



Influence of the Charge on the Reactivity of Azafullerenes

Yago García-Rodeja,^a Miquel Solà^b and Israel Fernández^{*a}

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The influence of the charge on the Diels-Alder reactivity of azafullerenes ($C_{59}N^+$ and $C_{59}N^-$) has been computationally explored by means of Density Functional Theory calculations. In addition, the regioselectivity of the process has been investigated and compared to the analogous cycloaddition reaction involving the parent neutral azahydro[60]fullerene $C_{59}NH$. It is found that the [4+2]-cycloaddition reaction between $C_{59}N^+$ and cyclopentadiene, which occurs concertedly through a synchronous transition state, proceeds with a lower activation barrier and is more exothermic than the analogous process involving $C_{59}NH$. In contrast, the anionic $C_{59}N^-$ counterpart is clearly less reactive. This reactivity trend is quantitatively analyzed in detail by means of the Activation Strain Model of reactivity in combination with the Energy Decomposition Analysis method. It is found that the frontier molecular orbital interactions are not responsible for the observed reactivity trend but the Pauli repulsion between closed-shells mainly governs the transformation.

Introduction

The chemistry of heterofullerenes is attracting a great deal of interest in recent years due to the significant structural and electronic modifications induced by the replacement of carbon atoms in the fullerene cage by different heteroatoms.¹ Among them, azafullerenes arguably constitute the most representative members of this family of compounds because they are the only class of heterofullerenes which have been synthesized in macroscopic quantities so far.² Thus, mono-azafullerenes $C_{59}N$ and $C_{69}N$ have been isolated as the stable dimers $(C_{59}N)_2$ and $(C_{69}N)_2$, respectively,³ and even their corresponding endohedral species $(H_2O@C_{59}N)_2$ and $(H_2@C_{59}N)_2$ have been prepared and fully characterized very recently.⁴ Moreover, the mono-azafullerene derivatives $C_{59}NH$ and $C_{59}NR_5$ could be also obtained on a preparative scale.^{2,5}

Not surprisingly, the presence of the nitrogen atom in the fullerenic cage strongly affects the electronic structure of the fullerene which may modify its properties. For instance, $C_{59}N$ -based donor-acceptor dyads have been successfully employed in organic solar cells.^{2c,6} As expected, the reactivity of these systems is also significantly affected. Indeed, we recently found that the parent azafullerene $C_{59}NH$ is comparatively less reactive than C_{60} in its Diels-Alder cycloaddition reaction with cyclopentadiene,⁷ a process typically used to produce novel fullerene derivatives with tunable properties.^{8,9} By means of the so-called Activation Strain Model (ASM)¹⁰ of reactivity in

combination with the Energy Decomposition Analysis (EDA) method,¹¹ this lower reactivity was ascribed to a much weaker interaction between the reactants along the entire reaction coordinate mainly as a result of a weaker $\pi(\text{diene}) \rightarrow \pi^*(\text{fullerene})$ interaction.

Strikingly, Murata and Hashikawa quite recently reported a facile access to the parent azafullerenyl cation $C_{59}N^+$,¹² a species first isolated by Reed and co-workers in 2003¹³ and previously detected by mass spectrometry in fragmentation reactions.¹⁴ In their work, Murata and Hashikawa found a strong intramolecular $C_{59}N^+ \cdots O^{\delta-}H_2$ interaction in the $H_2O@C_{59}N^+$ endohedral azafullerene cation.¹² In addition, this cationic heterofullerene, which is isoelectronic to the parent C_{60} fullerene, was found to be a key intermediate in many thermal reactions involving $(C_{59}N)_2$ in the presence of O_2 .¹⁵ More recently, the team formed by Murata and Hashikawa together with the Wang group reported the high-resolution photoelectron imaging of the anionic counterpart, $C_{59}N^-$, and also the corresponding dimer $(C_{59}N)_2^{2-}$.¹⁶ At variance to $C_{59}N^+$, the authors confirmed the occurrence of a significant coulombic repulsion between H_2O and $C_{59}N^-$ in the corresponding $H_2O@C_{59}N^-$ endohedral azafullerene anion.¹⁷

