1C_3C_2)$), especially in case of the open structures of $C_{60}CR^-$. At the same time, the distance between the C atom and the substituent R (d(C_2-R) for C_{60}HR systems and d(C_3-R) for C_{60}CHR systems) becomes shorter upon deprotonation. There is not a clear relation between the character of the R substituents and the change in geometry due to deprotonation in case of substituted hydrofullerenes but a quite reasonable tendency in methanofullerenes systems studied is found.

For the C_{60}CHR and $C_{60}CR^-$ series, the d(C_1-C_3) and d(C_2-C_3) are identical in case of the closed structures studied except for R= NR’$_2$ substituent where one bond length is larger than the other. The different behaviour of systems with NR’$_2$ can be understandable if one takes into account that the N atom has a pair of nonbonding electrons and the substituents of N place less symmetrically (the two R’ substituents are facing C_2-C_3 bond, (see Scheme 1) than in the case of other R substituents (O atom has also nonbonding electrons, but two pairs that are placed symmetrically with respect to the C_1-C_3 and C_2-C_3 bonds), see Scheme1. The elongation of the C_2-C_3 bond in C_{60}CHNR’$_2$ species may be attributed to hyperconjugation from the lone pair of the N atom to the σ^*(C_2-C_3) molecular orbital. Meanwhile, for open structures the d(C_2-C_3) is larger than the d(C_1-C_2) in general, except for R= NR’$_2$. In this latter

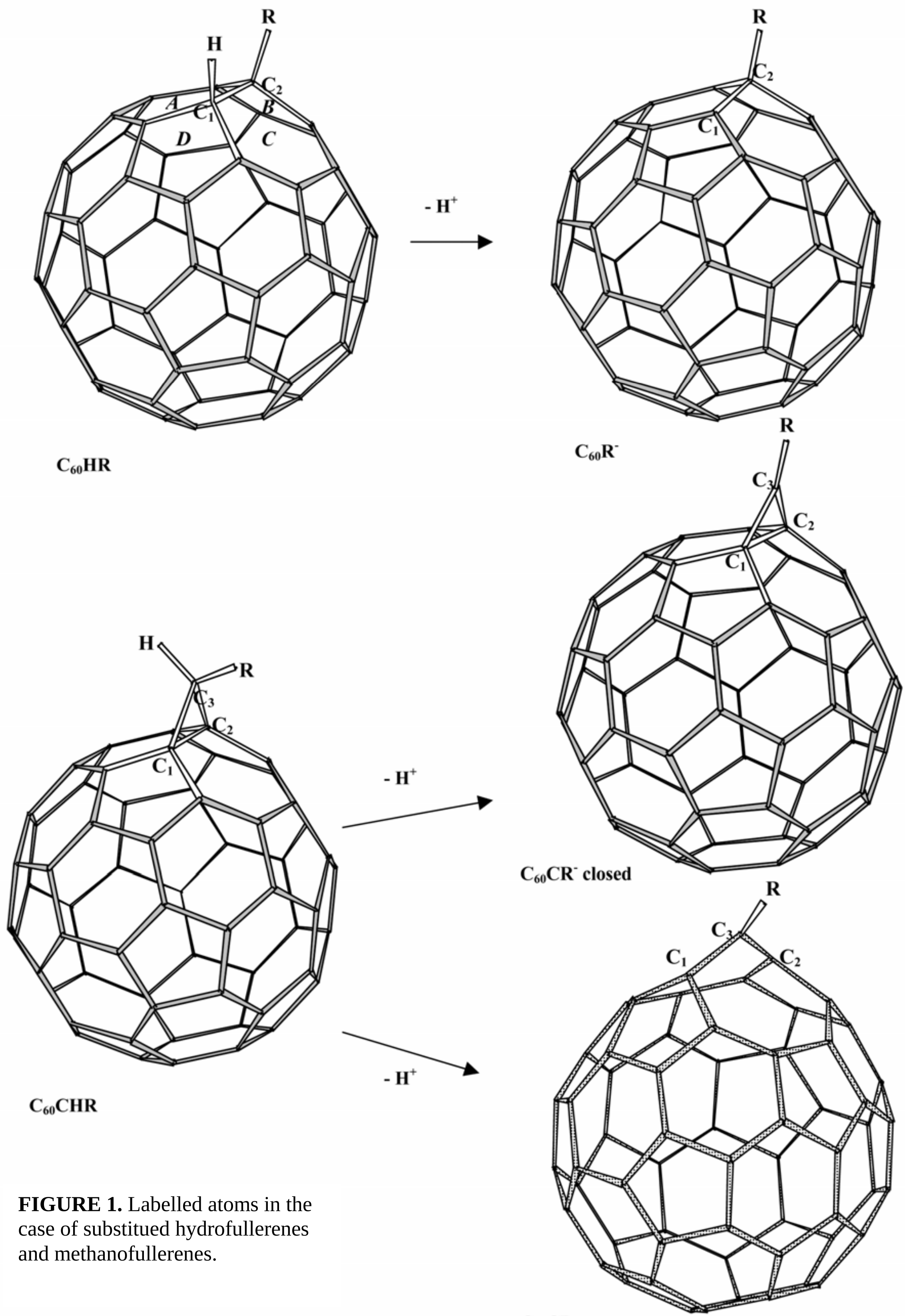
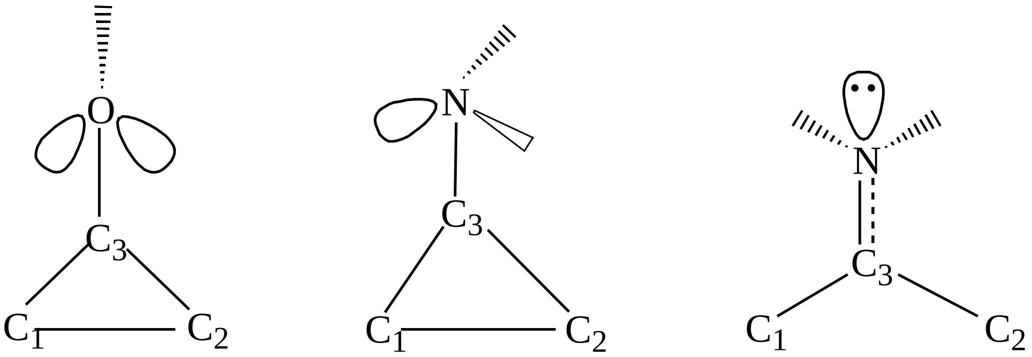


FIGURE 1. Labelled atoms in the case of substitued hydrofullerenes and methanofullerenes.

case, the lone pair is placed symmetrically in such a way that it can participate in the π structure (see Scheme 1)



SCHEME 1. Distribution of atoms and orbitals.

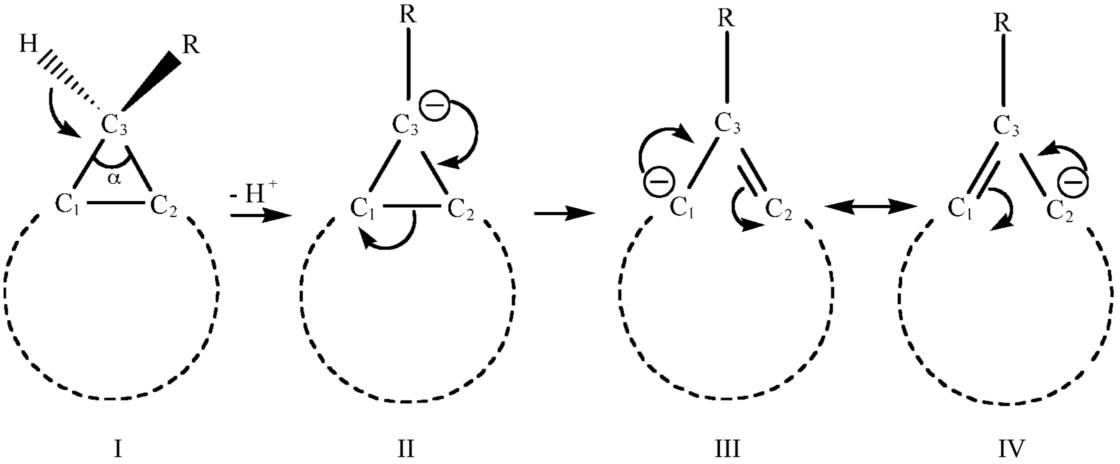


FIGURE 2. Deprotonation process in the case of methanofullerenes. Open and closed structure of the basic form.

In comparison with the corresponding acidic form, $C_{60}CHR$, generally these bond distances between the atoms of carbene fragment and the two C atoms of C_{60} become shorter, especially for the open form for which these two bonds are expected to have partial double bond character (see Fig. 2). Apart from that, when R is a OR' or NR'_2 π-donor type substituent, the shortening is less important for $C_{60}CR^-$ closed structures than in case of the $C_{60}CR^-$ open structures. The reverse effect is found for the rest of substituents. Ressonance structures of the type III and IV (see Fig. 2) are favoured due to the presence of π-donor substituents.

All these differences between the bond lengths in the reactive site of the C_{60} should have a relation with σ- and π-orbital interactions between the carbene C atom and the two C atoms of C_{60}. (For a discussion of the relative importance of the σ- and π-orbital interaction energy terms for carbenes see reference [41]). $C_{60}CR^-$ systems with R= OR or NR_2' substituents (which are carbene having a higher σ-character orbital interaction) tend to lengthen the d(C_3-R) distance and to shorten the bond between the carbene atom and the carbon atoms of C_{60}, meanwhile, systems with R= $CH=CH_2$, Ph, and C≡CH (which have a higher π-character orbital interaction) shorter d(C_3-R), and the bond between the carbene atom and the C_{60} carbon atom gets longer.

TABLE 1. Significant distances (Å) and angles (º) for the acidic and basic forms of the series considered, fully optimised at the AM1 level. (numbering, see Figure 1).

	d(C_1-C_2)	d(C_1-H)	d(C_2-R)	d(C_1-C_3)	d(C_2-C_3)	d(C_3-H)	d(C_3-R)	α($C_1C_3C_2$)
$C_{60}HR$								
H	1,552	1,126	1,126					
OH	1,565	1,131	1,414					
OCH_3	1,568	1,131	1,421					
NH_2	1,582	1,130	1,454					
$NHCH_3$	1,585	1,130	1,461					
$N(CH_3)_2$	1,586	1,130	1,470					
CH_3	1,562	1,128	1,521					
$CH{=}CH_2$	1,568	1,128	1,498					
Ph	1,569	1,128	1,504					
C≡CH	1,571	1,128	1,442					
$C_{60}R^-$								
H	1,491		1,120					
OH	1,493		1,411					
OCH_3	1,493		1,420					
NH_2	1,505		1,449					
$NHCH_3$	1,506		1,454					
$N(CH_3)_2$	1,505		1,463					
CH_3	1,496		1,512					
$CH{=}CH_2$	1,498		1,490					
Ph	1,498		1,498					
C≡CH	1,498		1,440					
$C_{60}CHR$								
H	1,580			1,494	1,494	1,108	1,108	63,59
OH	1,574			1,508	1,508	1,114	1,382	62,93
OCH_3	1,575			1,507	1,507	1,111	1,397	62,91
NH_2	1,568			1,525	1,509	1,119	1,412	62,29
$NHCH_3$	1,569			1,524	1,510	1,119	1,417	62,27
$N(CH_3)_2$	1,569			1,525	1,508	1,124	1,421	62,24
CH_3	1,574			1,502	1,502	1,114	1,490	63,06
$CH{=}CH_2$	1,571			1,505	1,505	1,115	1,467	62,75
Ph	1,572			1,503	1,502	1,118	1,472	62,95
C≡CH	1,570			1,506	1,506	1,119	1,415	62,62
$C_{60}CR^-$ closed								
H	1,627			1,416	1,416		1,057	70,10
OH	1,577			1,524	1,524		1,380	62,34
OCH_3	1,578			1,522	1,522		1,392	62,46
NH_2	1,581			1,486	1,525		1,380	63,34
$NHCH_3$	1,581			1,490	1,524		1,388	63,29
$N(CH_3)_2$	1,589			1,495	1,475		1,384	64,70
CH_3	1,620			1,420	1,420		1,424	69,57
$CH{=}CH_2$	1,617			1,431	1,429		1,380	68,84
Ph	1,616			1,433	1,433		1,378	68,66
C≡CH	1,615			1,429	1,429		1,342	68,84
$C_{60}CR^-$ open								
H	2,299			1,363	1,443		1,100	109,97
OH	2,362			1,388	1,435		1,343	113,61
OCH_3	2,368			1,396	1,432		1,339	113,73
NH_2	2,377			1,433	1,433		1,326	112,11
$NHCH_3$	2,375			1,436	1,434		1,328	111,69
$N(CH_3)_2$	2,370			1,439	1,439		1,330	110,95
CH_3	2,282			1,376	1,447		1,464	107,89
$CH{=}CH_2$	2,236			1,398	1,441		1,418	103,93
Ph	2,212			1,421	1,421		1,416	102,24
C≡CH	2,210			1,419	1,420		1,375	102,28

From this analysis it emerges that the R substituent character influences the geometrical reorganization of the system upon deprotonation. This deprotonation mechanism will be discussed in more detail below. The deprotonation process in both cases has a different effect on the C_{60} structure: The C_{60} fragment in $C_{60}HR$ species became geometrically more modified than for $C_{60}CHR$ especies as shows the magnitude of $\Delta E(C_{60})_{def}$ value in Table 1 (calculated as $\Delta E(C_{60})_{def}= E_{C60}^{fragment} - E_{C60}^{optimized}$), after deprotonation the $C_{60}R^-$ systems partially recover the C_{60} structure (the $d(C_1-C_2)$ recovers partially its double bond character), whereas for the open $C_{60}CR^-$ species this process involves on elongation of the C_1-C_2 bond (the resonance structures III and IV become more important) with a more important rearrangement and change in bond lengths and electronic charge distribution.

B. Deprotonation process

In Figure 1, we have depicted the two possible conjugated base geometries for the methanofullerenes, where the C_1-C_2 bond remains closed or becomes broken because of the reorganization of the charges forced by the loss of the proton. The results for these two possible geometries of $C_{60}CR^-$ showed the closed structures to be more stable, at AM1 and B3LYP/6-31G*//AM1 levels of theory. According to the HF/3-21G//AM1 results the open structures are the most stable for R=OH, OCH_3, $CH=CH_2$, Ph and C≡CH. We have fully optimized some structures (R=H, OH, CH_3) at the HF/3-21G level and we have confirmed the higher stabilization of closed structures in front of their corresponding open structures at this level of theory. In Figure 2, a mechanism is proposed for the rearrangement that systems suffers upon deprotonation, where it is clear that the different localization of the negative charge upon deprotonation is the key to finally have a closed or open structure of the $C_{60}CR^-$ systems. We expected that it could have a relation with the donor or acceptor character of the R substituent, but the influence is quite weak.

In a previous work[42] we compared the stabilities between [6,6]- and [5,6]-derivatives for a series of $C_{60}X$ systems (X= CH_2, NH, NCH_3, NCOOH, PCH_3 and O). Concretely, we found that the relative stability of the isomer [5,6]-open with respect to [6,6]-closed structure increases slightly in order CH_2 < O < NH, and in particular, for X= O and NH the most stable isomer was [5,6]-open, followed by the [6,6]-closed and more separately by [6,6]-open. As far as the $C_{60}CH_2$ system was concerned, we found that at the B3LYP/6-31G**//AM1 level the closed [6,6]-regioisomer was more stable than the [6,6]-open by 1.5 kcal/mol. For the $C_{60}NH$ species we found that [6,6]-closed was 5.1 kcal/mol more stable than [6,6]-open. We found that $C_{60}CR^-$ open structures are less stable than the closed structures by 13.6 kcla/mol on average for the different substituents considered at the B3LYP/6-31G*//AM1 level.

In Table 2, the deprotonation energies are given for both series considered, calculated at HF/3-21G and B3LYP/6-31G* levels of theory at the same geometry (AM1 fully optimised). From the B3LYP/6-31G*//AM1 energy values it is clear that the deprotonation is an endothermic process and the closed structures are the thermodynamic product.

TABLE 2. Deprotonation energy (a.u.) at (a) HF/3-21G//AM1 and (b) B3LYP/6-31G*//AM1 levels for each system, calculated from the energies of the acidic ($E_{(HA)}$) and basic ($E_{(A-)}$) form.

	ΔE^a		ΔE^b	
C$_{60}$HR/ C$_{60}$R$^-$				
H	0,551287		0,525876	
OH	0,543240		0,525220	
OCH$_3$	0,543511		0,526113	
NH$_2$	0,536352		0,537367	
NHCH$_3$	0,545575		0,532816	
N(CH$_3$)$_2$	0,556157		0,530520	
CH$_3$	0,511109		0,540212	
CH=CH$_2$	0,545390		0,527624	
Ph	0,540395		0,550336	
C≡CH	0,542827		0,534062	
C$_{60}$CHR/ C$_{60}$CR$^-$	closed	open	closed	open
H	0,648125	0,647337	0,646160	0,596554
OH	0,613459	0,623578	0,604376	0,586769
OCH$_3$	0,612059	0,626793	0,610006	0,594606
NH$_2$	0,625752	0,609059	0,618732	0,594541
NHCH$_3$	0,620097	0,605464	0,628381	0,604377
N(CH$_3$)$_2$	0,621514	0,598748	0,606219	0,576850
CH$_3$	0,654385	0,650018	0,652242	0,615545
CH=CH$_2$	0,595032	0,612068	0,603465	0,599257
Ph	0,608776	0,627980	0,615395	0,603611
C≡CH	0,598421	0,620342	0,595362	0,591203

TABLE 3. Electronic delocalisation calculated from the Mulliken populations ($N_{C\ acid}$, $N_{H\ acid}$ and $N_{C\ base}$) for all the structures studied at HF/3-21G//AM1.

	$N_{C\ acid}$	$N_{H\ acid}$	$N_{C\ base}$	Δ	$N_{C\ base}$	Δ
C$_{60}$HR/ C$_{60}$R$^-$						
H	-0,311	0,290	-0,031	-0,570		
OH	-0,303	0,332	0,010	-0,645		
OCH$_3$	-0,302	0,332	-0,010	-0,624		
NH$_2$	-0,280	0,310	-0,008	-0,581		
NHCH$_3$	-0,276	0,310	-0,011	-0,575		
N(CH$_3$)$_2$	-0,274	0,314	-0,023	-0,566		
CH$_3$	-0,279	0,291	0,026	-0,596		
CH=CH$_2$	-0,270	0,300	0,035	-0,606		
Ph	-0,267	0,311	0,051	-0,629		
C≡CH	-0,274	0,314	0,032	-0,620		
C$_{60}$CHR/ C$_{60}$CR$^-$			closed	closed	open	open
H	-0,218	0,264	-0,290	-0,192	-0,017	-0,465
OH	0,346	0,283	0,336	-0,273	0,512	-0,449
OCH$_3$	0,357	0,252	0,378	-0,273	0,553	-0,448
NH$_2$	0,216	0,271	0,310	-0,365	0,529	-0,584
NHCH$_3$	0,248	0,269	0,347	-0,368	0,568	-0,589
N(CH$_3$)$_2$	0,273	0,265	0,360	-0,352	0,604	-0,596
CH$_3$	-0,100	0,265	-0,021	-0,344	-0,050	-0,315
CH=CH$_2$	-0,187	0,268	0,020	-0,475	-0,110	-0,345
Ph	-0,083	0,284	0,093	-0,460	-0,064	-0,303
C≡CH	-0,188	0,298	-0,007	-0,479	-0,182	-0,304

A prediction of the acidities (DMSO, 25°C) for these systems is made from their theoretically calculated deprotonation energies, using a previously set up correlation scheme.[25] If we apply this correlation equation to the calculated deprotonation energies for both series, pK_a values are found for the substituted hydrofullerenes ranging from 2 to 7, whereas for the methanofullerenes the values range from 17 to 32, thus showing a higher acidic character for the series of substituted hydrofullerenes. The values for the deprotonation energies show that a lower acidity is found for the closed and open structures in case of H and CH_3 substituents mainly, but for the rest of substituents there is not a clear tendency, as far as the acidity value is concerned.

The delocalisation of the negative charge resulting from the deprotonation process also plays an important role in the stabilisation of the conjugate base. From the values collected in Table 3, we can see that the electronic delocalization (Δ) is more important in case of the substituted hydrofullerenes, but again from the results it is not possible to find a direct relation with respect to the character of R substituent. These values are given as obtained from calculations at the HF/3-21G level of theory, in order to compare with previous results,[35] and the comparable B3LYP calculated values are available as supplementary material.

To further analyse the differences between the two basic forms of both series considered, we collected the charges of the atoms that belong to the reactive zone (see Table 4).

Despite the diversity of functional groups considered, the charge on the acidic H atom (see Table 3) is seen not to vary much throughout the series, but important differences can be seen for the deprotonated carbon atom. The deprotonated C atom again loses more charge after delocalisation than gained from the deprotonating H atom, as was the case for the substituted hydrofullerenes.[35] Nonetheless we can see that, although the deprotonated C atom loses less charge upon deprotonation in case of the methanofullerenes (see Table 3), in most cases C_1 and C_2 gain charge upon the deprotonation process (see Table 4). This shows that the charge originating from the deprotonation remains more localised in the addition region for the methanofullerenes as compared to the substituted hydrofullerene series. From the charges of the non-functionalised part of the cage (q(58C), see Table 4), we can indeed see that less charge is delocalised for the closed methanofullerene basic forms as compared to the substituted hydrofullerenes basic forms. On the other hand, the opening of the functionalised bond permits a higher delocalisation to the rest of the cage. Finally, the fact that the calculated charges on the H atom are found to be similar, despite the important differences in predicted acidity, further stresses the care that should be taken in predicting the acidity for this type of systems solely from properties measured or predicted for the acidic form, without taking the basic form into account.[6,43]

TABLE 4. Charges for the functional group R, the C_1, C_2 and C_3 carbon atoms, and the sum of the charges for the 58 non-functionalised carbon atoms of the cage at HF/3-21G //AM1 level for all systems.

	qR	qC_1	qC_2	qC_3	q(58C)
$C_{60}HR$					
H	0,289	-0,311	-0,311		0,044
OH	-0,265	-0,303	0,180		0,056
OCH_3	-0,281	-0,302	0,213		0,039
NH_2	-0,104	-0,280	-0,008		0,083
$NHCH_3$	-0,129	-0,276	0,037		0,057
$N(CH_3)_2$	-0,155	-0,274	0,083		0,033
CH_3	0,170	-0,279	-0,317		0,135
$CH{=}CH_2$	0,177	-0,270	-0,366		0,158
Ph	0,161	-0,267	-0,361		0,156
$C{\equiv}CH$	0,170	-0,274	-0,456		0,247
$C_{60}R^-$					
H	0,201	-0,031	-0,316		-0,854
OH	-0,305	0,010	0,120		-0,825
OCH_3	-0,337	-0,010	0,150		-0,824
NH_2	-0,171	-0,008	-0,043		-0,778
$NHCH_3$	-0,202	-0,011	-0,090		-0,778
$N(CH_3)_2$	-0,235	-0,023	0,028		-0,770
CH_3	0,104	0,026	-0,365		-0,765
$CH{=}CH_2$	0,116	0,035	-0,442		-0,709
Ph	0,093	0,051	-0,447		-0,697
$C{\equiv}CH$	0,131	0.032	-0,543		-0,618
$C_{60}CHR$					
H	0,263	-0,178	-0,177	-0,218	0,046
OH	-0,261	-0,215	-0,215	0,346	0,062
OCH_3	-0,290	-0,200	-0,200	0,357	0,081
NH_2	-0,149	-0,189	-0,174	0,216	0,025
$NHCH_3$	-0,172	-0,186	-0,179	0,248	0,020
$N(CH_3)_2$	-0,200	-0,173	-0,189	0,273	0,024
CH_3	0,101	-0,145	-0,145	-0,100	0,024
$CH{=}CH_2$	0,122	-0,121	-0,121	-0,187	0,039
Ph	0,046	-0,148	-0,153	-0,083	0,054
$C{\equiv}CH$	0,044	-0,122	-0,122	-0,188	0,090
$C_{60}CR^-$ closed					
H	0,134	-0,129	-0,129	-0,290	-0,586
OH	-0,358	-0,240	-0,240	0,336	-0,498
OCH_3	-0,417	-0,239	-0,239	0,378	-0,483
NH_2	-0,307	-0,223	-0,230	0,310	-0,550
$NHCH_3$	-0,352	-0,231	-0,227	0,347	-0,537
$N(CH_3)_2$	-0,397	-0,217	-0,213	0,360	-0,533
CH_3	-0,198	-0,110	-0,110	-0,021	-0,561
$CH{=}CH_2$	-0,340	-0,124	-0,098	0.020	-0,418
Ph	-0,517	-0,102	-0,102	0,093	-0,372
$C{\equiv}CH$	-0,665	0,018	0,019	-0,007	-0,365
$C_{60}CR^-$ open					
H	0.227	0.010	-0.112	-0.244	-0,881
OH	-0,250	-0,132	-0,244	0,512	-0,886
OCH_3	-0,251	-0,166	-0,203	0,553	-0,933
NH_2	-0,099	-0,192	-0,192	0,529	-1,046
$NHCH_3$	-0,099	-0,203	-0,202	0,568	-1,064
$N(CH_3)_2$	-0,100	-0,211	-0,211	0,604	-1,082
CH_3	0,028	0,003	-0,089	-0,050	-0,892
$CH{=}CH_2$	-0,119	0,013	-0,056	-0,110	-0,728
Ph	-0,259	-0,020	-0,020	-0,064	-0,637
$C{\equiv}CH$	-0,270	0,048	0,045	-0,182	-0,641

TABLE 5. HOMO and LUMO energies (a.u.), band gap energy difference ($\Delta\varepsilon$, in eV.), global hardness (eV) and softness (10^{-2} eV^{-1}), and magnetizabilities (χ_M, in cgs-ppm) at HF/3-21G//AM1 level for all systems.

	ε_{HOMO}	ε_{LUMO}	$\Delta\varepsilon$	η	S	χ_M
$C_{60}HR$						
H	-0,2862	-0,0240	0,2622	3,57	14,0	-360
OH	-0,2911	-0,0271	0,2640	3,59	13,9	-358
OCH_3	-0,2899	-0,0257	0,2642	3,59	13,9	-366
NH_2	-0,2876	-0,0243	0,2633	3,58	14,0	-362
$NHCH_3$	-0,2869	-0,0237	0,2632	3,58	14,0	-367
$N(CH_3)_2$	-0,2864	-0,0234	0,2630	3,58	14,0	-373
CH_3	-0,2857	-0,0230	0,2627	3,57	14,0	-363
$CH=CH_2$	-0,2864	-0,0233	0,2631	3,58	14,0	-364
Ph	-0,2862	-0,0234	0,2627	3,57	14,0	-390
$C\equiv CH$	-0,2888	-0,0255	0,2633	3,58	14,0	-366
$C_{60}R^-$						
H	-0,1078	0,0889	0,1967	2,68	18,7	-357
OH	-0,1207	0,0854	0,2060	2,80	17,8	-355
OCH_3	-0,1201	0,0858	0,2059	2,80	17,9	-359
NH_2	-0,1165	0,0879	0,2045	2,78	18,0	-358
$NHCH_3$	-0,1167	0,0878	0,2045	2,78	18,0	-362
$N(CH_3)_2$	-0,1171	0,0875	0,2046	2,78	18,0	-368
CH_3	-0,1096	0,0891	0,1987	2,70	18,5	-361
$CH=CH_2$	-0,1124	0,0876	0,2000	2,72	18,4	-361
Ph	-0,1143	0,0859	0,2001	2,72	18,4	-381
$C\equiv CH$	-0,1163	0,0855	0,2018	2,75	18,2	-362
$C_{60}CHR$						
H	-0,2898	-0,0244	0,2654	3,61	13,8	-359
OH	-0,2938	-0,0289	0,2649	3,60	13,9	-374
OCH_3	-0,2880	-0,0234	0,2646	3,60	13,9	-365
NH_2	-0,2888	-0,0252	0,2636	3,59	13,9	-369
$NHCH_3$	-0,2876	-0,0246	0,2631	3,58	14,0	-373
$N(CH_3)_2$	-0,2871	-0,0244	0,2627	3,57	14,0	-374
CH_3	-0,2887	-0,0238	0,2649	3,60	13,9	-367
$CH=CH_2$	-0,2888	-0,0244	0,2644	3,60	13,9	-366
Ph	-0,2882	-0,0235	0,2647	3,60	13,9	-395
$C\equiv CH$	-0,2909	-0,0257	0,2652	3,61	13,9	-370
$C_{60}CR^-$ closed						
H	-0,1004	0,0801	0,1805	2,46	20,4	-354
OH	-0,1326	0,0781	0,2107	2,87	17,4	-360
OCH_3	-0,1354	0,0771	0,2125	2,89	17,3	-366
NH_2	-0,1147	0,0777	0,1925	2,62	19,1	-367
$NHCH_3$	-0,1213	0,0766	0,1980	2,69	18,6	-372
$N(CH_3)_2$	-0,1161	0,0767	0,1929	2,62	19,1	-373
CH_3	-0,0881	0,0787	0,1667	2,27	22,0	-359
$CH=CH_2$	-0,0870	0,0702	0,1573	2,14	23,4	-365
Ph	-0,0906	0,0660	0,1566	2,13	23,5	-387
$C\equiv CH$	-0,1044	0,0700	0,1743	2,37	21,1	-366
$C_{60}CR^-$ open						
H	-0,0938	0,0875	0,1812	2,47	20,3	-355
OH	-0,0894	0,0896	0,1791	2,44	20,5	-385
OCH_3	-0,0854	0,0917	0,1770	2,41	20,8	-389
NH_2	-0,0763	0,0997	0,1760	2,39	20,9	-392
$NHCH_3$	-0,0747	0,1011	0,1757	2,39	20,9	-399
$N(CH_3)_2$	-0,0722	0,1024	0,1746	2,38	21,1	-405
CH_3	-0,0912	0,0885	0,1797	2,45	20,4	-361
$CH=CH_2$	-0,0956	0,0805	0,1761	2,40	20,9	-350
Ph	-0,0979	0,0742	0,1721	2,34	21,4	-371
$C\equiv CH$	-0,1096	0,0754	0,1850	2,52	19,9	-348

C. Global aromaticity

In Table 5, the HOMO and LUMO energies are given, together with the band gap. When comparing the two series considered, we find a slightly higher band gap for the methanofullerene as compared to the respective substituted hydrofullerenes, except for the $NHCH_3$ and the $N(CH_3)_2$ derivatives. The HOMO-LUMO gap ($\Delta\varepsilon$) is an estimate of the chemical hardness, and the latter property has been proposed as a measure of the global aromaticity[27,44,45] (for recent reviews on the use of DFT based reactivity and stability descriptors, see references [46-48]). For this, the calculated values for the global hardness and softness are also given in Table 5.

The deprotonation of a given system, for both the substituted hydrofullerene and methanofullerene series, shows a clear increase in softness, with a higher effect in the latter series. This is expected to be due to the creation of an electron rich environment in the carbene addition region, since in this case, less electron density is transposed to the fullerene cage upon deprotonation (see Part B, Table 4).

As a further prediction of the global aromaticity, the magnetisabilities χ_M are given in Table 5. In almost all cases, the carbene system is found to be more aromatic as compared to its substituted hydrofullerene counterpart with the same functional group, and this for both the acidic and the basic forms. In general, a slight decrease in global aromaticity can be seen upon deprotonation, coinciding with a lowered stability. For the methanofullerene series, a clear influence of the functional group can again be discerned in the basic form. Indeed, in the case of an OR' or NR'_2 functional group, a lower band gap and a higher magnetisability can be found for the open structure, whereas the closed structure is found more aromatic in case of an alkyl addend.

D. Local aromaticity

In order to make a further interpretation of the similarities and differences between the analysed substituted hydrofullerene and methanofullerene series considered, their local aromaticity is analysed. To this end, NICS were calculated in the geometrical ring centres for all rings of each system. In Table 6, these values are given for the rings of, and surroundings, the addition site, with the numbering of the rings according to Figure 3.

When considering the substituted hydrofullerene series, little effect can be seen from the difference in functional group. The local aromatic pattern seems to be little influenced by the different characters of these functional groups. This can be brought in accordance with our previous results showing the electron deficiency of the fullerene cage, together with its high global softness, to greatly influence the charge transfer between the functional group and the cage.[35] For the deprotonated systems however, more important differences can be discerned in the vicinity of the deprotonated site.

When now comparing the local aromaticity between the respective acidic and basic forms, clear differences in NICS can be seen upon deprotonation, for all the rings of the fullerene cage. The resulting negative charge is seen to cause a general reorganisation of the electron density over the cage, clearly influencing the local aromatic pattern.

TABLE 6. NICS (ppm-cgs) for selected rings (**bold** = pentagon ring) and in the middle of d(C_1-C_2) for the $C_{60}CR^-$ open form, calculated at HF/3-21G//AM1 using the GIAO method.

	A	**B**	C	**D**	E	**F**	G	H	I	**J**	K	L
$C_{60}HR$												
H	1,1	**0,7**	1,1	**0,7**	-9,4	**1,1**	-9,4	-7,8	-9,4	**1,1**	-9,4	-7,8
OH	1,0	**1,6**	1,0	**0,9**	-9,3	**1,4**	-9,4	-7,9	-9,3	**1,4**	-9,3	-8,0
OCH_3	0,9	**1,3**	0,9	**0,7**	-9,3	**1,4**	-9,2	-8,0	-9,2	**1,4**	-9,3	-8,1
NH_2	1,0	**1,5**	1,2	**0,9**	-9,4	**1,1**	-9,4	-8,0	-9,3	**1,2**	-9,3	-8,0
$NHCH_3$	1,0	**1,1**	1,1	**0,7**	-9,4	**1,1**	-9,5	-7,9	-9,1	**1,2**	-9,3	-8,0
$N(CH_3)_2$	0,7	**1,3**	1,2	**0,8**	-9,3	**1,1**	-9,5	-8,0	-9,1	**1,1**	-9,3	-8,0
CH_3	0,9	**1,0**	0,9	**1,0**	-9,4	**1,1**	-9,3	-7,9	-9,3	**1,1**	-9,4	-7,8
$CH=CH_2$	1,0	**1,2**	1,0	**0,8**	-9,4	**1,1**	-9,1	-7,9	-9,3	**1,1**	-9,4	-7,9
Ph	1,4	**1,8**	1,4	**0,9**	-9,3	**1,2**	-9,0	-7,9	-9,0	**1,2**	-9,3	-7,9
C≡CH	0,9	**1,1**	0,9	**0,7**	-9,4	**1,1**	-9,4	-7,9	-9,4	**1,1**	-9,4	-8,0
$C_{60}R^-$												
H	2,8	**3,7**	2,8	**-3,7**	-7,8	**-1,3**	-9,8	-4,4	-9,8	**1,3**	-7,8	-6,2
OH	0,2	**5,6**	0,2	**-0,3**	-7,5	**1,0**	-9,4	-4,3	-9,4	**-1,0**	-7,5	-5,7
OCH_3	-0,2	**5,4**	0,2	**0,4**	-7,5	**1,1**	-9,2	-4,5	-9,2	**-1,1**	-7,5	-5,7
NH_2	0,2	**5,0**	1,0	**-1,6**	-7,7	**0,2**	-9,6	-4,5	-9,6	**0,5**	-8,1	-5,9
$NHCH_3$	0,3	**4,8**	1,1	**-1,7**	-7,8	**0,3**	-9,4	-4,5	-9,5	**0,6**	-8,1	-5,9
$N(CH_3)_2$	0,1	**5,0**	0,7	**-1,3**	-7,9	**0,4**	-9,4	-4,5	-9,4	**0,7**	-8,0	-5,9
CH_3	1,7	**3,9**	1,7	**-2,7**	-7,9	**-0,8**	-9,7	-4,3	-9,7	**-0,8**	-7,9	-6,0
$CH=CH_2$	1,6	**4,3**	2,1	**-2,8**	-7,9	**0,5**	-9,4	-4,4	-9,7	**-0,8**	-7,8	-6,0
Ph	2,2	**5,2**	2,2	**-2,4**	-7,8	**0,3**	-9,4	-4,5	-9,3	**-0,3**	-7,8	-5,9
C≡CH	1,7	**4,6**	1,7	**-2,9**	-8,0	**-0,5**	-9,7	-4,4	-9,7	**0,5**	-8,0	-6,1
$C_{60}CHR$												
H	-4,2	**1,2**	-4,2	**1,2**	-8,8	**2,8**	-8,8	-7,3	-8,8	**2,8**	-8,8	-7,3
OH	-3,9	**0,8**	-3,8	**0,8**	-8,8	**2,7**	-8,8	-7,4	-8,9	**2,4**	-8,9	-7,4
OCH_3	-3,3	**1,0**	-4,0	**1,0**	-8,8	**3,0**	-8,7	-7,3	-8,9	**2,5**	-8,9	-7,3
NH_2	-3,9	**0,8**	-3,6	**1,0**	-8,8	**2,6**	-8,8	-7,4	-8,9	**2,4**	-8,9	-7,3
$NHCH_3$	-3,8	**0,7**	-3,5	**0,9**	-8,8	**2,6**	-8,9	-7,4	-8,9	**2,4**	-8,9	-7,3
$N(CH_3)_2$	-2,7	**0,6**	-3,8	**1,1**	-8,8	**2,6**	-8,8	-7,4	-9,0	**2,4**	-8,9	-7,3
CH_3	-4,5	**1,2**	-3,9	**1,2**	-8,8	**2,9**	-8,8	-7,3	-8,8	**2,6**	-8,8	-7,3
$CH=CH_2$	-4,1	**1,2**	-3,9	**1,2**	-8,8	**2,8**	-8,8	-7,3	-8,8	**2,6**	-8,8	-7,3
Ph	-4,0	**1,4**	-3,8	**1,4**	-8,8	**2,7**	-8,9	-7,3	-8,7	**2,7**	-8,7	-7,2
C≡CH	-4,2	**1,2**	-4,3	**1,2**	-8,8	**2,9**	-8,8	-7,4	-8,8	**2,6**	-8,8	-7,4
$C_{60}CR^-$ closed												
H	-1,2	**2,7**	-1,2	**2,7**	-8,7	**2,9**	-8,7	-6,8	-8,7	**2,9**	-8,7	-6,8
OH	-2,2	**1,8**	-1,8	**1,8**	-8,8	**2,3**	-8,8	-6,5	-9,0	**1,7**	-9,0	-6,5
OCH_3	-2,3	**1,8**	-2,0	**1,8**	-8,8	**2,4**	-8,8	-6,5	-9,0	**1,8**	-9,0	-6,5
NH_2	-2,5	**1,9**	-1,0	**1,3**	-8,8	**1,8**	-9,0	-6,4	-9,2	**1,6**	-9,1	-6,6
$NHCH_3$	-2,5	**1,8**	-1,0	**1,3**	-8,9	**1,9**	-9,0	-6,4	-9,2	**1,6**	-9,1	-6,7
$N(CH_3)_2$	-1,5	**1,4**	-0,7	**1,6**	-8,9	**1,9**	-8,8	-6,7	-9,2	**1,8**	-9,2	-6,6
CH_3	-1,3	**2,6**	-0,9	**2,6**	-8,6	**2,9**	-8,6	-6,8	-8,6	**3,0**	-8,6	-6,8
$CH=CH_2$	-1,8	**2,0**	-1,8	**2,2**	-8,7	**2,8**	-8,7	-6,9	-8,7	**2,8**	-8,7	-6,9
Ph	-1,8	**2,1**	-1,8	**2,1**	-8,6	**2,8**	-8,6	-6,9	-8,6	**2,8**	-8,6	-6,9
C≡CH	-1,9	**2,1**	-1,9	**2,1**	-8,8	**2,7**	-8,6	-7,0	-8,8	**2,7**	-8,8	-7,0
$C_{60}CR^-$ open												
H	4,1	**-0,8**	8,7	**9,4**	-8,9	**-2,6**	-7,3	-6,8	-6,4	**-6,4**	-9,7	-5,2
OH	8,4	**-4,5**	14,1	**-0,0**	-10,7	**-7,5**	-9,5	-7,9	-9,4	**-11,2**	-10,8	-7,3
OCH_3	8,8	**0,4**	14,0	**-4,5**	-9,4	**-8,3**	-10,6	-7,1	-10,9	**-12,0**	-9,3	-7,9
NH_2	8,7	**-3,8**	11,7	**-3,8**	-10,6	**-10,0**	-10,6	-7,6	-10,6	**-11,7**	-10,6	-7,6
$NHCH_3$	10,5	**-3,1**	8,6	**-4,0**	-10,6	**-11,3**	-10,6	-7,5	-10,6	**-10,2**	-10,6	-7,6
$N(CH_3)_2$	9,3	**-3,5**	9,3	**-3,5**	-10,6	**-11,0**	-10,6	-7,5	-10,6	**-11,0**	-10,6	-7,5
CH_3	3,5	**-0,0**	7,0	**9,0**	-9,0	**-2,3**	-7,5	-6,9	-7,0	**-5,9**	-9,9	-5,3
$CH=CH_2$	-3,1	**5,7**	-3,2	**10,4**	-7,2	**2,0**	-6,8	-6,1	-6,8	**1,4**	-7,8	-5,1
Ph	-5,7	**8,8**	-5,7	**8,8**	-6,9	**3,6**	-6,5	-5,6	-6,9	**3,6**	-6,5	-5,7
C≡CH	-7,1	**9,0**	-7,0	**9,1**	-6,6	**4,4**	-6,2	-5,6	-6,6	**4,4**	-6,2	-5,6