The isolation and/or detection of these charged azafullerenes prompted us to explore their not very well understood reactivity in comparison to our previous study on the reactivity of the parent neutral $C_{59}NH$ system.⁷ Therefore, herein we report a detailed investigation on the influence of the charge on the Diels-Alder reactivity of azafullerenes which is based on the application of the ASM-EDA approach, a method which has proven to be extremely useful to our current understanding of the reactivity of fullerenes^{7,18} and strongly related systems.¹⁹

^aDepartamento de Química Orgánica I and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040-Madrid, Spain. e-mail: israel@quim.ucm.es

^bInstitut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, C/ Maria Aurèlia Capmany, 69, 17003-Girona, Spain.

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Theoretical Methods

Computational Details

To enable possible direct comparison, we have used the same level of theory to that used in our previous studies on the reactivity of the neutral $C_{59}NH$ azafullerene⁷ and C_{60} .^{18a} Geometry optimizations of the molecules were performed without symmetry constraints using the Gaussian03²⁰ optimizer together with Turbomole 6.0.1²¹ energies and gradients at the BP86²²/def2-SVP²³ level of theory using the D3 dispersion correction suggested by Grimme et al.²⁴ and the resolution-of-identity (RI) approximation.²⁵ This level is denoted RI-BP86-D3/def2-SVP. Reactants and cycloadducts were characterized by frequency calculations, and have positive definite Hessian matrices. Transition states (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.²⁶

The program package ADF²⁷ was used for single-point energy refinements at the BP86-D3 level, in conjunction with a triple- ζ -quality basis set using uncontracted Slater-type orbitals (STOs) augmented by two sets of polarization functions with a frozen-core approximation for the core electrons.²⁸ Auxiliary sets of s, p, d, f, and g STOs were used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.²⁹ This level of theory is denoted BP86-D3/TZ2P+//RI-BP86-D3/def2-SVP. Solvent effects (solvent = toluene) have been taken into account in ADF by means of the Conductor like Screening Model (COSMO)³⁰ of solvation using the optimized geometries at the gas-phase. This level is therefore denoted COSMO(toluene)-BP86-D3/TZ2P+//RI-BP86-D3/def2-SVP.

Activation Strain Analyses of Reaction Profiles and Energy Decomposition Analysis

As the theoretical background and applications of ASM and EDA methods have been reviewed recently,^{10,11} herein we only briefly described the basics of these approaches. Within the ASM method,¹⁰ also known as *distortion/interaction model*,^{10c,31} the potential energy surface $\Delta E(\zeta)$ is partitioned, along the reaction coordinate ζ , into two contributions, namely the strain $\Delta E_{\text{strain}}(\zeta)$ associated with the deformation (or distortion) experienced by the individual reactants during the transformation, plus the interaction $\Delta E_{\text{int}}(\zeta)$ between these increasingly deformed reactants (eq. 1):

$$\Delta E(\zeta) = \Delta E_{\text{strain}}(\zeta) + \Delta E_{\text{int}}(\zeta) \quad (1)$$

Herein, the reaction coordinate is defined as the projection of the IRC onto the shortest C...C bond forming distance between the azafullerene and cyclopentadiene reactants.

Within the EDA method,¹¹ the interaction energy can be further decomposed into the following chemically meaningful terms (eq. 2):

$$\Delta E_{\text{int}}(\zeta) = \Delta V_{\text{elstat}}(\zeta) + \Delta E_{\text{Pauli}}(\zeta) + \Delta E_{\text{orb}}(\zeta) + \Delta E_{\text{disp}}(\zeta) \quad (2)$$

The term ΔV_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the deformed reactants and is usually attractive. The Pauli repulsion ΔE_{Pauli} comprises the destabilizing interactions

between occupied orbitals and is responsible for any steric repulsion. The orbital interaction ΔE_{orb} accounts for bond pair formation, charge transfer (interaction between occupied orbitals on one moiety with unoccupied orbitals on the other, including HOMO-LUMO interactions), and polarization (empty-occupied orbital mixing on one fragment due to the presence of another fragment). Finally, the ΔE_{disp} term takes into account the interactions which are due to dispersion forces.