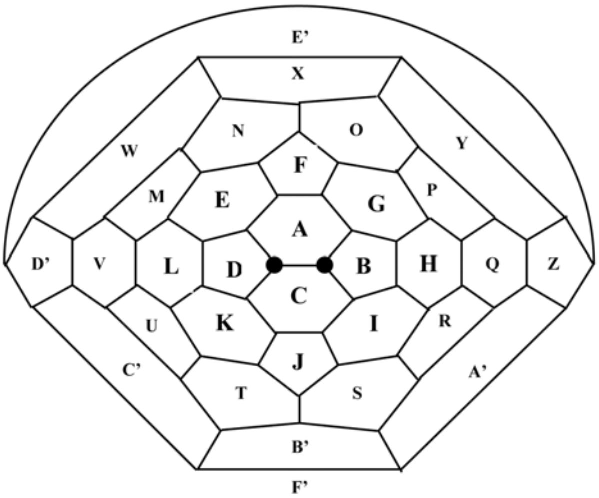


FIGURE 3. Schlegel diagram with labelled rings follwing the spin rule.

Also in the case of the methanofullerenes, little influence from the functional group type can be discerned in the local aromaticity, although more important as compared to the substituted hydrofullerenes. We note that the rings of the central pyracylenic unit, numbered A and C, can have a different NICS due to the carbene functional group facing only one of these rings.

For the methanofullerenes, upon deprotonation, the local aromatic pattern is more altered in the case of open structures with respect to their corresponding closed structures. The NICS values of the 5- and 6-membered rings show a less regularity of values depending on the susbtituent R of the system with respect to substituted hydrofullerenes series. There is a clear relation with the localization of the electrons in the rings A and C (see Table 6) measured by NICS values. In case of $C_{60}CR^-$ open systems where the R substituents OR' and NR'$_2$ type are closer to the two rings,A and C, because the angle α is larger, there is a higher localization (more positive NICS values) in these rings thanks of its donor character and this effect is more remarkable than for systems with R=H or CH_3 substituents, and for the rest of R substituents studied, where its acceptor character explains a higher aromatic character of the A and C rings. Going from $C_{60}CHR$ structures to $C_{60}CR^-$ open structures, one can note that A and C rings become less aromatic in case of R= H, OH, OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$ and CH_3 and more aromatic in case of conjugated R substituent ($CH=CH_2$, Ph and C≡CH); meanwhile rings B and D, and F and J, become more aromatic for the first group of R subtituents (R= H, OH, OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$ and CH_3) and less aromatic for the second group ($CH=CH_2$, Ph and C≡CH). From this, it seems clear that the donor substituents help to localize electrons in the vicinity of the addition site of carbene. The relatively high negative values of NICS values in the 5-membered rings F and J, can be understandable as a result of a reorganization of the system, when rings A and C show a higher localization, F and J show a higher delocalization. Apart from addition site, little difference is indeed seen in the NICS for the remainder of the fullerene. This clearly demonstrates the lack of interaction between the 'carbene' part of the system and the fullerene cage. As was already predicted from the results in the previous parts of this section, the electron density originating from the deprotonation does not delocalise over the fullerene cage, as it is, on the contrary, the case for the substituted hydrofullerenes.

IV. CONCLUSIONS.

An *ab initio* study of the properties of a series of substituted hydrofullerenes ($C_{60}HR$) and a series of methanofullerenes ($C_{60}CHR$), (R= H, OH, OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$, CH_3, $CH=CH_2$, Ph and C≡CH) has been performed. Their reactivity has been analysed, based on their geometrical, energetic and electronic properties.

The formation of C_{60}HR systems from C_{60} is found to have a more important perturbation for the fullerene cage than the carbene addition to C_{60}, both in terms of geometrical and electronic structure. The difference in functional groups does not have an important influence, since little differences are found in geometric, and magnetic properties for the groups considered.

The acidity for the methanofullerenes is predicted to be much lower as compared to the substituted hydrofullerenes. Use of their acidic properties for further functionalisation will thus be less applicable for the latter series. The negative charge resulting from the deprotonation process will be more localised to the addition region in the case of the methanofullerene series, C_{60}CHR, as compared to the substituted hydrofullerene series, C_{60}HR. The influence of the substituent is found to be larger than for the equivalent C_{60}HR.

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SUPLEMENTARY MATERIAL

TABLE 3 ampl. Electronic delocalisation calculated from the Mulliken populations ($N_{C\ acid}$, $N_{H\ acid}$ and $N_{C\ base}$) for all the structures studied at B3LYP/6-31G*//AM1 level.

	$N_{C\ acid}$	$N_{H\ acid}$	$N_{C\ base}$	Δ	$N_{C\ base}$	Δ
$C_{60}HR$/ $C_{60}R^-$						
H	-0,239	0,178	0,013	-0,431		
OH	-0,289	0,210	-0,004	-0,495		
OCH_3	-0,299	0,209	-0,020	-0,488		
NH_2	-0,266	0,192	-0,034	-0,423		
$NHCH_3$	-0,271	0,191	-0,052	-0,410		
$N(CH_3)_2$	-0,269	0,195	-0,054	-0,409		
CH_3	-0,277	0,178	-0,013	-0,442		
$CH=CH_2$	-0,281	0,186	-0,023	-0,444		
Ph	-0,270	0,193	0,010	-0,473		
C≡CH	-0,286	0,199	-0,024	-0,461		
$C_{60}CHR$/ $C_{60}CR^-$			closed	closed	open	open
H	-0,310	0,181	-0,654	0,163	-0,183	-0,308
OH	0,149	0,181	0,052	-0,084	0,244	-0,276
OCH_3	0,169	0,155	0,099	-0,085	0,264	-0,250
NH_2	0,028	0,171	0,030	-0,173	0,264	-0,407
$NHCH_3$	0,052	0,168	0,046	-0,162	0,284	-0,400
$N(CH_3)_2$	0,029	0,164	0,033	-0,168	0,292	-0,427
CH_3	-0,090	0,167	-0,212	-0,045	0,006	-0,263
$CH=CH_2$	-0,144	0,166	0,033	-0,343	-0,032	-0,278
Ph	-0,210	0,184	-0,062	-0,332	-0,143	-0,251
C≡CH	-0,302	0,198	-0,238	-0,262	-0,277	-0,223

5.6. Article VI:

Addition patterns of $C_{60}F_n$ studied by means of global and local aromaticity analysis

M. Cases, G. Van Lier and P. Geerlings

Addition pattern of $C_{60}F_n$ studied by means of global and local aromaticity analysis

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ABSTRACT

Two series of $C_{60}F_n$ systems (addition pattern *T* (n=2,4,6,…18) and addition pattern *S* (n=2,4,6,…20)) have been studied theoretically, in order to analyse the two possible addition patterns, *T* and *S* by means of global and local aromaticity calculation. $C_{60}F_n$ systems have been fully optimized at the AM1 level to analyse geometric changes along the series of systems, the fluorine atoms addition to C_{60} clearly distortions its spherical geometry. NICS and magnetizabilities have been carried out at HF/3-21G//AM1 level, using CSGT and GIAO methods, to analyse the local (for each 5- or 6-membered ring centre) and global (for each system) aromatic character, respectively. From the changing of NICS values after a new pair of fluorine atoms attached to C_{60}, we show that one can predict the preferential next [6,6]-bond susceptible to be attacked, in case of both addition patterns defined. And from the magnetizabilities values one confirms that the fluorination reaction goes on until higher fluorinated systems in order to get structures more and more aromatic.

Keywords: $C_{60}F_n$ (n= 2, 4, 6, 8, 10, 12, 14, 16, 18, 20), S and T addition pattern, global and local aromaticity

INTRODUCTION

Lastly, there has been a significant interest in fluoro derivatives of C_{60} because they have been shown to be promising synthons as enhanced acceptors in donor-acceptors diads, thanks of their characteristics (good solubility, high reactivity towards nucleophiles and enhanced dienophilicity of the unsubstituted part of the cage, as a result of electron withdrawal by fluorines).[1]

Fluorine addition to the C_{60} fullerene can be afforded with a variety of agents.[2-11] The inability to control the reaction provides a complex mixture of products with varying numbers of fluorine atoms attached to the carbon cage and difficults the isolation of early compounds of fluorine addition. The situation has changed few years ago, the different fluorofullerene derivatives characterized have became in number a wide kind of C_{60} derivatives involving a single addend type. At the beginning of the fluorofullerenes synthesis and characterization the number of fluorine atoms attached to C_{60} were so large (48, 36, 18 and more recently 20[12]), but now it is possible to isolate fluorofullerenes with a few number of fluorines attached (2,4,6,8,16) by optimization of the reaction conditions.[1] A deep study of these isolated compounds respect their geometric, energetic and electronic characteristics can help to understand how and why the multiple addition to C_{60} takes place.

All fluorofullerene structures present two dominant features, *the fluorine atoms are attached to the cage as fluorine pairs across [6,6]-bonds*, and *the evidence of the tendency to create structures with increased aromaticity relative to the fullerene precursor*, the aromatic character of the fluorofullerenes increases in order of increasing the number of fluorine atoms attached to the cage. Because fullerenes are partially aromatic, addition of the first fluorine pair increases localization of the electrons remaining double bonds of the same hexagon, so that further addition in this hexagon becomes favourable.[13]

Similar features present hydrofullerenes, and comparison between isostructural $C_{60}X_n$ systems (X= H, F, n= 18(*T*), 20(*S*), 36(*T*))[14, 15] show that the addition pattern in both type of C_{60} derivatives follows a contiguous addition pathway, when a [6,6]-bond is attacked, then one of its adjacent [6,6]-bond is the preferential bond to be nextly attacked, and go on.[16, 17]

From the different fluoroderivatives of C_{60} characterized at experimental level, two possible addition pattern have been defined, the *S* and *T* called addition patterns.[1]

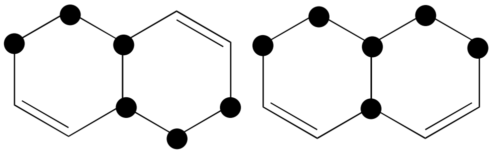


FIGURE 1. S and T addition patterns.

The first addition of a pair of fluorine atoms takes place at [6,6]-bond (1,2-fluoroderivative $C_{60}F_2$ is formed), the second pair is attached to one of the adjacent [6,6]-bond of the same hexagon firstly attacked (1,2,3,4-fluoroderivative $C_{60}F_4$ is formed), and then at time of the third pair of fluorine atoms attachment depending on which adjacent [6,6]-bond is chosen, the first *T* or first *S* isomer is formed, $C_{60}F_6$-*T* or $C_{60}F_6$-*S* isomers. The *S* isomer of $C_{60}F_6$ can be isolated, meanwhile the *T* isomer no because it undergoes further fluorination more rapidly to give the $C_{60}F_8$.[13] Continuous pair fluorine atoms addition to C_{60} follows the *T* pattern until lead ultimately to $C_{60}F_{18}$ formation, and in case of the *S* pattern (called also the zigzag addition) results only in the formation ultimately of $C_{60}F_{20}$. Boltalina et al.[6] reported the $C_{60}F_{18}$ isomer with C_{3v} symmetry as the more stable, which presents a distorted cage structure, because all the fluorine atoms are bounded to one hemisphere of C_{60} cage in the way that lead a planar 6-membered ring centred with 18 sp^3C atoms around and then other hemisphere is made up of 24 sp^2C atoms, and a flattened equatorial belt of 12 sp^2C atoms separates the two hemispheres. Avent et al.[18] previously reported the possible isolation and characterization of $C_{60}F_{16}$, both respect to *T* addition pattern, and more recently Boltalina *et al.*[13] reported the possible isolation and characterization of $C_{60}F_8$. In case of *S* addition pattern only the $C_{60}F_{20}$ have been isolated and characterized after $C_{60}F_6$-*S*, and named "Saturnene" in view of its unique structure comprising flattened poles and extended equator of sp^3C atoms.

In this present work we study the different systems of $C_{60}F_n$ series for the *T* addition pattern (n= 2, 4, 6,…18), which provides the $C_{60}F_{18}$ structure at end point, and for the *S* addition pattern (n= 2, 4, 6,… 20), which provides the $C_{60}F_{20}$ structure at end point of fluorinating process of C_{60}. The relative energetic stabilities between series, and between the structures of a same series, and comparison with their magnetizabilities values are given to confirm that the increasing of number of fluorine atoms attached to C_{60} provides structures with a higher global aromatic character. Analysis of the geometries, especially related with the possibility to predict bonds with a higher double bond character (shorter C-C bond length, the experimental value for C_{60} is 1.401Å length for [6,6]-bond (30 bonds)[19], and at AM1 1.385Å, in C_{60}) in order to compare with the possible predictable [6,6]-bond additions preferential on base of the NICS values. In case of C_{60} molecule the NICS values of its pentagons ring centres is +5.1ppm and +6.8ppm for its hexagons ring centres at HF/3-21G//AM1. These values are expected to change when new pairs of fluorine atoms added to C_{60} structure, we will show how on base of these NICS values for each system it is easy to know the local aromaticity of each pentagon and hexagon and can predict localized electron site.

COMPUTATIONAL DETAILS

All geometries ($C_{60}F_n$ systems (addition pattern *T* (n= 2, 4, 6,…18) and addition pattern *S* (n= 2, 4, 6,…20)) were fully optimized at the semiempirical AM1 level of theory[20] using the AMPAC program.[21] The AM1 method has been preferred over other semiempirical methods because it yields reliable results for the geometries of C_{60}. Single point calculations using the AM1 fully optimised geometries at HF/3-21G were performed using GAUSSIAN98.[22]

From the HOMO-LUMO gap one can calculate the T value as HOMO-LUMO energy separation multiplied by the number of carbon atoms conjugated in the system studied. $C_{60}F_2$ (58C), $C_{60}F_4$ (56C), $C_{60}F_6$ (54C), … This value seems to be preferred as an index of kinetic stability.[23-26]

Global aromaticity in terms of the molecular magnetizability for each system is calculated, using the CSGT method,[27] in order to know if the tendency of increasing aromaticity respect to precursor derivative in the series studied is clear and if it has some relationship with the energy stability of each system.

The local aromaticity of a ring is described by its ability to support diamagnetic ring (i.e. diatropic) currents, which can be described by the nucleus-independent chemical shift or NICS.[28] It has been calculated at the geometrical centres of each 5- and 6-membered rings of the cage, determined by the non-weighted mean of ring atom coordinates, using the GIAO method.[29]

Molecular magnetizabilities and NICS values were both calculated at the *ab initio* HF/3-21G level of theory, using GAUSSIAN98 program, at the AM1 fully optimised geometries. It is important to remark that DFT methods do not provide systematically better NMR results than Hartree-Fock, because no current functionals include a magnetic field dependence.

RESULTS AND DISCUSSION

A large number of systems have been studied and in order to better present the results we will separate this section in several subsections corresponding each one to some close $C_{60}F_n$ systems in the fluorinating process of C_{60}. In Table 1 are gathered the energy, HOMO-LUMO gap, T index value and magnetizability of each system studied. See figure 2 to know the numbering of the C atoms of C_{60} where F atoms are attached for each structure considered.

TABLE 1. Energy at HF/3-21G//AM1 (a.u.), HOMO-LUMO gap (a.u.), T index value, and χ (cgs-ppm) for systems studied.