Results and Discussion

We first considered the Diels-Alder cycloaddition reaction involving the cationic $C_{59}N^+$ azafullerene and cyclopentadiene. Similar to the neutral $C_{59}NH$ system, this cationic fullerene also exhibits 16 chemically reactive C–C [6,6]-bonds (see Figure 1). Moreover, this species also presents an additional C–N [6,6]-bond (bond 17) which can be also reactive in a [4+2]-cycloaddition with cyclopentadiene. Although two possible cycloadducts per [6,6]-bond can be formed depending on the approach of the diene, our calculations indicate that the energy barrier differences between both approaches can be considered as negligible (< 0.7 kcal/mol, see ESI). For this reason, herein we only present and discuss the data derived from the most favorable approach.

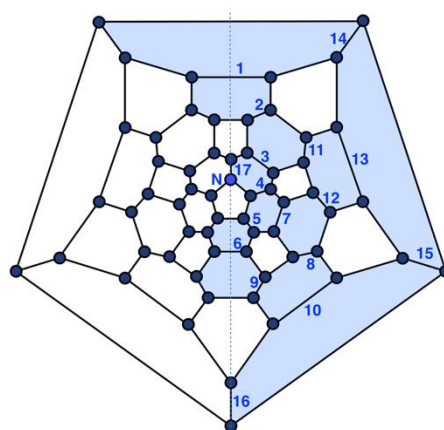


Fig. 1. Reactive [6,6]-bonds in the considered azafullerenes.

The computed reaction profile for the process involving $C_{59}N^+$ and cyclopentadiene resembles those computed for the analogous reaction involving C_{60} or $C_{59}NH$ (Figure 2).⁷ Therefore, regardless of the bond involved in the process, the [4+2]-cycloaddition proceeds concertedly through a relatively synchronous transition state (TS) from an initial van der Waals complex (RC) which lies approximately ca. -12 kcal/mol below the reactants (Table 1). According to the data in Table 1, the reaction occurs preferentially, both kinetically and specially thermodynamically, on [6,6]-bond 4. Although this contrasts to the neutral $C_{59}NH$ system where bond 3 was found to be the most reactive one,⁷ in both cases the most reactive C–C belongs to the six-membered ring where the nitrogen atom is present. It should be however noted that the rest of the bonds exhibit similar activation barriers ($\Delta\Delta E^\ddagger < 2$ kcal/mol), which suggests

that the regioselectivity of process involving $C_{59}N^+$ is predicted to be rather low.³² Despite that, it becomes clear that the cationic azafullerene is clearly more reactive than the neutral system ($\Delta\Delta E^\ddagger = 3.8$ kcal/mol, $\Delta\Delta E_R = -6.7$ kcal/mol) and even, than the parent C_{60} fullerene ($\Delta\Delta E^\ddagger = 1.0$ kcal/mol, $\Delta\Delta E_R = -5.1$ kcal/mol). This finding is consistent with our chemical intuition because the positive charge in the fullerene should greatly enhance the dienophile character of the fullerene. This is confirmed by the computed LUMO energy of these dienophiles: -7.72 eV ($C_{59}N^+$) $<$ -4.26 eV (C_{60}) $<$ -4.20 eV ($C_{59}NH$). A similar enhancement of the exohedral Diels-Alder reactivity, as compared to C_{60} , was found in the cationic endohedral fullerene $Li^+@C_{60}$.^{18c,33}

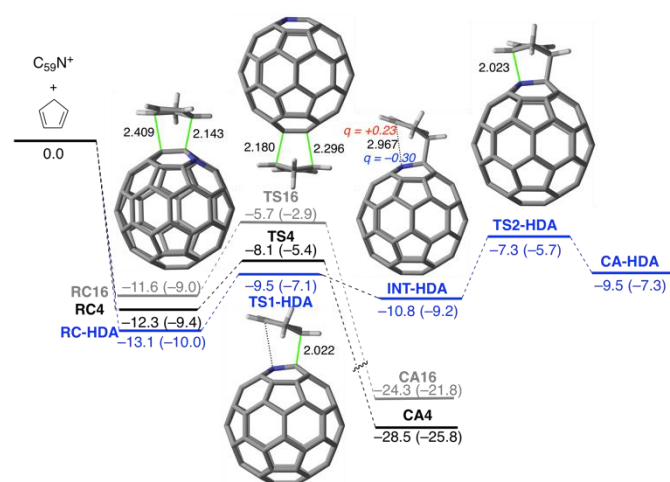


Fig. 2. Computed reaction profiles for the Diels-Alder reactions between cyclopentadiene and $C_{59}N^+$ on the most reactive [6,6]-bond 4 (black lines) and least reactive bond 16 (gray lines). The competitive hetero-Diels-Alder reaction (HDA) is shown in blue. Relative energies and bond distances are given in kcal/mol and angstroms, respectively. All data have been computed at the BP86-D3/TZ2P+//RI-BP86-D3/def2-SVP level. Values within parentheses indicate calculations in solution at the COSMO(toluene)-BP86-D3/TZ2P+//RI-BP86-D3/def2-SVP level.

Table 1. Computed energies (in kcal/mol, at the BP86-D3/TZ2P+//RI-BP86-D3/def2-SVP level) for the Diels-Alder cycloaddition reactions between cyclopentadiene and $C_{59}N^+$, most reactive bond of $C_{59}NH$ and C_{60} on C-C [6,6]-pyraclyenic bonds.

[6,6]-bond	ΔE_{RC}^a	ΔE^\ddagger^b	ΔE_R^c	$\Delta\Delta E^\ddagger^d$	$\Delta\Delta E_R^e$
1	-11.9	5.2	-25.1	1.0	3.4
2	-11.8	4.3	-26.8	0.1	1.7
3	-12.7	4.9	-23.8	0.7	4.7
4	-12.3	4.2	-28.5	0.0	0.0
5	-11.4	4.9	-23.4	0.7	5.1
6	-11.9	5.7	-24.2	1.5	4.3
7	-11.7	4.6	-26.0	0.4	2.5
8	-11.5	5.0	-25.3	0.8	3.2
9	-11.4	5.2	-24.9	1.0	3.6
10	-11.5	5.0	-24.9	0.8	3.6
11	-12.4	4.5	-26.1	0.3	2.4
12	-11.4	5.1	-25.2	0.9	3.3
13	-11.8	4.9	-25.0	0.7	3.5
14	-11.0	5.2	-24.7	1.0	3.8
15	-11.1	5.2	-24.6	1.0	3.9
16	-11.6	5.9	-24.3	1.7	4.2
$C_{59}NH$ (bond 3) ^f	-7.9	8.0	-21.8		
C_{60}	-7.1	5.2 ^g	-23.4 ^g		

^a Reactant complex (RC) energy: $\Delta E_{RC} = E(RC) - E(C_{59}N^+) - E(CP)$. ^b Activation energy: $\Delta E^\ddagger = E(TS) - E(RC)$. ^c Reaction energy: $\Delta E_R = E(\text{cycloadduct}) - E(C_{59}N^+) - E(CP)$. ^d $\Delta\Delta E_{TS} = \Delta E^\ddagger(TS_i) - \Delta E^\ddagger(TS_4)$. ^e $\Delta\Delta E_R = \Delta E_R(\text{bond } i) - \Delta E_R(\text{bond } 4)$. ^f Data taken from reference 7 (computed at the same level of theory). ^g Experimental values of activation energy and reaction energy are 6.9 and -19.8 kcal/mol, respectively.³⁴