$C_{60}F_n$	Energy	HOMO-LUMO (gap)	T	χ
$C_{60}F_2$	-2456,8228	0,267	15,5	-369
$C_{60}F_4$	-2654,6233	0,268	15,0	-397
$C_{60}F_6$-S	-2852,4267	0,272	14,7	-425
$C_{60}F_6$-T	-2852,4207	0,269	14,5	-421
$C_{60}F_8$-S	-3050,2312	0,275	14,3	-455
$C_{60}F_{10}$-S	-3248,0365	0,289	14,4	-488
$C_{60}F_{12}$-S	-3445,8395	0,293	14,0	-501
$C_{60}F_{14}$-S	-3643,6421	0,293	13,5	-515
$C_{60}F_{16}$-S	-3841,4452	0,299	13,1	-529
$C_{60}F_{18}$-S	-4039,2453	0,301	12,7	-549
$C_{60}F_{20}$-S	-4237,0764	0,349	14,0	-571
$C_{60}F_8$-T	-3050,1926	0,251	13,1	-444
$C_{60}F_8$-T(T+1)n	-3050,2256	0,280	14,6	-451
$C_{60}F_{10}$-T	-3248,0306	0,274	13,7	-461
$C_{60}F_{10}$-T(T+2)n	-3248,0314	0,286	14,3	-481
$C_{60}F_{12}$-T(T+3)	-3445,8368	0,295	14,2	-489
$C_{60}F_{14}$-T(2T+1)	-3643,6443	0,298	13,7	-504
$C_{60}F_{16}$-T(2T+2)	-3841,4647	0,299	13,2	-515
$C_{60}F_{18}$-T(3T)	-4039,2932	0,321	13,5	-530
$C_{60}F_{12}$-Tn	-3445,8362	0,293	14,1	-492
$C_{60}F_{14}$-Tn	-3643,6430	0,300	13,8	-499
$C_{60}F_{16}$-Tn	-3841,4473	0,301	13,2	-517
$C_{60}F_{18}$-Tn	-4039,2565	0,314	13,2	-536

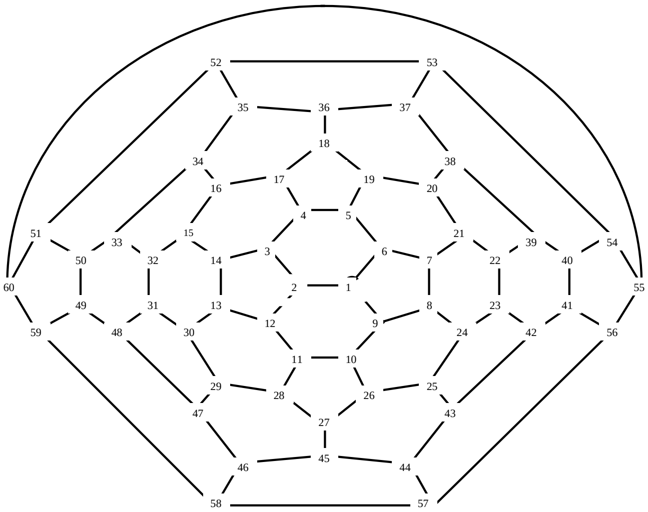


FIGURE 2. Numbering for the C atoms of C_{60} where F atoms are attached.

$C_{60}F_2$, $C_{60}F_4$

These are the two common first fluorofullerenes of both series, *T* and *S*. The addition of fluorine atoms to C_{60} as mentioned takes place across a [6,6]-bond of the cage instead on a 5,6-bond. Generally the additions to C_{60} take place at [6,6]-bond which is a bond with a higher double bond character, and in this case it occurs also because if one compares the two possible structures, 1,2-$C_{60}F_2$ and 2,3-$C_{60}F_2$, the former is 24.7 kcal/mol more stable than the latter. The reason is as showed in this kind of addition the strain which appears in the pentagon when after the addition it would be necessary the location of one double bond on it.

The second pair of fluorine atoms addition takes place in one adjacent [6,6]-bond (3,4-, 5,6-, 9,10- or 11,12- are equivalent [6,6]-bonds) of 1,2-([6,6]-bond). The octahedral addition (18,36- or 27,45-) yield a system that is a little less reactive (higher kinetic stability as predicted by T value), has a higher magnetizability value and it is 6.2 kcal/mol less stable than 1,2,3,4-$C_{60}F_4$.

The third pair of fluorine atoms additions, if one takes in consideration that the continuous fluorinating process takes place in adjacent [6,6]-bonds of the previous [6,6]-bonds attacked, then clearly can distinguish between two possibilities: 9,10- and 11,12-, which will correspond to $C_{60}F_6$-S and $C_{60}F_6$-T isomers, respectively. From the NICS values of $C_{60}F_4$ (Fig 3b) seems that the electrons are more located in 9,10-([6,6]-bond) than in 11,12-([6,6]-bond).

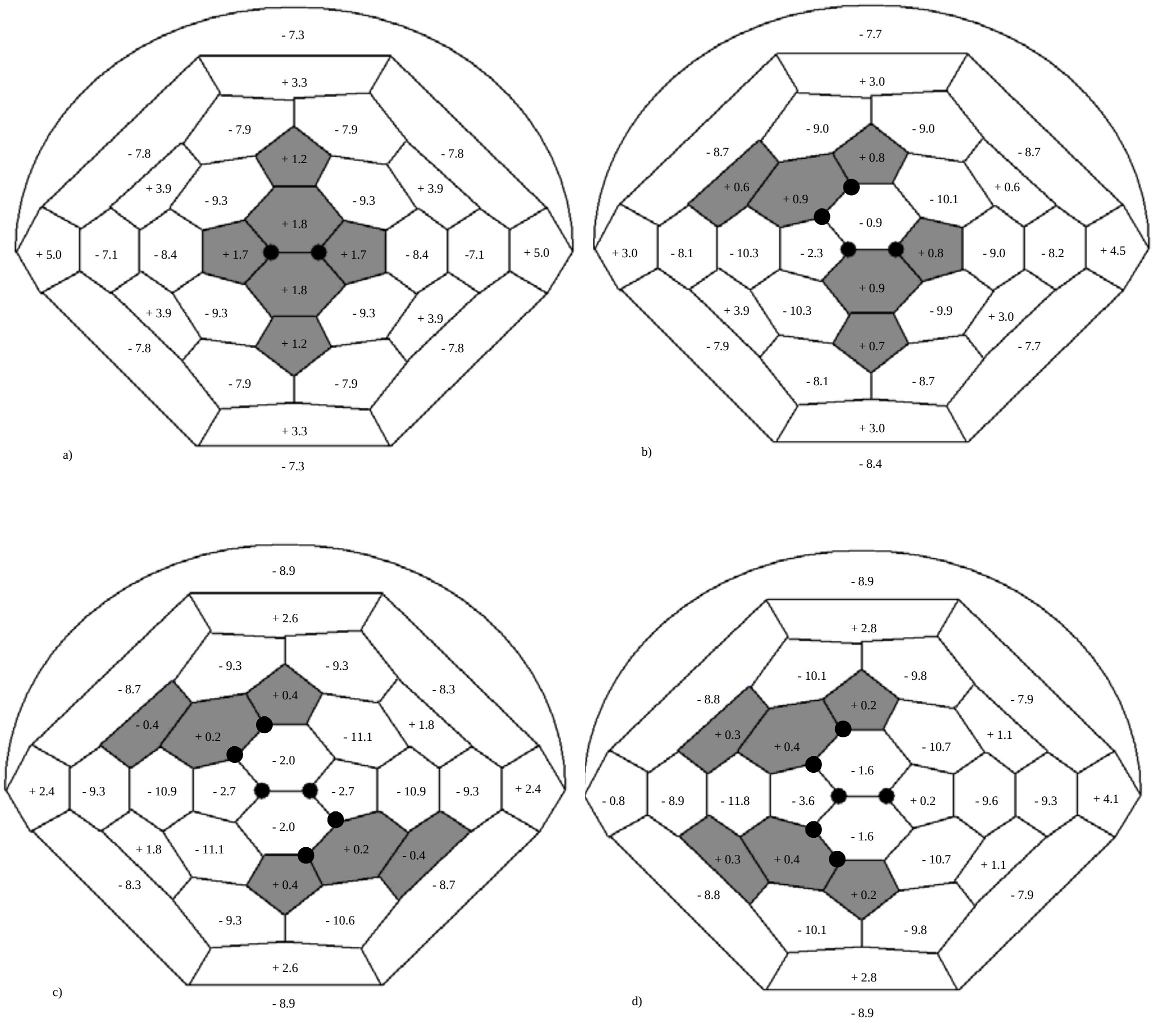


FIGURE 3. NICS values of a) $C_{60}F_2$, b) $C_{60}F_4$, c) $C_{60}F_6$-S and d) $C_{60}F_6$-T.

$C_{60}F_6$-T, $C_{60}F_6$-S

These are the both possible isomers for $C_{60}F_6$ fluorofullerene derivative (see Figure 3c and d). Only $C_{60}F_6$-S has been isolated and this is understandable because it is also the most stable product (at HF/3-21G//AM1 (3.8kcal/mol), at HF/3-21G (4.1kcal/mol) and HF/6-31G*//HF/3-21G (15.1kcal/mol) level of theory). Moreover, both of them have the highest global aromaticity and kinetic stability values. Both isomers can be formed from the previous $C_{60}F_4$ fluorofullerene derivative, meanwhile $C_{60}F_6$-S can be isolable, $C_{60}F_6$-T can be expected to readily undergo further fluorination at higher rate than $C_{60}F_6$-S.

From $C_{60}F_6$-S until $C_{60}F_{20}$

Zigzag continuous addition pattern conducts clearly to the $C_{60}F_{20}$, the “Saturnene” fluorofullerene derivative, and one can know from the NICS values calculated for each structure, which is the preferential [6,6]-bond (adjacent to the previous attacked) where new pair of fluorine atoms adds to the cage. For each new higher fluorofullerene derivatives, the [6,6]-bond chosen is one which the two C atoms of this bond belong to one hexagon and two pentagons with NICS values quite close to 0 value, mainly they are negative (negative NICS values correspond to diatropic ring currents which represent aromatic character of the ring), but they have increased their value from more negative to less negative thanks of the previous addition in the same hexagon which has help to localize the electrons.

$C_{60}F_n$-S isomers present a high geometric symmetry which can be observed also in case of NICS values of hexagons and pentagons of the cage, for this reason two equivalent [6,6]-bonds are possible preferential [6,6]-bonds to explain the new pair of fluorine atoms addition for each structure.

From the exhotermic energy reaction values (see Fig. 5) the formation of $C_{60}F_6$-S, $C_{60}F_8$-S and $C_{60}F_{10}$-S is favourable, but then for $C_{60}F_{12}$-S, $C_{60}F_{14}$-S and $C_{60}F_{16}$-S structures it becomes less favourable especially until the formation of $C_{60}F_{18}$-S which has the less negative exothermic energy of reaction of the S series. Then the next addition of two fluorine atoms helps to finally stabilize the structure and $C_{60}F_{20}$-S becomes a really favourable product of reaction and its high stability explains its possible isolation.

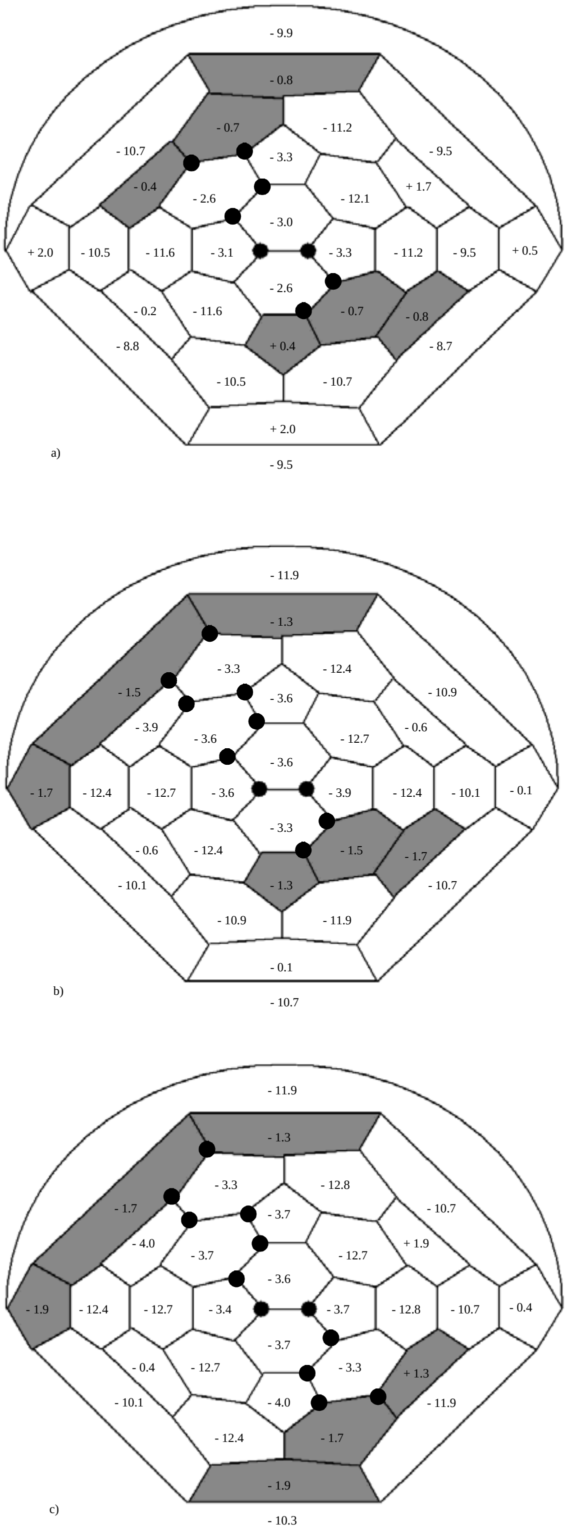
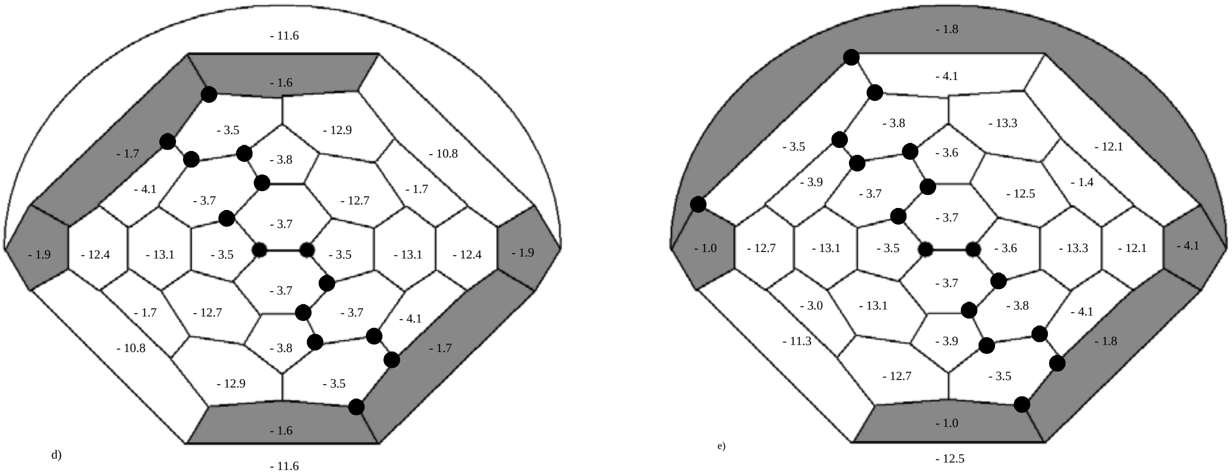
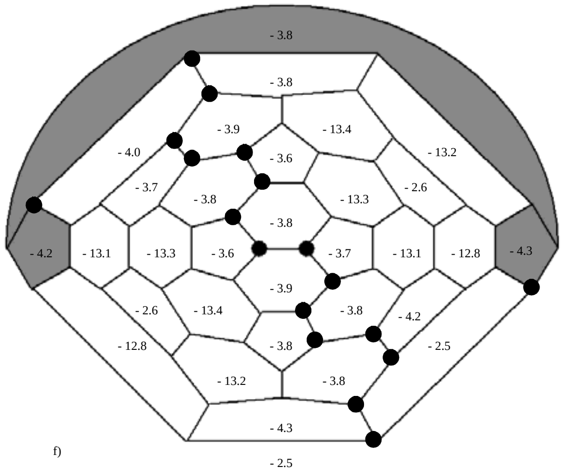


FIGURE 4.1. NICS values of $C_{60}F_n$-S (n= 8, 10, 12).





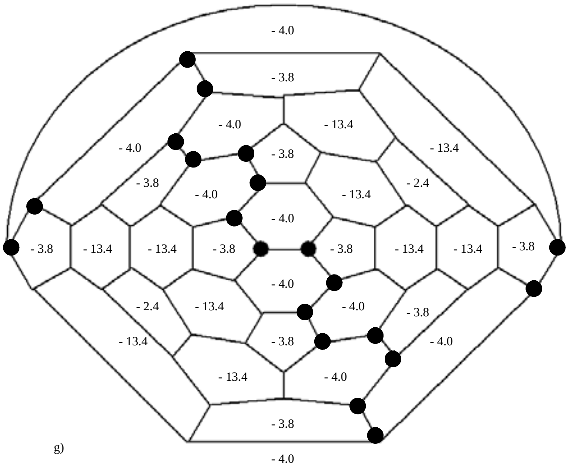


FIGURE 4.2. NICS values of $C_{60}F_n$-S (n= 14, 16, 18, 20).

The T values also show how changes the kinetic stability of these S compounds, from $C_{60}F_6$-S to $C_{60}F_{18}$-S T value decreases, they are species more reactive and less stable and for this reason they have not been possible to be isolated. Continuous fluorine addition provides finally a structure, the $C_{60}F_{20}$-S, which has a higher T value in comparison with its precursors and that explains its stability and possible isolation.

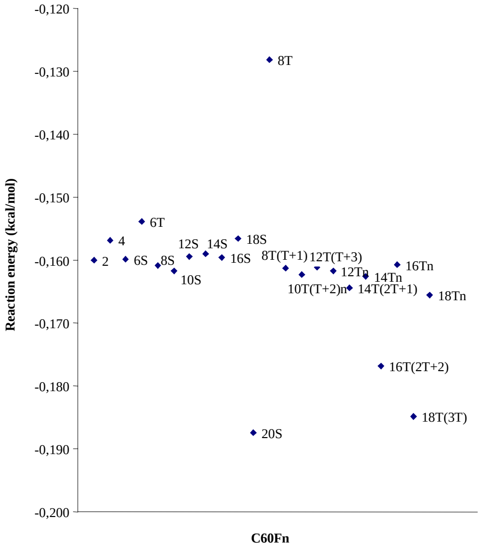


FIGURE 5. Energy of reaction ([energy of $C_{60}F_n$-S] – [energy of $C_{60}F_{n-1}$-S] – [energy of F_2]) (kcal/mol) at HF/3-21G//AM1 level vs. $C_{60}F_n$.

From $C_{60}F_6$-T until $C_{60}F_{18}$

As said before, $C_{60}F_6$-T undergoes quite rapidly to $C_{60}F_8$-T. In Figure 3d, the NICS values of

$C_{60}F_6$-T show as preferential [6,6]-bonds, where the pair of F atoms should be added because the electrons are more located, the 16,17- or 28,29- ([6,6]-bond), which belong to one hexagon and two pentagons with NICS values quite close to 0 value, they are positive (positive NICS values correspond to paratropic ring currents which represent antyaromatic character of the ring), but they have decreased their value from more positive to less positive thanks of the previous addition in the same hexagon which has help to localize the electrons and get a global more aromatic structure in comparison with $C_{60}F_6$-S isomer (see Fig 9).