Different to $C_{59}NH$, the C-N bond in $C_{59}N^+$ denoted as bond-17 in Figure 1 may also undergo a hetero-Diels-Alder (HDA) reaction with cyclopentadiene. As depicted in Figure 2, this cycloaddition reaction occurs stepwise via the formation of the intermediate **INT-HDA**, where the new C-C bond is already formed.³⁵ According to the data in Figure 2, this alternative reaction is only slightly kinetically favored ($\Delta\Delta E^\ddagger = 0.6$ kcal/mol at the gas-phase and $\Delta\Delta E^\ddagger = 1.1$ kcal/mol in toluene solution) over the cycloaddition reaction involving the C-C bond-4. Despite that, the latter process is strongly favored from a thermodynamic point of view ($\Delta\Delta E_R = -19.0$ kcal/mol at the gas-phase and $\Delta\Delta E_R = -18.5$ kcal/mol in solution). In case the product of the HDA process is formed, it will easily revert to the reactant complex **RC-HDA** that is more stable by about 3 kcal/mol. From **RC-HDA**, the reaction will evolve preferably through **RC4** and **TS4** to generate the cycloadduct involving the bond 4. Therefore, this alternative HDA reaction seems to be not competitive under the experimental conditions typically used for Diels-Alder reactions involving fullerenes (i.e. room temperature or moderate heating in non-polar benzene/toluene solvents).^{8,9}

We then focused on the reactivity of the anionic $C_{59}N^-$ azafullerene. Once again, we considered all the possible cycloaddition reactions at the sixteen different C-C [6,6]-bonds together with the analogous HDA reaction involving the C-N bond-17. Similarly, in all cases involving the C-C bonds, the cycloaddition proceeds concertedly via a synchronous six-membered transition state from an initial reactant complex (**RC**, see Figure 3). In this particular case, the most reactive bond is found to be the [6,6]-bond 2, which at variance to $C_{59}NH$ or

$C_{59}N^+$, does not belong to the six-membered ring where the heteroatom is present (Table 2). Moreover, bonds 3 and 4, that are among the most reactive in $C_{59}N^+$ become, in comparison to the rest of the bonds, less reactive in $C_{59}N^-$. This change of reactivity can be very likely attributed to the increased Pauli repulsion of the π -bonds near the nitrogen in the anionic system.

Not surprisingly, this anionic azafullerene is even less reactive than the neutral $C_{59}NH$ system from both kinetic and thermodynamic points of view ($\Delta\Delta E^\ddagger = 2.5$ kcal/mol, $\Delta\Delta E_R = -4.8$ kcal/mol, for the most reactive bonds), which is qualitatively consistent with the significant destabilization of the LUMO (-1.18 eV) induced by the negative charge.³⁶ Therefore, the following Diels-Alder reactivity is found: $C_{59}N^+$ ($\Delta E^\ddagger = 4.2$ kcal/mol) $>$ C_{60} ($\Delta E^\ddagger = 5.2$ kcal/mol) $>$ $C_{59}NH$ ($\Delta E^\ddagger = 8.0$ kcal/mol) $>$ $C_{59}N^-$ ($\Delta E^\ddagger = 10.5$ kcal/mol). In addition, no clear relationship between the bond length of the reactive bonds and the computed reactivity trend can be found (see Table S3 in the E.S.I.). Interestingly, the increase in the energy barrier when going from C_{60} to $C_{59}N^-$ in the DA cycloaddition with cyclopentadiene ($\Delta\Delta E^\ddagger = 5.3$ kcal/mol) is very similar to that found when comparing C_{60} and C_{60}^{2-} ($\Delta\Delta E^\ddagger = 5.9$ kcal/mol at the BP86-D2/TZP//BP86-D2/DZP level).³⁷ It is worth noting that $C_{59}N^-$ and C_{60}^{2-} are isoelectronic species. In addition, it was reported that the analogous cycloaddition involving the parent C_{60} fullerene prefers the corannulenic [5,6]-bond over the pyracenenic [6,6]-bond when reduced by 4-6 electrons (C_{60}^{n-} , $n = 4-6$).³⁶ We were curious to explore if this unusual regioselectivity might also occur in anionic $C_{59}N^-$. However, our calculations indicate that the [5,6]-cycloaddition is clearly unfeasible in view of the much higher barrier ($\Delta E^\ddagger = 15.8$ kcal/mol vs $\Delta E^\ddagger = 10.5$ kcal/mol) computed for this alternative approach of the cyclopentadiene.