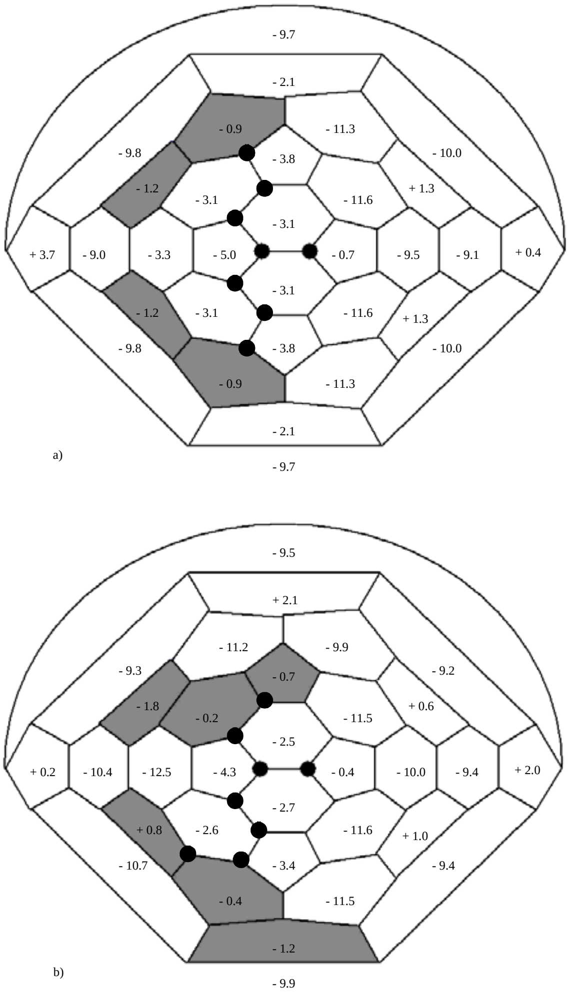


FIGURE 6. NICS values of a) $C_{60}F_8$-T [13] and b) $C_{60}F_8$–T(T+1)n (proposed from the NICS values of the previous fluorofullerene $C_{60}F_6$-T).

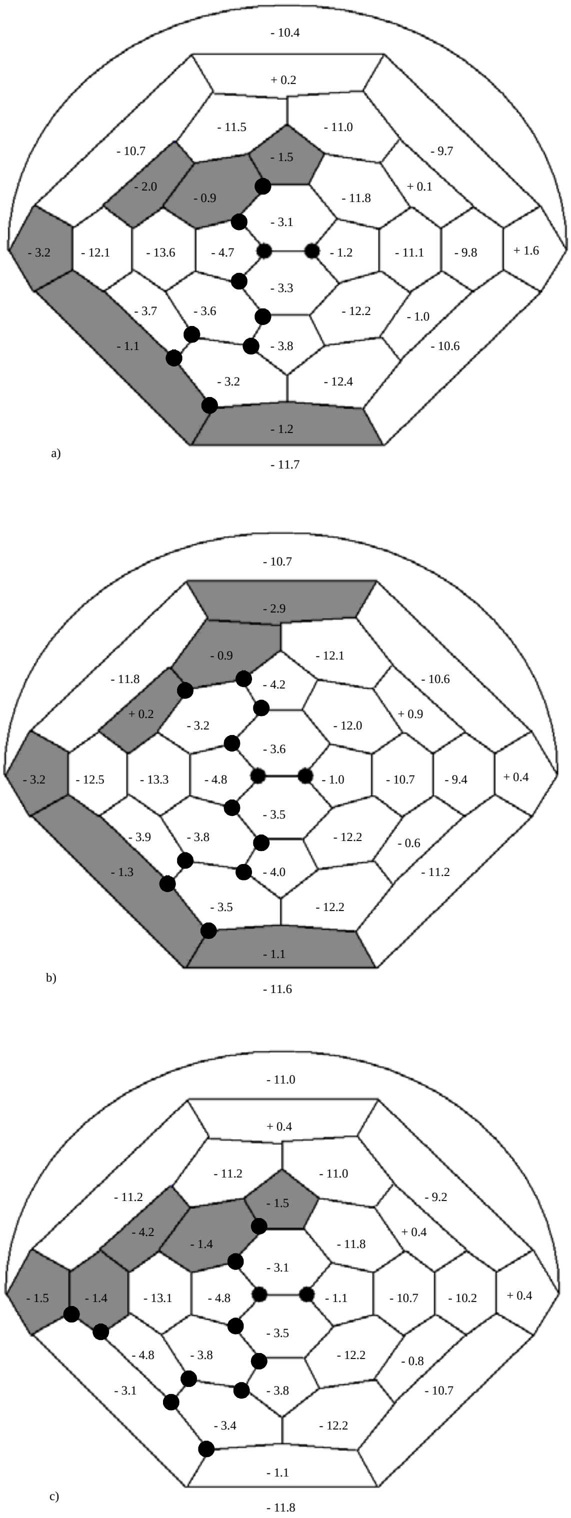


FIGURE 7. NICS values of a) $C_{60}F_{10}$-T(T+2)n, b) $C_{60}F_{12}$-T(T+3) and c) $C_{60}F_{12}$-Tn.

Experimentally have been reported[13] the structure of $C_{60}F_8$-T as Figure 6a shows, which in comparison with the proposed from the NICS analysis of $C_{60}F_6$-T, Figure 6b (shall us to call it $C_{60}F_8$-T(T+1)n), is less stable and so it can be predicted to be more reactive also as predicted by the T value. The exothermicity of structure 6b is clearly more negative than of structure 6a, and also the magnetizability value, which confirms the quite difficulty to isolate the $C_{60}F_8$-T fluorofullerene derivative (Fig 6a).

The next $C_{60}F_n$-T which have been isolated are $C_{60}F_{16}$-T and $C_{60}F_{18}$-T. On base of NICS values of the two structures of Figure 6, the $C_{60}F_8$-T is more symmetrical than $C_{60}F_8$-T(T+1)n, and in case of $C_{60}F_8$-T(T+1)n is possible to find a clear preferential [6,6]-bond to be attacked, the 46,47-([6,6]-bond) and get the next fluorofullerene derivative structure, $C_{60}F_{10}$-T. The higher exhotermic energy of reaction for the formation of $C_{60}F_{10}$-T from $C_{60}F_8$-T would suggest that this $C_{60}F_{10}$-T should be possible to be isolated, but this is not the case during the fluorinating of C_{60} process, and also this structure presents a global aromaticity measured in terms of magnetizability quite smaller than its precursor $C_{60}F_8$-T, and as it is well known the advance of the reaction takes place in order of getting more aromatic structures. So from this point of view seems quite difficult that $C_{60}F_8$-T could have been isolated with such structure proposed.

If one considers the $C_{60}F_{10}$-T(T+2)n, Fig. 7a, as the structure of $C_{60}F_{10}$-T derivative predicted from the NICS values of $C_{60}F_8$-T(T+1) structure, then the following fluorofullerene derivatives could be the $C_{60}F_{12}$-T(T+3) or the $C_{60}F_{12}$-Tn showed in Figure 7b and 7c.

The main difference between these two isomers of the $C_{60}F_{12}$ is what the distribution of F atoms added let to have in the structure, one benzenoid central ring or two benzenoid central rings, respectively. Obviously, the structure with two benzenoid rings, $C_{60}F_{12}$-Tn, is more aromatic and less stable than the other, the $C_{60}F_{12}$-T(T+3). From this point two possible routes can be defined as shows Figure 8.

Following the NICS criteria applied until now, if one takes the $C_{60}F_{12}$-Tn structure then the next [6,6]-bond preferential to be attacked for F atoms addition are the 16,17- or 35,50-([6,6]-bond), which belong to one hexagon and two pentagons with NICS values quite close to 0. If the additions take place for instance at 33,50-([6,6]-bond), one obtains the structure pitched on Fig 8a. Going on with this pattern analysis, from this new structure $C_{60}F_{14}$-T(2T+1) one can get the $C_{60}F_{16}$-T(2T+2) structure (Figure 8b) which corresponds to the structure experimentally isolated, and further fluorine addition gives place to the following $C_{60}F_{18}$-T(3T) derivative structure (Figure 8c) which corresponds also to the isolated C_{3v} isomer, the most stable. These three fluorofullerenes derivatives, $C_{60}F_{14}$-T(2T+1), $C_{60}F_{16}$-T(2T+2) and $C_{60}F_{18}$-T(3T) are more stable and less aromatic than the three isomer structures, $C_{60}F_{14}$-Tn, $C_{60}F_{16}$-Tn and $C_{60}F_{18}$-Tn (Figure 8 d, e and f, respectivelly) which can be defined from the $C_{60}F_{12}$-Tn (Fig 7c) following the NICS criteria applied.

From all results reported one can make some general remarks which are nextly exposed:

-Analysis of the geometries shows that the C-C length of [6,6]-bonds where fluorine atoms are

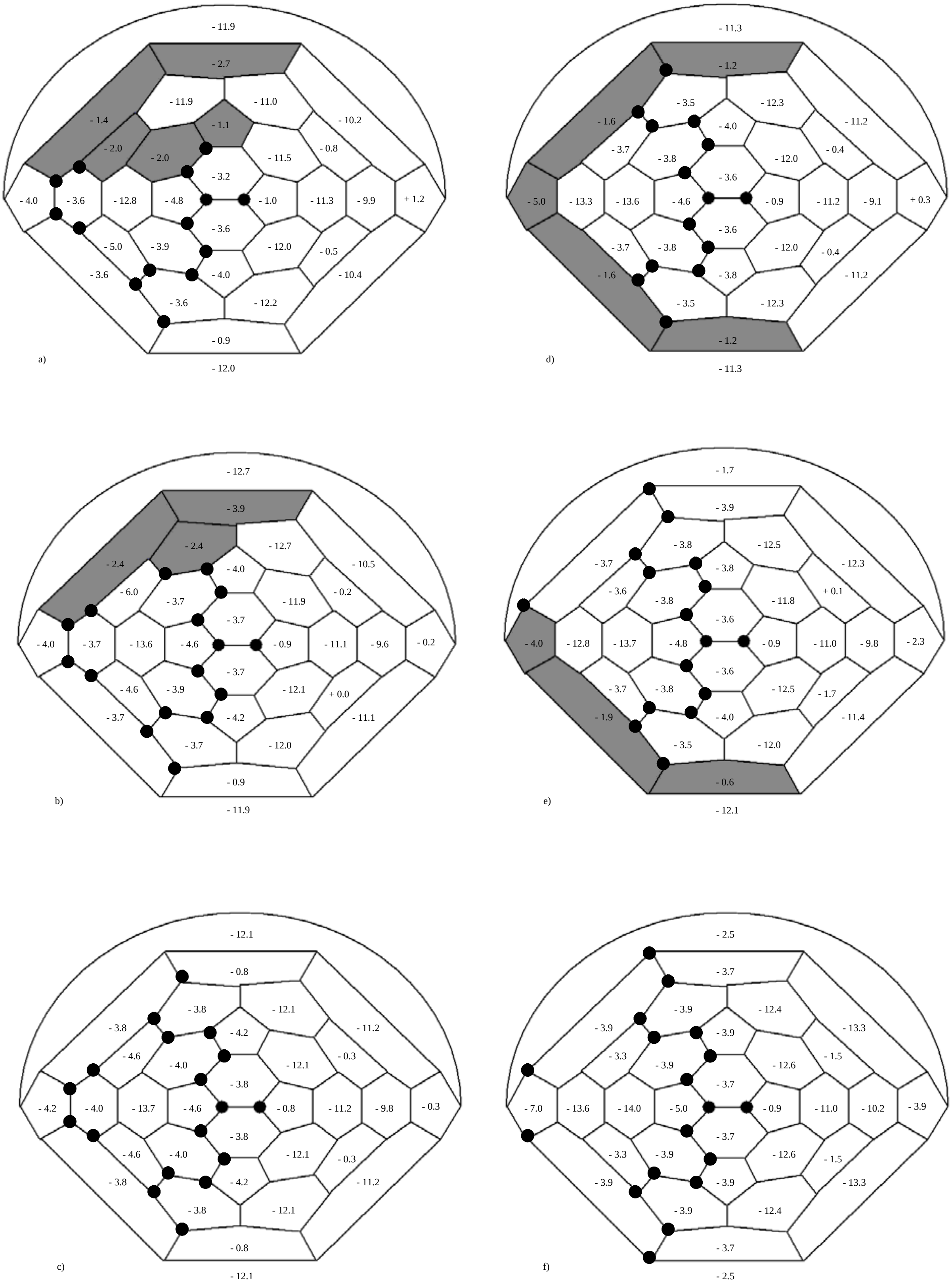


FIGURE 8. NICS values of a) $C_{60}F_{14}$-T(2T+1), b)$C_{60}F_{16}$-T(2T+2), c) $C_{60}F_{18}$-T(3T), d) $C_{60}F_{14}$-Tn, e) $C_{60}F_{16}$-Tn and f) $C_{60}F_{18}$-Tn.

added ranging from 1.62 Å to 1.58 Å when number of fluorine atoms added increases. The shortening of these C-C bonds explains the distortion of C_{60} cage. Following the NICS criteria to know which is the preferential next [6,6]-bond attacked, in all cases, the [6,6]-bond chosen is also the shortest [6,6]-bond close to previous attacked, this length is over 1.367 Å. The shortening of a bond also helps to explain its higher double bound character. In terms of aromaticity analysis, sometimes it has been said that between different aromaticity criteria should not have necessarily any relationship, but here we found that geometric and magnetic criteria have a reasonable relationship.

-Reactions are predicted to be exothermic. This exothermicity is ever seen to increase upon increasing fluorination. This shows the driving force of these reactions and can explain why only recently $C_{60}F_2$ and other lower fluorofullerenes were isolated and characterized. The subsequent fluorination stays only if a system with high stability is obtained, other $C_{60}F_n$ isomers were considered, but they were less stable (they do not follow T or S pattern) .

-Global aromaticity as predicted by magnetizability and the HOMO-LUMO gap generally follows the same tend. In a number of cases discrepancies are seen, but mostly the kinetic most stable system also has the highest magnetizability, and is thus the less reactive isomer with HOMO-LUMO gap larger (see Table 1).

-As the local aromaticity is expected to yield an indication of the addition pathway that would be followed upon subsequent addition, it can be expected that the most aromatic isomer would be found upon each addition. In order to analyse this, a number of methods are possible. First, the global aromaticity could be used, as predicted by the magnetizability and/or by the HOMO-LUMO gap. Also the kinetic stability should give an indication in this direction. A summation over the NICS values should also give an indication of the global aromaticity, as here the different contributions from the local ring currents should be taken into account. The question however remains in if a global sum over all NICS should be considered, or if one should take into account the conjugation of the system. In other words, it is possible that the occurrence of high aromatic regions and low aromatic regions is preferred over a more levelled distribution. A clear correspondence is seen from the results between the general summation of NICS and the global aromaticity as predicted by the magnetizability calculation.

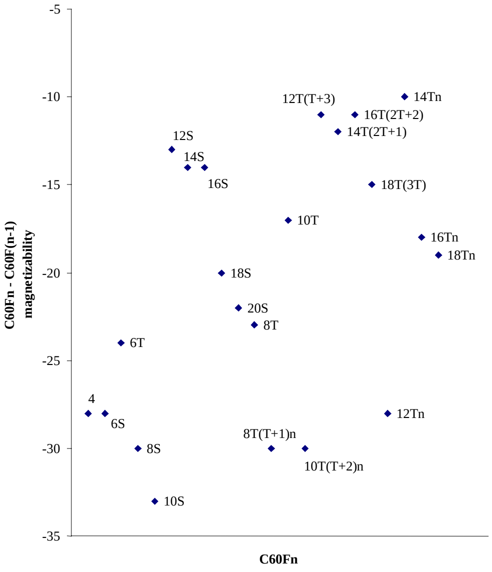


FIGURE 9. Relative Magnetizabilities (cgs-ppm) vs $C_{60}F_n$.

CONCLUSIONS

In case of the two series of fluorofullerenes studied, the $C_{60}F_n$-T (n=2,4,6,…18) and the $C_{60}F_n$-S (n=2,4,6,…20) series, the search for a relationship between the aromaticity of the system, both local and global, and the addition pattern occurring, following considerations were made:

· Addition is expected at the most reactive bond. In a conjugated system such as C_{60}, this can be expected to occur at the less delocalized site (NICS values more positive). This could be predicted by taking the NICS values of the rings surrounding a possible addition site into account and determine the preferential [6,6]-bond nextly attacked.

· The subsequent addition occurring until a system is obtained with increasing of aromaticity, this could be a driving force for the fluorination process. Global aromaticity as predicted by magnetizability of the system, as well as by the HOMO-LUMO gap, could therefore give us an indication of the direction of addition is taking. Between two possible isomers of $C_{60}F_6$, the $C_{60}F_6$-T and –S, the most stable is the less aromatic, and which has been isolated. $C_{60}F_n$-S isomers are more aromatic than $C_{60}F_n$-T series, that can explain why in $C_{60}F_n$-T route of fluorination more different structure have been able to be isolated.

·An additional indication of the addition pathway can possibly be shown by the stability of the different isomeric reactions possible. Furthermore, the kinetic stability of the possible products can give an indication of relative stability and reactivity to further addition.

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5.7. Article VII:

Analysis of S, T and O_h addition patterns of $C_{60}O_n$ by means of local and global aromaticity

M. Cases, G. Van Lier and P. Geerlings

Analysis of S, T and O_h addition patterns of $C_{60}O_n$ by means of local and global aromaticity

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ABSTRACT

S, *T* and O_h addition patterns of multiple addition of oxygen atoms to C_{60} have been studied at theoretical level. $C_{60}O_n$ (n= 1, 2, 3,…10) systems have been fully optimized at AM1 level. NICS values for each pentagon and hexagon ring centre of the cage and magnetizability of each system have been calculated at HF/3-21G//AM1 level to local and global aromaticity analysis, using CSGT and GIAO methods, respectively. From NICS values one can recognise in which region of the cage, pentagons and hexagons, presents a higher or lower aromatic character and then predicts the most probable addition site. Our results seem clearly to defend for epoxide fullerenes formation the preference for following an *S* or O_h addition pattern and clearly not *T* addition pattern in contrast to fluorofullerenes case. And from the magnetizabilities values one confirms that the progressive addition of oxygen atoms to C_{60} goes on until higher epoxides fullerenes derivatives in order to get structures more and more aromatic. It seems evident that the advance of multiple addition of oxygen atoms to C_{60} takes place under kinetic control rather than by thermodynamics, and this explains the difficulty of isolation fullerene derivatives with a low degree of oxygenation.

Keywords: $C_{60}O_n$ (n= 1, 2, 3,… 10), multiple addition, addition pattern, global and local aromaticity, NICS

INTRODUCTION

Since the fullerene soot produced by Krätschmer-Huffman method,[1] the fullerene oxides were the first fullerene derivative found to exist. They can be formed by a wide of methods (photooxidation, ozonolysis, by reaction with dimethildioxirane,…).[2-4] In 1992, Creegan et al. synthesized and studied one of the first fullerene derivatives, the [6,6]-closed epoxide isomer of $C_{60}O$.[5] [6,6]-bond type of C_{60} is the most reactive bond type of the cage, because of its higher double bond character, and usually the addition to this type of C-C bond is which provides the most stable product of reaction, rather than to a [5,6]-bond. Although theoretical calculations suggested that it should be possible to isolate another $C_{60}O$ isomer of comparable stability, that [5,6]-open oxidoannulene (an ether structure) and after over ten years of [6,6]-closed $C_{60}O$ characterization, Weisman et al. [6] described the photochemical synthesis and characterization of the [5,6]-open $C_{60}O$ (oxa-homo[60]fullerene). The two $C_{60}O$ isomers show distinct photophysical properties apart from their absorption spectra. Their stability is quite relative,[7] both of them are fullerene oxide derivatives, [6,6]-closed $C_{60}O$ is an epoxide fullerene derivative meanwhile [5,6]-open $C_{60}O$ corresponds to an ether fullerene derivative, and becomes more difficult to get it in large amounts. The fullerene oxides show a rich chemistry in reactions both with fullerenes, and with themselves, they are thermally labile and readily liberate the attached oxygen upon heating, but exist an especial great interest in the fullerene epoxide [6,6]-closed $C_{60}O$ reactivity, because is the simplest fullerene derivative and the key fullerene oxidation product that plays an important role in the synthesis of various organic, organometallic and polymeric fullerene derivatives.[4, 8-19] The epoxide is one of the most versatile functionalities and provides easy access to further modifications.[20]

C_{60} readily reacts with oxygen to form $C_{60}O_n$, and that explains the difficulty to isolate the low degree of oxygenation derivatives of C_{60}.[21] Then one can talk about multiple addition of oxygen atoms to C_{60} and it would be useful to know more about the possible addition patterns which can drive this multiple addition. As said, the preferential C-C bond of C_{60} to be attacked for an oxygen atom are the [6,6]-bonds, they seem to have a clearer localization of the π-electrons of the rings in comparison with [5,6]-bonds. Until now, there is evidence for even higher levels of oxygen addition, depending on the method of synthesis used, observations of $C_{60}O_n$, where n=2-5 with lesser amounts for n=6 and possibly n=7, have been observed in the mass spectra of fullerene oxides.[20, 22, 23]

Other kind of epoxide fullerene derivatives has been found from the fluorofullerenes derivatives. They arise from nucleophilic substitution of fluorine atoms by OH and then subsequent elimination of HF ($C_{60}O_9$ and $C_{60}O_{18}$ are each isostructural with the $C_{60}X_{18}$ and $C_{60}X_{36}$, respectively, where X= H and F),[24, 25] but also numerous fluorinated compounds such as $C_{60}F_{16}O_5$, $C_{60}F_{18}O_5$ and $C_{60}F_{10}O_9$ were also observed in addition to extraordinary species containing up to 18 oxygen atoms plus 8 or 10 fluorine atoms.[26-30]

Apart from the experimental studies about epoxides fullerene derivatives, theoretical calculations have been performed in order to know stabilities between the amount of all possible isomers for each number of oxygen atoms attached to the cage of C_{60}.[21, 31, 32] There are indeed eight possible regioisomers of $C_{60}O_2$ and 43 isomers of $C_{60}O_3$, and this is in light of the multiple reacting centres available in fullerene cluster. However, only a few of these isomers have been so far isolated as both bis- and tris-oxides of C_{60} are shown to be highly unstable.[5, 22, 33]

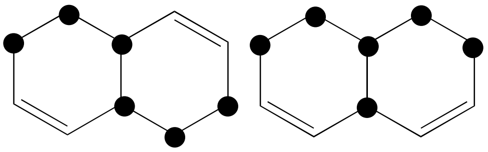


FIGURE 1. S and T addition patterns.

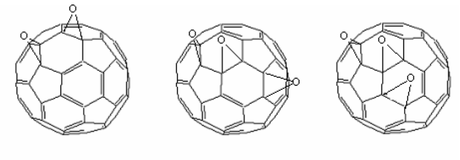


FIGURE 2. a) $C_{60}O_2$ more stable isomer, b) $C_{60}O_3$, isomer S and c) $C_{60}O_3$, isomer T.

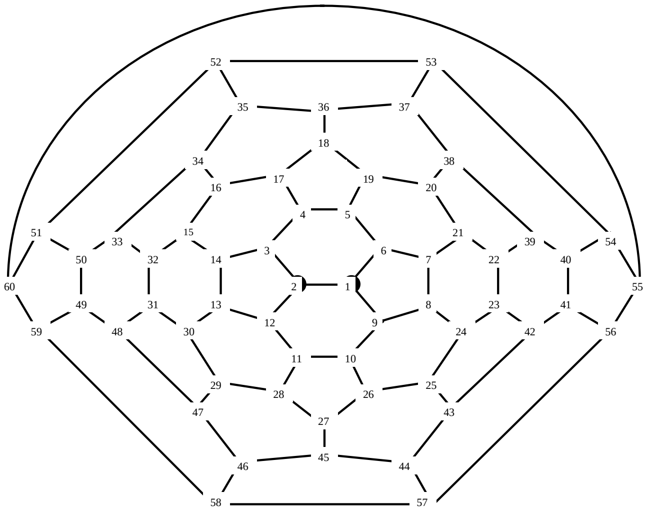


FIGURE 3. Numbering for the C atoms of C_{60} where O atoms are attached.

As other kind of multiple addition to C_{60} (hydrogenation and fluorination),[34-36] the consecutive oxygen atoms addition seems clearly to take place in the adjacent [6,6]-bond of previous C-C bonds where oxygen atom has added. Frusco et al., reported the charactherization of the two possible $C_{60}O_3$ isomers, the triepoxides S and T named (see Figure 2).[34-37] The T isomer ((1,2),(9,10),(8,24)-$C_{60}O_3$) could be formed from (1,2),(9,10)-$C_{60}O_2$ or from (1,2),(8,24)-$C_{60}O_2$, while the S isomer might arise from epoxidation of (25,26)-([6,6]-bond) in (1,2),(9,10)-$C_{60}O_2$ structure (see Fig. 3 to know the corresponding number of C atoms where oxygen atom are defined to be added). These results show as theoretical study done for Curry and co-authors that the reactivity of buckminsterfullerene with oxygen is local, and [6,6]-double bonds adjacent to an existing epoxide functionality are more easily oxidized than the others.[21] For this reason seems quite evident that addition patterns like *T* or *S* addition pattern will be the most probable to explain the multiple addition of oxygen atoms to C_{60}, and one can neglect the possibility of have an O_h addition pattern.

In this work we present our analysis by means mainly of local aromaticity for all the $C_{60}O_n$ systems chosen. This kind of analysis was used to understand the fluorination addition pattern in a previous work.[ref] The good agreement between theoretical and experimental results takes now us to study this other possible multiple addition to C_{60} in case of oxygen addition to the cage. Our purpose here is to show from the NICS values which is the most probable addition pattern in case of oxygenation of C_{60} cage when one considers *T*, *S* or O_h addition patterns. And with the energy stabilities and magnetizabilities values for each system studied we could contribute to the discussion about if this oxygenation process is controlled by kinetics rather than thermodynamics as suggested Slanina et al.[38, 39]

COMPUTATIONAL DETAILS

All geometries ($C_{60}O_n$ systems (n= 1, 2, 3,…10) corresponding to *T*, *S* and O_h addition patterns) were fully optimized at the semiempirical AM1 level of theory[40] using the AMPAC program.[41] The AM1 method has been preferred over other semiempirical methods because it yields reliable results for the geometries of C_{60}. Experimental distances for [5,6]- and [6,6]- type bonds on C_{60} are 1.458 and 1.401Å,[42] respectively, and theoretical calculations reproduce these bonds with 1.464 and 1.385Å length at AM1 and with 1.453 and 1.369Å at HF/3-21G level. Single point calculations using the AM1 fully optimised geometries at HF/3-21G were performed using GAUSSIAN98,[43] and the HOMO-LUMO gap was calculated as also the T index value which can be defined as HOMO-LUMO energy separation multiplied by the number of carbon atoms conjugated in the system studied. This value seems to be preferred as an index of kinetic stability.[44-47]

The local aromaticity of a ring is described by its ability to support diamagnetic ring (i.e. diatropic) currents, which can be described by the nucleus-independent chemical shift or NICS. It has been calculated at the geometrical centre of each 5- and 6-membered rings of the cage, determined by the non-weighted mean of ring atom coordinates, using the GIAO method.[48] Negative and positive values of NICS correspond to diatropic (aromatic) and paratropic (antyaromatic) rings, respectively. In case of C_{60} molecule, the NICS values of its pentagons ring centre is +5.1ppm and -6.8ppm for its hexagons ring centre at HF/3-21G//AM1. These values are expected to change when the degree of oxygenation of the cage increases, because the addition will help to distinguish between more and less aromatic regions of the cage.

Global aromaticity in terms of the molecular magnetizability for each system is calculated, using the CSGT method,[49] in order to know if the tendency of increasing aromaticity respect to precursor derivative in the series studied is clear and if it has some relation with the energy stability of each system.

NICS and molecular magnetizabilities values were both calculated, using GAUSSIAN program, at HF/3-21G level at the AM1 fully optimised geometries. It is important to remark that DFT methods do not provide systematically better NMR results than Hartree-Fock, because no current functionals include a magnetic field dependence.

RESULTS AND DISCUSSION

In this section we will present the results obtained from the calculations carried out for all the $C_{60}O_n$ systems studied in several subsections to better explain them and help the reader to follow our discussion.

Three different addition patterns have been considered: T, S and O_h, in case of oxygen atoms addition to C_{60}. The corresponding energy, HOMO-LUMO gap, T index value and magnetizability of each system are gathered in Table 1. We have labelled each C atom of the cage with a number as Figure 3 shows to make easier to name addition bonds for each structure.

$C_{60}O$, $C_{60}O_2$: adjacent addition (T or S) or O_h pattern?

Generally the additions to C_{60} take place to the most reactive type of C-C bond, the [6,6]-bond type, which has a higher double bond character in comparison with the other type of C-C, the [5,6]-bond. For this reason, we have just studied fullerene epoxide derivatives with [6,6]-bond addition.

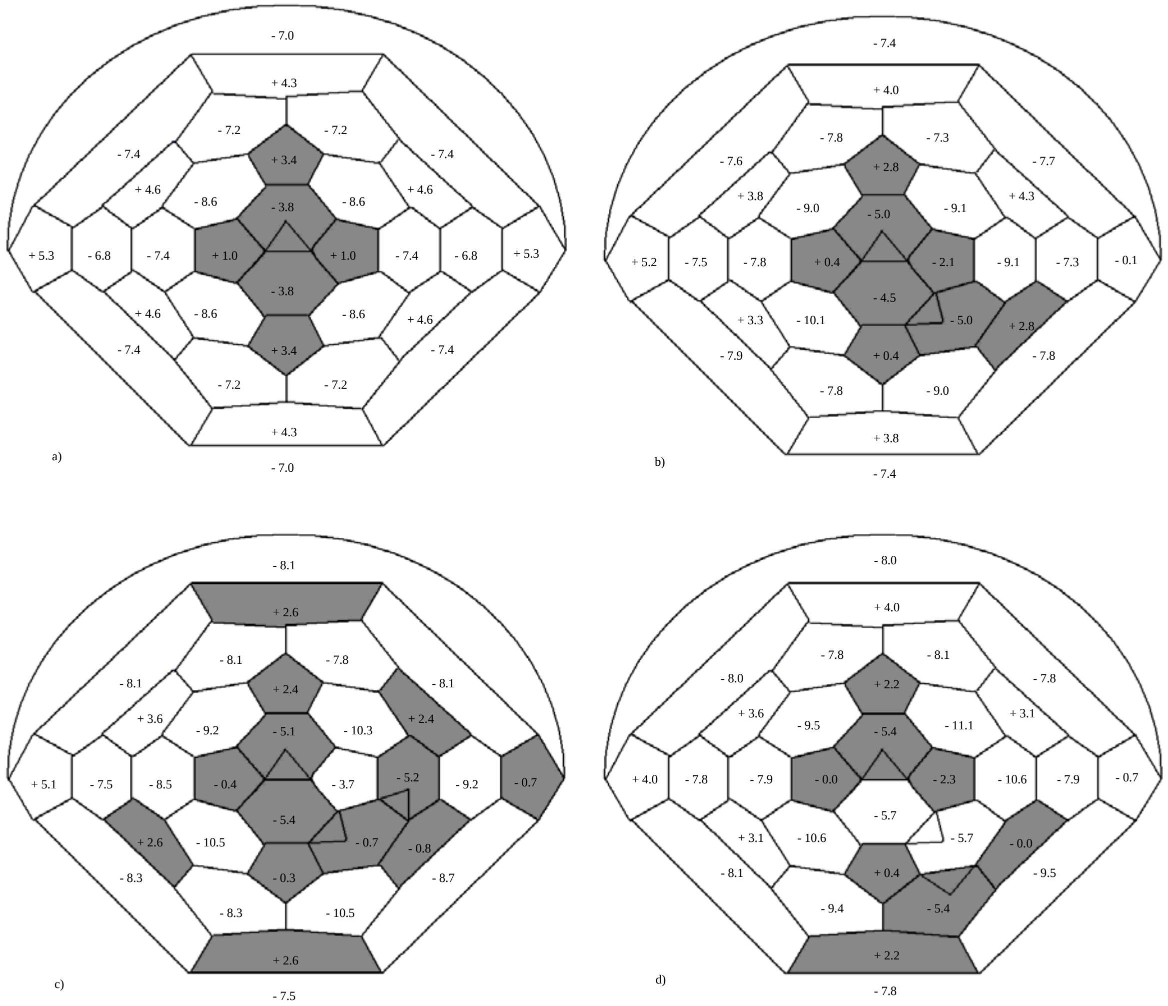


FIGURE 4. NICS values of a) $C_{60}O$ and b) $C_{60}O_2$, c) $C_{60}O_3$-T and d) $C_{60}O_3$-S.

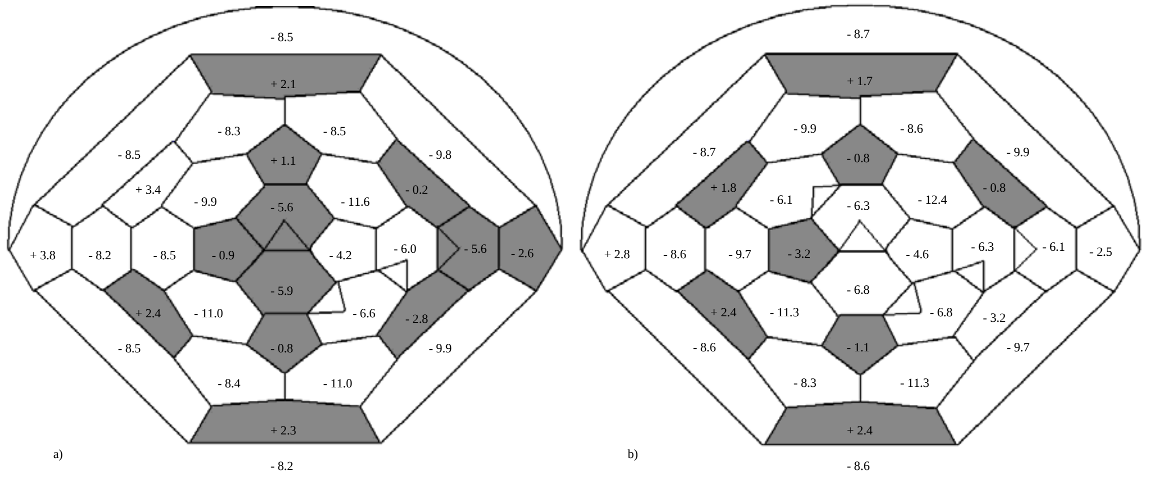


FIGURE 5. NICS values of a) $C_{60}O_4$-T and b) $C_{60}O_5$-T.

TABLE 1. Energy at HF/3-21G//AM1 (a.u.), HOMO-LUMO gap (a.u.), T index value, and χ (cgs-ppm) for systems studied.

$C_{60}O_n$	Energy	HOMO-LUMO (gap)	T	χ
$C_{60}O$	-2333,4181	0,269	15,6	-358
$C_{60}O_2$	-2407,8128	0,270	15,1	-377
$C_{60}O_3$-S	-2482,2066	0,271	14,6	-396
$C_{60}O_3$-T	-2482,2049	0,271	14,6	-396
$C_{60}O_4$-T	-2556,5991	0,276	14,4	-416
$C_{60}O_5$-T	-2630,9922	0,276	13,8	-429
$C_{60}O_4$-S	-2556,6000	0,273	14,2	-413
$C_{60}O_5$-S	-2630,9938	0,282	14,1	-433
$C_{60}O_6$-S	-2705,3869	0,280	13,4	-446
$C_{60}O_7$-S	-2779,7797	0,283	13,0	-459
$C_{60}O_8$-S	-2854,1728	0,284	12,5	-472
$C_{60}O_9$-S	-2928,5627	0,286	12,0	-487
$C_{60}O_{10}$-S	-3002,9669	0,305	12,2	-503
$C_{60}O_2$-O_h	-2407,8030	0,263	14,7	-372
$C_{60}O_3$-O_h	-2482,1893	0,340	18,4	-393
$C_{60}O_4$-O_h	-2556,5760	0,291	15,1	-414
$C_{60}O_5$-O_h	-2630,9617	0,292	14,6	-426
$C_{60}O_6$-O_h	-2705,3475	0,315	15,1	-435

The addition of the first O atom to the cage provides the formation of (1,2)-$C_{60}O$ epoxide derivative. This is the first step of the oxygenation of C_{60} cage, and the second addition of an O atom could take place in eight different possible [6,6]-bonds of the cage, and then eight possible isomers should be considered.[21] Two clear kinds of way can be taken, the second addition takes place in an adjacent [6,6]-bond of the previous [6,6]-bond where O atom has been attached (in the same hexagon), or it takes place in an octahedral position respect to the first [6,6]-bond attacked. The first option could be explained for the T or S addition pattern models and the second would correspond to an O_h addition pattern. From the NICS values showed in Figure 4a, the pentagons and hexagons which have the two C atoms of the first [6,6]-bond attacked, present an increasing of electron localization because they are lower and more positive than other ones of the cage (positive NICS values correspond to paratropic ring currents which represent antiaromatic character of the ring). The [6,6]-bonds 18,36-, 22,23-, 27,45-, 31,32- and 55,60-corresponding to the O_h positions respect to 1,2-([6,6]-bond) belong to hexagons and pentagons which their centre ring NICS values show that they are more aromatic and consequently that means that they have their electron π more delocalized. Calculations shows also that (1,2),(9,10)-$C_{60}O_2$ is more stable than $C_{60}O_2$-O_h, it has a higher T index value and it is more aromatic, it presents a higher magnetizability value. At this point then, seems quite clear the preference for an adjacent addition pattern instead of an O_h pattern.

$C_{60}O_n$-S or $C_{60}O_n$-T ?

In base of (1,2),(9,10)-$C_{60}O_2$ formation, if the next O atom addition takes place to the 8,24- or to 25,26-([6,6]-bond), the $C_{60}O_3$ isomer will be the $C_{60}O_3$-T or the $C_{60}O_3$-S, respectively. [5,6]- and 3,4-([6,6]-bond) are equivalent to 8,24- and 25,26-([6,6]-bond). Local aromaticity analysis (see Fig. 4b) shows that C atoms of 25,26-([6,6]-bond) have more localized the electrons because they belong to two pentagons and two hexagons with centre ring NICS values more positive. The stability and the global aromaticity of both isomers, $C_{60}O_3$-S and $C_{60}O_3$-T, are quite similar, nevertheless S isomer is more stable, and less aromatic globally. These results confirm what was predicted from other theoretical studies[21] that the reactivity of C_{60} with oxygen is local, and adjacent [6,6]-bonds to an existing epoxide functionality are more easily oxidized than the others, it will be discussed below.

Figure 5 shows the $C_{60}O_4$-T and $C_{60}O_5$-T structures, which correspond following the T addition pattern and using the criteria of considering the [6,6]-bond preferentially attacked as that which their C atoms belong to pentagons and hexagons with more positive centre ring NICS values. Addition to 22,23-([6,6]-bond) of $C_{60}O_3$-T provides the $C_{60}O_4$-T formation and then the next [6,6]-bond where O atom is added is the 3,4-([6,6]-bond). To continue with the T addition pattern, the next C-C bond attacked should be the 16,17- or the 39,40-([6,6]-bond), they are equivalent, and that is exactly what NICS analysis predicts (see Figure 5b), but then from $C_{60}O_6$-T (i. e., addition to 16,17-([6,6]-bond)) the next $C_{60}O_n$-T (n= 7, 8,…) do not follow the T addition pattern, the seventh O atom is predicted to attack the 34,35-([6,6]-bond) instead of 18,36- or 39,40-([6,6]-bond). The next additions of O atoms follow a more S type addition pattern. From these results seems then quite clear that the multiple addition with a T addition pattern of oxygen to C_{60} cage can be possible until 5 and 6 O atoms added, not further.

$C_{60}O_n$-S (n= 4, 5, 6, 7, 8, 9 and 10)

As we found in a previous work about fluorination addition pattern study,[ref] local aromaticity analysis by NICS values, can help to understand the series of S structures here with $C_{60}O_n$-S systems. In base of $C_{60}O_3$-S isomer formation, the 3,4- and the 43,44-([6,6]-bond), which are equivalent, have C atoms which belong to two pentagons and two hexagons with more positive centre ring NICS values, and then the $C_{60}O_4$-S formation is predicted (see Fig. 6b). Continuous zigzag addition pattern (S pattern) conducts clearly as Figure 6 shows to the $C_{60}O_{10}$-S structure which is equivalent geometrically to $C_{60}F_{20}$-S.[50] As happened with $C_{60}F_n$-S series, these S structures present a high geometric symmetry which can be observed also in case of NICS values of hexagons and pentagons of the cage, for this reason two equivalent [6,6]-bonds are possible preferential [6,6]-bonds to explain the new O atom addition for each structure. From T index values (Table 1), one can note that S structures present a high stability. Moreover, $C_{60}O_n$-S are less aromatic globally than their equivalent structures of $C_{60}F_n$-S series. This can remark that the cyclopropanetype-addition of O atoms to C_{60} does not help to delocalize electrons along the different 3-membered rings (C-O-C).

$C_{60}O_n$-O_h (n= 2, 3, 4, 5 and 6)

Values of energies in Table 1 show how these O_h structures are less stable than they corresponding T or S isomers. In contrast, if one considers their T index values, then it seems that octahedral isomers are more kinetically stable than the respective T or S isomers. The global aromaticity is predicted by magnetizability values lower than in case of T or S isomers. It is in agreement with the fact that structures more stable are less aromatic, especially because the chemistry of fullerenes is suggested to proceed in such a manner that the reaction products become as aromatic as possible.

As we did with the other two types of addition patterns analysed, in this work we present the analysis on base of local aromaticity terms (centre ring NICS values) the different possible isomers of O_h addition pattern. In Figure 7 are picked the more stable isomers which follow an O_h addition pattern. From the NICS values, it is quite clear to predict the next octahedral position where O atom will be attached, and with this evident easiness to predict the next preferential [6,6]-bond where O attaches as in case of S series, it seems that O_h addition pattern should be a reasonable multiple addition pattern to explain the oxygenation of C_{60} cage.

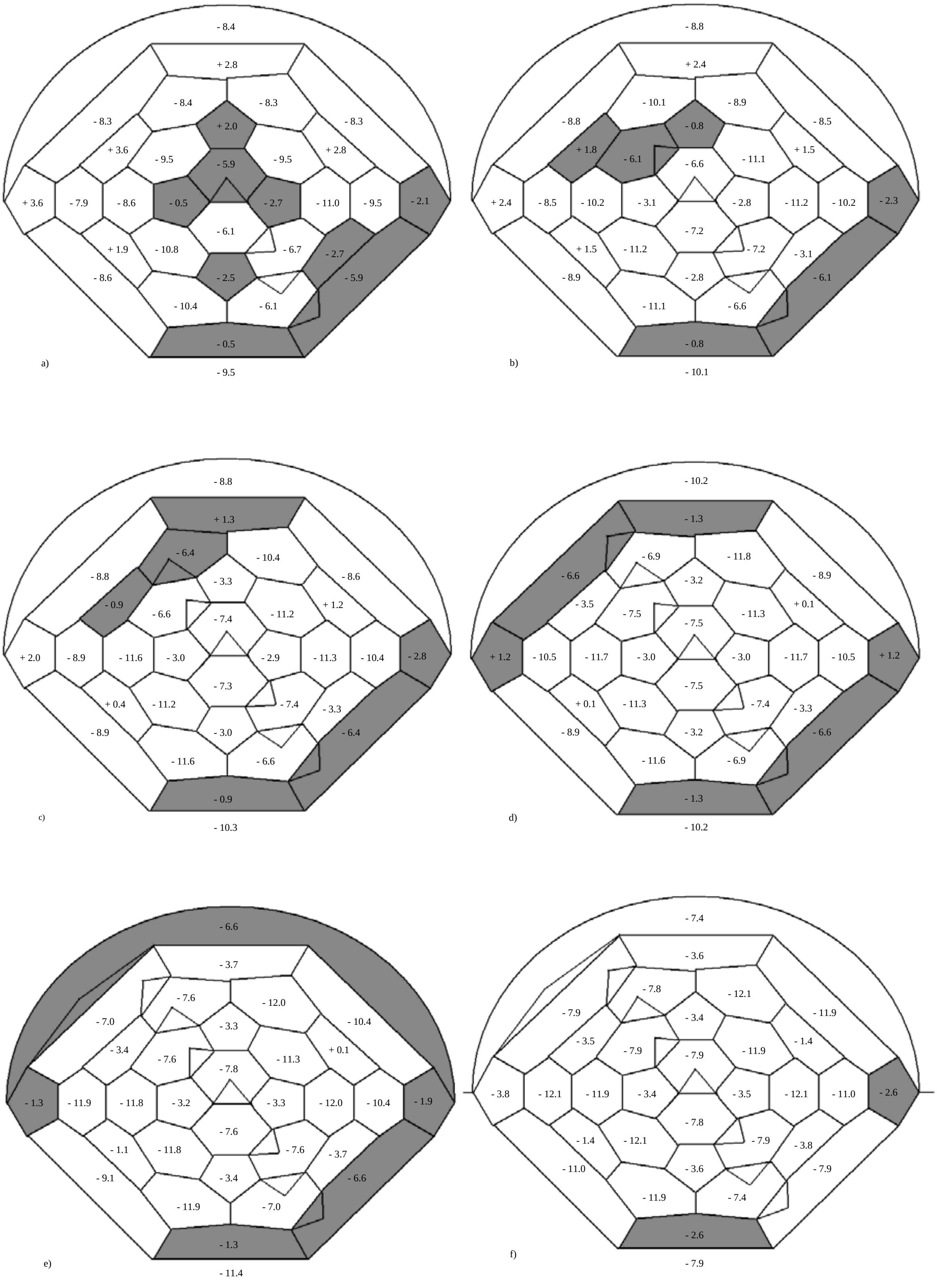


FIGURE 6.1. NICS values of $C_{60}O_n$-*S* (n= 4, 5, 6, 7, 8, 9).

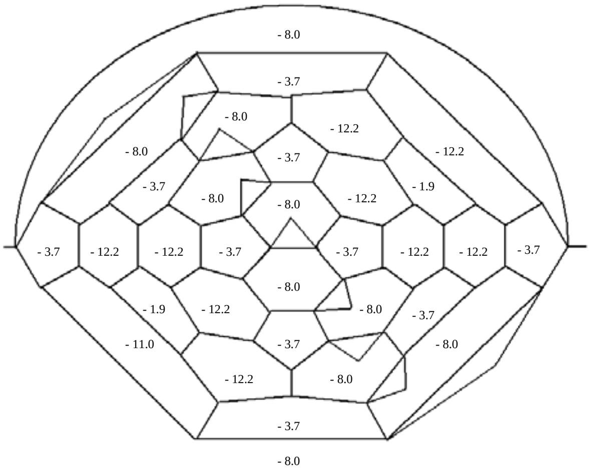
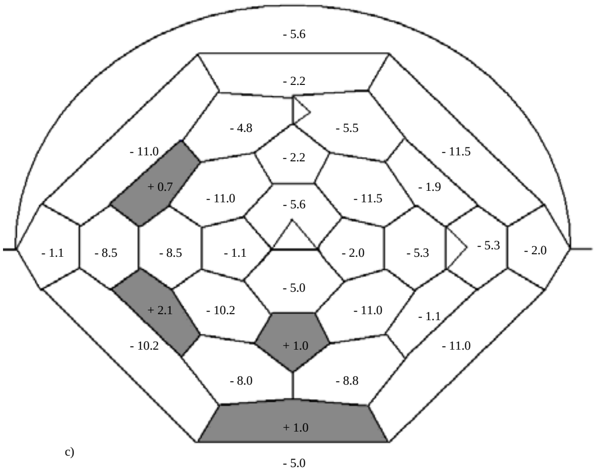
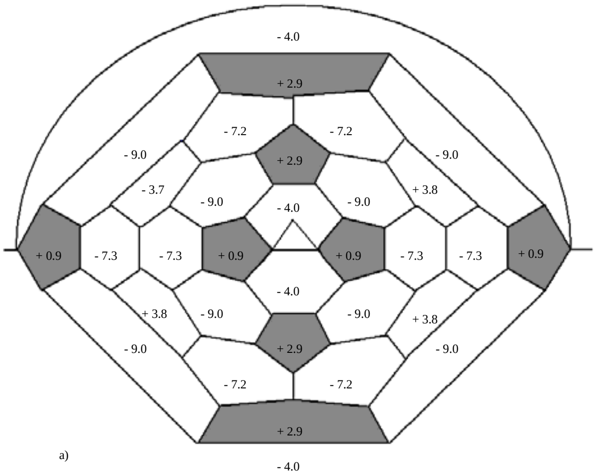


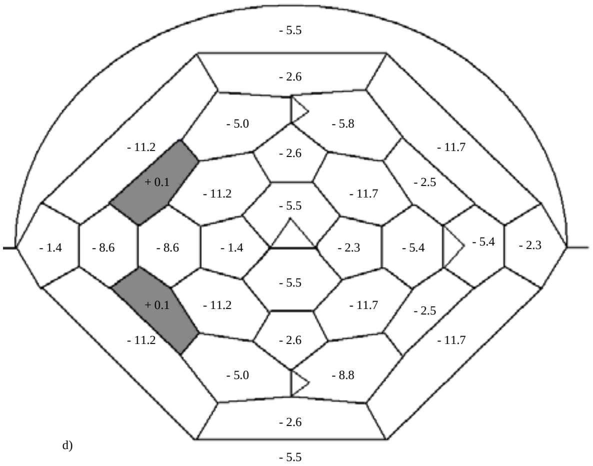
FIGURE 6.2. NICS values of $C_{60}O_{10}$-*S*.



c)



a)



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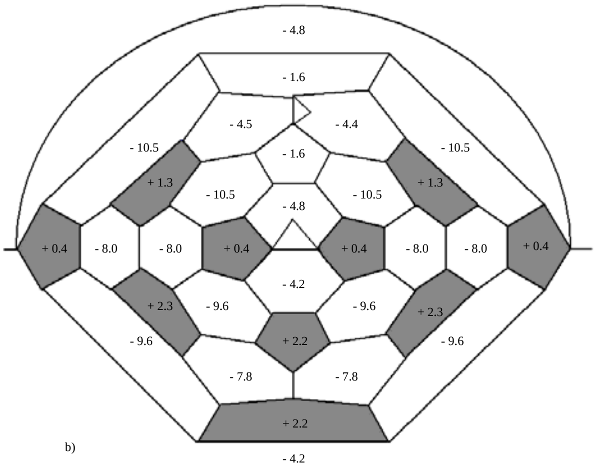
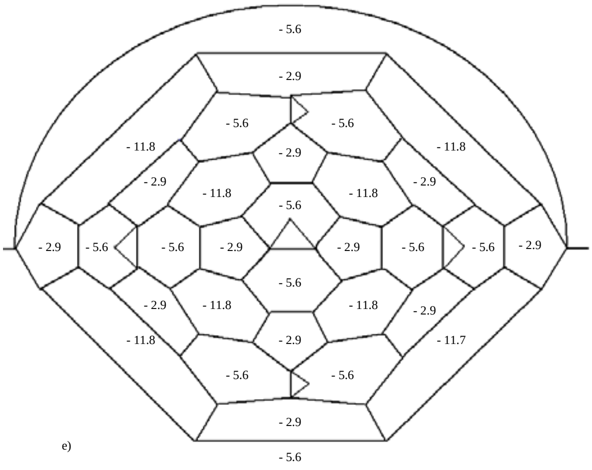


b)



e)

FIGURE 7. NICS values of $C_{60}O_n$-O_h (n= 2, 3, 4, 5 and 6).

After this detailed analysis of the different series, a geometric analysis of the different structures considered shows in general that the C-C length of the [6,6]-bonds where O atoms are added ranging from 1.545 to 1.525 Å when the number of O atoms attached to the cage increases, and the [6,6]-bond preferential to be nextly attacked predicted by NICS criteria applied corresponds with the shortest C-C [6,6]-bond close to previous [6,6]-bonds attacked, with values around 1.375 Å. The NICS values positive and negative help to know the higher or lower aromatic character of a ring, when they are positive represent a ring with a high antiaromatic behaviour and that should mean that the C-C bond have different lengths, the shortest ones corresponding to bonds with higher double bound character and the longest to simple bounds. For these systems as we found in case of fluorofullerenes, exists a clear relationship between geometric and magnetic aromaticity criteria.

CONCLUSIONS

For the three series of fullerene epoxides studied, the $C_{60}O_n$-S, -T and -O_h (n= 1, 2, 3, …), the analysis by means of local and global aromaticity has help to understand which can be the most probable addition pattern which the oxygenation of C_{60} can follow. As other previous studies show in case of multiple hydrogenation and fluorination of the cage, our study shows that exists a clear preference for a multiple adjacent addition, when a [6,6]-bond is attacked, then the close [6,6]-bonds to this first ([6,6]-bonds in the same hexagon) are the preferential site to be nextly attacked, but just two of the three [6,6]-bond of one hexagon are susceptible to be attacked. In case of $C_{60}O_n$ systems, the S addition pattern can be perfectly predicted using the centre ring NICS values analysis, for n= 1, 2, 3,…,10 they are described.

The other two addition pattern considered, we find that could be possible to get $C_{60}O_n$ with T pattern for n= 3, 4, 5 and 6, but not further, our NICS analysis predicts for $C_{60}O_n$-T with n=7, 8,… a zigzag preferential addition. O_h isomers can be clearly defined on base of this NICS analysis, however they are less stable than their corresponding T or S isomers.

With this second work using this NICS analysis in order to predict the next position for an specific addition, seems quite clear that it could be a useful technique to take in consideration when multiple addition take place to the cage of C_{60}.

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6. CONCLUSIONS

In general words, the most remarkable conclusions that one can take out from all these computational chemistry studies performed in relation with single and multiple addition to C_{60}, can be summarised in the next ten ideas:

FIRST:

The [5,6] and [6,6]-bonds of C_{60} have (show) similar reactivity when a direct cycloaddition of a singlet oxycarbonylnitrene, i. e. $NCOOCH_3$, takes place to the C_{60}, the [5,6]- and [6,6]-attacks having similar barriers and exothermicities. The [5,6]-open and [6,6]-closed adducts are the most stable products, because the other structures require the introduction of two double bonds in two 5-membered rings of C_{60}. Accordingly to this, the addition to [5,6]-bonds is possible and not exclusively at [6,6]-bonds and that explains the 10% of [5,6] product isolated experimentally.

SECOND:

A 1,3-dipolar cycloaddition of an azide, i.e. N_3CH_3, to the C_{60} provides as the most stable triazoline adduct respect to the six possible isomers, the [6,6]-closed adduct, thanks mainly to a more favourable orbital interaction between the azide and the two C atoms attacked of the C_{60} surface. Our calculations confirm that this intermediate in the monoimino-[60]fullerenes formation process is stable enough to be isolated when working at mild conditions. Meanwhile, the losing of N_2 of this [6,6]-closed triazolinic intermediates provides as the most stable aziridinic adduct the [5,6]-open isomer because the N_2 molecule sterically prevents the nitrene substituent from adding to the originally attacked [6,6]-bond and forces the nitrene substituent to attack either of the two adjacent [5,6]-ring junctions.

THIRD:

The stepwise mechanism of N_2 extrusion from a [6,6]-closed triazolinic adduct can be explained by two possible vias depending on the order followed to break the C-N and N-N bonds in the process of losing N_2. A zwitterionic intermediate species is located between the two TSs identified in the most feasible mechanism. It has been located in a very shallow minimum and it means that it should be very difficult to isolate or even detect.

FOURTH:

Considering a series of $C_{60}X$ derivatives, where X = NH, NCH_3, $NCOOCH_3$, O, CH_2 and PCH_3, the [5,6]-open and the [6,6]-closed isomers have similar stabilities and are the more stable adducts. It was observed that the substitution of H by bulkier substituents leads to a destabilization of the [5,6]-open adduct as compared to the [6,6]-closed isomer. The same result is obtained when N is substituted by P. Electron acceptor and electron withdrawing substituents do not have a large effect on the relative stability of the [5,6]-open and [6,6]-closed adducts provided that the steric effect being similar.

FIFTH:

The preference in the case of $C_{60}NH$ system or an addition to [5,6] or [6,6]-bond of C_{60} to yield the [5,6]-open or [6,6]-closed adducts can be explained in the first place because the overlap between the LUMO orbitals of the open fullerene and the HOMO orbitals of the addends is larger and secondly because the opening of the [5,6]-bond does not need to introduce a large amount of strain energy in the addend in comparison with the corresponding [6,6]-closed isomer.

SIXTH:

Charge and energy decomposition analysis show that the σ-donation from a carbene fragment to the $Cr(CO)_5$ fragment is stronger than the π-back-donation. In contrast, the electron back-donation amount is more directly related to the structural and electronic characteristics of the pentacarbonyl Chromium Fischer Carbene complexes, $(CO)_5Cr=C(X)R$, than the electron donation amount. The reason for this larger influence of back-donation values and π orbital interaction energies is that they are more scattered over a large range of values depending on the carbene substituents, while charge donation values and σ orbital interaction energies are more constant. For a given R substituent (R = H, CH_3, $CH=CH_2$, Ph and $C\equiv CH$), back-donation increases in the order H > OH > OCH_3 > NH_2 > $NHCH_3$, that is, it becomes larger with the decrease in the π-donor character of X substituent. Interestingly, the X substituent has a larger effect on the $Cr\text{-}C_{carbene}$ bonding than the R substituent.

SEVENTH:

A series of substituted hydrofullerenes, $C_{60}HR$, in comparison with a series of methanofullerenes, $C_{60}CHR$, have a higher acidic character. In both series the more donor or acceptor character of the R substituent (R= H, CH_3, $CH{=}CH_2$, Ph, C≡CH, OH, OCH_3, NH_2, $NHCH_3$ and $N(CH_3)_2$) does not have a remarkable influence in their reactivity. The R substituent character is found to have somewhat influence on the geometrical reorganization around the addition site in each system upon deprotonation, especially in case of $C_{60}HR$ series.

EIGHTH:

The formation of $C_{60}HR$ systems from C_{60} is found to produce a more important perturbation for the fullerene cage than the carbene addition to C_{60}, $C_{60}CHR$ systems, both in terms of geometrical and electronic structure. Upon deprotonation $C_{60}R^-$ systems partially recover the C_{60} structure, whereas for $C_{60}CR^-$ open species this process involves a more important rearrangement and change in bond lengths and electronic charge distribution. The delocalization of the negative charge resulting from the deprotonation process, mainly on the C_{60} cage, also plays an important role in the stabilization of the conjugate base. It has been showed that the $C_{60}CR^-$ closed structures were more favourable than their corresponding open structures in agreement with previous works showing that the [6,6]-open structures were less stable than the [6,6]-closed ones.

NINTH:

In case of the two series of fluorofullerenes studied, the $C_{60}F_n$-T (n= 2, 4, 6, …, 18) and $C_{60}F_n$-S (n= 2, 4, 6, …, 20) series, a relationship is found between the aromaticity of the systems (both the local and the global calculated by NICS and magnetizabilities respectively) and the addition pattern occurring. The consecutive F atoms addition to the C_{60} cage takes place at the less delocalized site which corresponds always to a [6,6]-bond type close to a previous [6,6]-bond attacked. Taking NICS values of the centres of rings surrounding of the addition site into account it is possible to predict the preferential [6,6]-bond nextly attacked. At the same time, global aromaticity together with the stability analysis of the systems can therefore give an indication of the direction of addition is taking, and help to predict species more susceptible to be isolated.

TENTH:

Similarly to $C_{60}F_n$ series, the $C_{60}O_n$ fullerene derivatives show a preference for a multiple adjacent addition, the consecutive O atom addition takes place at [6,6]-bonds close to [6,6]-bonds previously attacked. The NICS values of the rings around the addition region of C_{60} surface show S pattern as the most favourable adjacent addition pattern in comparison with T pattern, and also NICS values can help to predict an O_h multiple addition, although this pattern of addition is found to be less probable.

For all that, it is clear to summarise that the single or multiple addition to C_{60} takes place in different way dependently mainly on the addend characteristics and consequently they play an important role on the fullerenes derivatives structure.

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8. ANNEX

LIST OF OTHER PUBLICATIONS:

- **"Pristine and Silicon-Substituted Small-Carbon-Clusters and Fullerenes: Electronic Structure and Reactivity"**

  M. Solà, J. M. Cabrera-Trujillo, F. Tenorio, O. Mayorga, M. Cases, M. Duran and J. Robles

  Reviews In Modern Quantum Chemistry: A Celebration Of The Contributions Of R.G. Parr, Ed., K. D. Sen, World Scientific, Singapore, 46 (2002) 1367-1420.

- **"Local Softness versus Density of States as Reactivity Index"**

  L. T. Nguyen, M. Cases, G. Van Lier, F. De Proft, P. W. Fowler and P. Geerlings

  J. Phys. Chem. A, 2003, 107(35), 6837.

- **"Electron Pairing Analysis in Fischer-Type Chromium-Carbene Complexes $(CO)_5Cr{=}C(X)R$ ($X = H, OH, OCH_3, NH_2, NHCH_3$ and $R = H, CH_3, CH{=}CH_2, Ph, C{\equiv}CH$)"**

  J. Poater, M. Cases, X. Fradera, M. Duran and M. Solà

  Chem. Phys., 2003, 294, 129.

LIST OF CONTRIBUTIONS TO CONFERENCES:

Conference: Física de la material condensada: Aplicaciones de la teoría del funcional de la densidad y otros métodos de la química cuántica.
City/Country: Laredo (Spain)
Dates: 29th June – 2nd July, 1999.
Type of contribution: Communication
Title: Cicloadición 1,3-dipolar entre la CH_3N_3 y la molécula C_{60}. Estudio del mecanismo de reacción.
M. Cases, M. Duran, M. Solà

Conference: V GIRONA SEMINAR ON MOLECULAR SIMILARITY
City/Country: Girona (Spain)
Dates: 12th – 20th July, 2001.
Type of contribution: Short communication
Title: Application of the ADF-QM/MM method to study [60]fullerenes cycloadditions.
M. Cases, L. Cavallo, M. Duran, M. Solà

Conference: 27eme Congres des Chimistes Théoriciens d'Expressió Latine
City/Country: Toulouse (France)
Dates: 3rd – 7th September, 2001.
Type of contribution: Poster
Title: Theoretical studies of Diels-Alder Cycloadditions to C_{60} using Hybrid Methods.
M. Cases, L. Cavallo, S. Irle, K. Morokuma, M. Duran, M. Solà

Conference: Electronic Structure and Chemical Reactivity
City/Country: Bellaterra (Spain), UAB
Dates: 19th – 20th September, 2001.
Type of contribution: Poster
Title: Structural and Electronic Properties of the Series of Fischer Carbenes.
M. Cases, G. Frenking, M. Duran, M. Solà

Conference: NANOTEC02
City/Country: Brighton (England)
Dates: 28th – 31st August, 2002.
Type of contribution: Poster
Title: *Ab initio* study of the reactivity of $C_{60}HR$ and $C_{60}CHR$ derivatives.
M. Cases, G. Van Lier, M. Duran, M. Solà, P. Geerlings
Type of contribution: Communication
Title: *Ab initio* Study of the Aromaticity in the Fullerenes and Carbon Nanotubes.
G. Van Lier, M. Cases, M. Duran, M. Solà, P. Geerlings

Conference: ESPA2002
City/Country: Sevilla (Spain)
Dates: 10th – 13th September, 2002.
Type of contribution: Poster
Title: Deprotonation of $C_{60}HR$ and $C_{60}CHR$, a chemical and physical properties study.
M. Cases, G. Van Lier, M. Duran, M. Solà, P. Geerlings

Conference: VI GIRONA SEMINAR ON MOLECULAR SIMILARITY
City/Country: Girona (Spain)
Dates: 21th – 24th July, 2003.
Type of contribution: Short communication
Title: Global and Local aromaticity analysis to study Addition patterns of $C_{60}F_n$ series.
M. Cases, G. Van Lier, R. Taylor, P. Geerlings

Conference: DFT2003
City/Country: Brussels (Belgium)
Dates: 7th – 12th September, 2003.
Type of contribution: Poster
Title: A Computational Chemistry Study of Single and Multiple

M. Cases, G. Van Lier, P. Geerlings, M. Duran, M. Solà

AGRAÏMENTS

… totes aquestes pàgines que precedeixen a aquest últim apartat són la meva tesi sobre paper, i ara voldria amb unes paraules dir una mica com l'he viscut dient la meva amb agraïments, anècdotes... (avís: sóc de les que "quilometrejo" fàcilment, els que em coneixeu ja ho sabeu, però tranquils que no ha donat per un segon volum ☺, intentaré ser breu, però hi ha molt per dir encara!).

Tot això no hagués pogut ser possible sense que un bon dia en Miquel Solà m'hagués proposat aquesta opció: fer el doctorat a l'IQC. Per què no? em vaig dir i a fer pre-inscripció, matrícula, cursos, paperassa per demanar beques, donar classes com a professora associada durant un any, tornar a fer paperassa de beca... i sí, al final la UdG me la va donar. Gràcies a aquesta beca he pogut dur a terme tota aquesta investigació.

On? Doncs a l'IQC, primer als "barracons" i finalment al C3 de la Facultat de Ciències.

Amb qui? Amb tota una bona tropa ☺

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Què dir? Primer donar les gràcies als jefes per donar-me la possibilitat de formar part d'aquest grup de recerca capdavanter en moltes estadístiques, però sobretot a en Miquel Solà per la seva dedicació setmana a setmana per tal que uns objectius que poc a poc ens anàvem proposant per portar a terme, precisament es portessin a terme i que poc a poc anessin donant resultats per formar part de la meva tesi. Agraeixo el teu esforç i constància en la supervisió del meu treball i crec que hem fet una bona feina.

I a la resta, doncs dir-vos que heu estat uns molt bons companys de feina, de cafès (ja ho sé: no sóc dels que baixen cada dia), de xerrades, d'excursions... de dinars, sopars... especialment "els meus nens" que dic jo dels meus companys de despatx, amb ells he compartit el dia a dia. Quan vaig entrar era la novata, i poc a poc ens hem anat passant el títol, ara acabo la tesi com a veterana dins el despatx, i em fa gràcia haver viscut els vostres principis en aquest món de la Química Computacional. Molta sort a tots plegats tropa!

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Per proximitat, i per tenir-hi una bona infiltrada, voldria tenir un record també per la gent del LEQUIA, hi ha qui a vegades m'ha preguntat: ara treballes aquí doncs?, no, però tampoc em faria res, els hi he contestat. Alguna vegada per posar-me una mica massa pel mig m'ha tocat una ruixada d'aigua i tot (eh Helio ;-)). Anna i Sebas (primer vau ser alumnes meus, i ara companys de fatigues de doctorat, ei jo ja us veia molt professionals), Clàudia (ves per on el món és petit, i qui sap potser algun dia de petites ens devíem creuar per les Planes, o vam jugar amb les mateixes Barbies de la Neus).

Als conserges (Narcís, Josep, Tresa, Sònia, Paqui), els "operates", a les secretàries de facultat, a les noies de fotocòpies i a la gent del bar, dir-vos que sou una bona plantilla, m'heu ajudat sempre que us he necessitat.

La beca de la UdG, m'ha mantingut dins l'equip de professorat tots els anys de tesi i per tant m'ha donat l'oportunitat de donar classes pràctiques i de problemes als estudiants de la UdG, tot un honor. He tingut alumnes de Química i alumnes de Ciències Ambientals, ben diferents uns d'altres, no entraré en detalls que amb anècdotes també podria escriure un llibre, però de tots m'he sentit orgullosa quan poc a poc veia que els feia entrar una mica més en el món de la Química, els de Química a la química física i els de Ciències Ambientals a la química general. Recordo el primer dia de classe de problemes, jo allà a la tarima de la E4 amb la pissarra darrera i davant una tropa d'alumnes, em sentia segura, però un "estar nerviosa" que es va sentir de fons quan em vaig girar a escriure, em va acabar d'ajudar. Sí estava nerviosa perquè tenia una gran responsabilitat i no podia fallar "als meus alumnes". Sempre he intentat recordar què era el que agraïa més com a alumne per part d'un professor i he intentat fer-ho tan bé com he pogut. Cada curs he procurat conèixer el màxim de noms, per allò d'acostar-me més a vosaltres, potser no recordaré els vostres noms, però sí les cares;-). M'ha agradat haver contribuït a la vostra formació com a químics uns i com a mediambientalistes els altres, sort en el futur professional a tots plegats!

Gràcies a l'IQC, UdG, DURSI i al DAAD, he viatjat pel món, ja sigui per assistir a congressos, escoles, cursos o bé per fer estades de més o menys durada, i m'ha servit per molt. D'una banda per conèixer molta gent, per aprendre, per portar a terme col·laboracions amb altres grups i com no, per fer turisme.

He anat pel món representant a l'IQC i coneixent a molta gent com deia, aquí de forma ràpida i cronològica els vull destacar: la gent de la 2ona Escola de Química Teòrica a Palma de Mallorca, els "QVATREROS" (la tropa que vam fer entre físics de Madrid, País Basc i Valladolid, i químics de Tarragona) al congrés de Laredo, la gent de Marburg (Alemanya)(Hi vaig anar gràcies a una beca del Deutscher Akademischre Austauschdienst, sense saber ni "papa" d'alemany, només me'n vaig penedir una vegada que vaig equivocar-me de bus i resulta que la parada final era a un "manicomi", el conductor em va fer baixar, com que jo parlava de tot menys alemany suposo que es pensava que allà era on m'havia de quedar ☺. Sort d'un altre bus on el conductor era un jove en pràctiques i parlava anglès i em va tornar al centre. Al grup d'en Frenking tenien una bona tradició, reunir el grup una vegada a la setmana i fer reunió informativa sobre aspectes relacionats amb el grup i la seva recerca ben acompanyats d'un tall de pastís casolà i una tassa de cafè. Encara tinc present la imatge de qui ells anomenaven per la seva aparença "el Yeti" tot cridant pel passadís: "Coffee is ready, coffee is ready", i amb la cafetera en mà deixant el rastre de l'aroma per convèncer a la gent, "follow me" semblava…), la penya del curs de Doctorat de Castelló (vam tenir hores de discussions científiques, les millors les del "caos", però les vam saber alternar bé amb la diversió, car la city deixava molt que desitjar, teníem tot un privilegi, la nostra estada a Castelló era en un hotel de 3 que a última hora havia substituït la residència militar que ens esperava en un principi, tots recordem els litres de suc de taronja del bufet lliure que teníem per esmorzar… i tot va canviar quan vam descobrir el Botànico! D'aquella colla, primer en van sorgir molts mails, el temps ha donat per fer "reencuentros" a Barcelona, Girona, Galícia, Cuenca, Madrid, Navarra… , i per tenir nous amics, especialment la Cris i la Nicole i els Xapis (els 2 Xavis i en Javi)), la gent d'Atlanta (especialment la Takako, la japonesa i companya de pis, com vam disfrutar menjant pastissos! i juntament amb l'Akiko recordo aquell dia que em van portar a un restaurant Tailandès, que després d'unes cullerades d'un plat amb només el primer nivell de 7 o 8 en referència a la fortalesa de les espècies, vaig entendre perquè hi havia un cambrer anant amunt i avall tota* *l'estona assegurant-se que tots els clients tinguessin la copa plena d'aigua-gel i perquè l'aire condicionat estava "a tope" que semblava que fóssim en una nevera, una bona experiència, això de tenir dues japoneses partint-se de riure d'una catalana,… i de la Marizel, ella molt treballadora, molt complidora, tinc el record allà al bus quan ja ens acomiadàvem, em vaig quedar amb un cor petit de deixar-te allà), els estudiants de la European Summer School a Riolo Terme (Itàlia)(hi havia de tot, bé europeus, russos i japonesos per generalitzar, els cambrers de l'hotel-balneari on ens allotjàvem ens portaven molt bé, acostumats als "iaios"..., allà ja no hi vaig anar sola representant l´IQC, en Jordi i l´Ana també hi eren, i a més a més també gent de la penya de Castelló, vam fer un bon grupet, entre els "espanyols" i en JeanRaphael, l'Olaf i l'Eugeniuz, les hores de classe a classe, les hores de menjar a menjar que allà es menjava molt bé, i la resta doncs convivència entre cultures. El millor: una autèntica pizza italiana després d'haver pujat (i per tant baixat) 500 escales i tenir Bolonya als teus peus. El pitjor: l'excursió "al campo" a la qual els sud-europeus ens vam negar a seguir, després d'un dinar més que contundent pretenien que amb el sol de les 3 de la tarda féssim muntanya amunt, ens van deixar fer, clar la "siesta" deien ells), els estudiants "espanyols" (diferents generacions del Curs de Doctorat Interuniversitari de Química teòrica) al CHITEL a Toulouse o l´ESPA de Sevilla, i a tots els belgues que em van ajudar a viure a Brussel·les i repetir l´estada subvencionades pel DURSI una i l'altra per la UdG: en Greg i el Prof. Paul Geerlings, en Frank, la Greet, en Pierre, l´Stephan, en Loc, la Martine, la Meryem, en Röul, la Geike, i tota la tropa d'amics d'en Greg que no són pocs...*

Tots ells no els hagués conegut sinó hagués fet el doctorat i per això són especials, són amics que he fet a partir del doctorat però que els tinc per sempre.

Paral·lelament durant aquests anys he aprofitat per posar-me al dia amb els idiomes i en especial agraeixo als diferents professors del Servei de Llengües Modernes les hores de classe compartides, per la seva humanitat i professionalitat; a en Patrick, la Julie i la Mary Jane d´anglès, del primer vaig aprendre a deixar de ser sorda i muda respecte l'anglès, de la segona vaig aprofundir amb piles de vocabulari (o almenys es va intentar☺) i amb la tercera millorar la fluïdesa en el parlar; a l'Ute i la Dankmute per aconseguir que després d'aquests anys pugui dir que l'alemany no és tan complicat d'aprendre, sobretot perquè elles me l'han sabut ensenyar amb molt de dinamisme; a la Bea de francès que amb un curs de principiant de només quasi un any em va ajudar a atrevir-me a anar d'estada a Brussel·les i aquests últims mesos amb la Mar he recuperat les bases de la gramàtica i l'expressió de la nostra llengua, el català, sort de no haver-lo hagut d'aprendre perquè mira que n'és de complex...

I com no, que ja us devíeu pensar que no diria res de vosaltres dues, les dues "mosqueteres" perfectes, Teia i Imma, per mi heu estat una gran troballa en la meva vida, quantes hores viscudes!!! Juntes hem passat moltes coses, vam començar compartint convivència en un pis d'estudiants i vam posar fonaments a la nostra amistat. Quantes "batalletes" per explicar... ui si en podríem escriure un llibre! (si no podem tenir futur científic, qui sap, podria ser una opció). M'heu obert casa vostra des del primer moment i m'hi he sentit com a casa. Juntes hem viatjat de vacances, primer a Port Aventura (encara se'm revolta l'estómac pensant amb el Dragon-Kan), després a la Vall d´Aran (el millor: tot baixant pel Port de la Bonaigua amb el CLIO tot esquivant cavalls salvatges i vaques per la carretera, encara recordo quan a un cavall li volíem fer foto i jo tenia millor angle, paro el cotxe al mig de la carretera, baixo el vidre, obro la càmera, enfoco i iiijjiiii se sent, el cavall venia de sobte a galop cap a nosaltres, tiro la camera a la *copilot, trec el fre de mà, i accelerada "a tope"!), després a Carcassone (ostres tot i la patinada amb el cotxe un parell de dies abans vau confiar amb mi (i amb el CLIO) i cap "à la France", vam reviure la vida medieval i vam dormir entre muralles), i aquells dies a Santa Pau (jo primer amb el meu "quemaco" a tort i a dret passejant per la Fageda d'en Jordà per primera vegada, i després quina tarda-vetllada jugant a cartes, a "tocat i enfonsat"... a la vora de la llar de foc, quina que en queia a fora!). El que deia, moltes "batalletes"... ei gràcies per estar per tot arreu (encara recordo la vostra megapostal per felicitar-me el dia del meu aniversari quan estava a Marburg, ho vau aconseguir va arribar el vespre abans), sempre us he tingut al meu costat, vosaltres sabeu que també m'hi teniu, pels bons i els no tan bons moments, per riure o plorar juntes, som un bon equip! Teia ànims per la teva tesi i tu Imma amb el projecte.*

Gràcies

Gracias

Thank you

Vielen Dank

Merci

de la vostra Montse, Montserrat o Montserrateta, a tots us ho dic, sense tots vosaltres i la meva família aquesta tesi potser si que hagués estat possible, però no l'hagués viscut igual!

Voldria a part de donar les gràcies, amb unes paraules fer referència als diferents familiars que durant aquest temps han anat marxant, m'agrada pensar que un cop acabada aquesta etapa de la meva vida us sentiríeu contents per la meva feina, per això a tu <u>tiet Sebastià</u> (ostres te'n vas anar de cop, això si amb el cotxe ben net, mai el portaré tan net com el teu!), a tu <u>tia Antònia</u> (era petita quan va morir el meu avi, però tu com a bona germana me'n parlaves), a vosaltres dos padrinets, <u>Maria i Aleix</u> (això de la Química Física us sonava molt fort!, aprofita aquesta oportunitat nena, em dèieu, crec que ho he fet. De vosaltres he après molt i us dono les gràcies per ser tan generosos i donar-me una família tan gran, som una bona tropa "els carboners"), i a tu <u>Maria</u> (saps, no sabia si era el millor venir-te a veure de visita, però és que el blau intens dels teus ulls i el teu somriure eren tot un regal! admiro la teva força-fe-vida); a tots us vull tenir ben presents i si pogués tan sols picar-vos l'ullet, no dubteu que ho faria, ;-) va per vosaltres.

Girona, Juliol de 2003