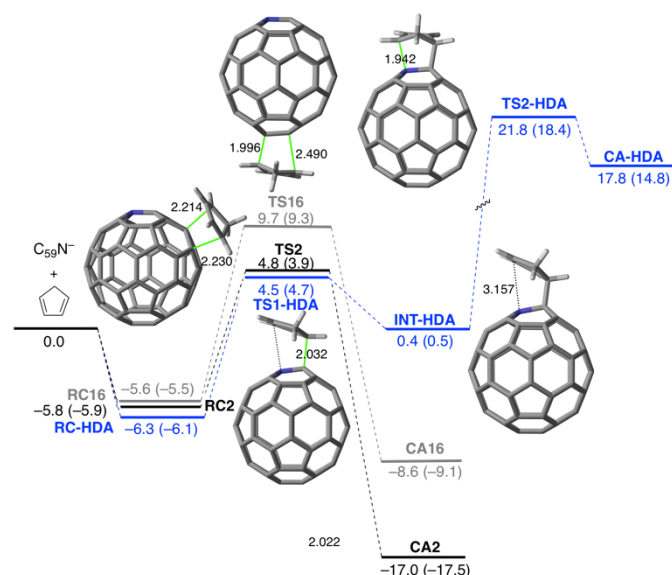


Fig. 3. Computed reaction profiles for the Diels-Alder reactions between cyclopentadiene and $C_{59}N^-$ on the most reactive [6,6]-bond 2 (black lines) and the least reactive bond 16 (gray lines). The competitive hetero-Diels-Alder reaction (HDA) is shown in blue. Relative energies and bond distances are given in kcal/mol and angstroms, respectively. All data have been computed at the BP86-D3/TZ2P+//RI-BP86-D3/def2-SVP level. Values within

parentheses indicate calculations in solution at the COSMO(toluenes)-BP86-D3/TZ2P+//RI-BP86-D3/def2-SVP level.

Table 2 Computed energies (in kcal/mol, at the BP86-D3/TZ2P+//RI-BP86-D3/def2-SVP level) for the Diels-Alder cycloaddition reactions between cyclopentadiene and $C_{59}N^-$.

[6,6]-bond	ΔE_{RC}^a	ΔE^\ddagger^b	ΔE_R^c	$\Delta\Delta E^\ddagger^d$	$\Delta\Delta E_R^e$
1	-6.2	10.8	-16.8	0.3	0.2
2	-5.8	10.5	-17.0	0.0	0.0
3	-5.6	11.6	-13.4	1.1	3.6
4	-6.4	11.7	-15.7	1.2	1.2
5	-5.6	12.6	-11.3	2.1	5.7
6	-6.1	10.8	-17.1	0.3	-0.1
7	-5.3	15.1	-11.0	4.6	6.0
8	-5.6	12.5	-13.6	2.0	3.4
9	-6.1	11.2	-15.9	0.7	1.0
10	-5.9	12.1	-14.4	1.6	2.6
11	-5.6	13.2	-11.5	2.7	5.5
12	-6.0	11.8	-14.1	1.3	2.8
13	-5.3	14.0	-12.1	3.5	4.9
14	-6.0	11.4	-15.2	0.9	1.8
15	-5.9	12.2	-13.7	1.7	3.3
16	-5.6	15.3	-8.6	4.8	8.4

^a Reactant complex (RC) energy: $\Delta E_{RC} = E(RC) - E(C_{59}N^-) - E(CP)$. ^b Activation energy: $\Delta E^\ddagger = E(TS) - E(RC)$. ^c Reaction energy: $\Delta E_R = E(\text{cycloadduct}) - E(C_{59}N^-) - E(CP)$. ^d $\Delta\Delta E_{TS} = \Delta E^\ddagger(TS_i) - \Delta E^\ddagger(TS_j)$. ^e $\Delta\Delta E_R = \Delta E_R(\text{bond } i) - \Delta E_R(\text{bond } 2)$.

As clearly shown in Figure 3, the alternative HDA reaction involving $C_{59}N^-$, which again occurs stepwise, is clearly unfeasible in view of the computed endothermicity of the process ($\Delta E_R = +17.8$ kcal/mol) and specially, of the high barrier computed for the final ring-closure step involving the transition state **TS2-HDA** ($\Delta E^\ddagger = 21.4$ kcal/mol). This high barrier height can be ascribed to the unfavorable electronic repulsion between the π -system of the cyclopentadienyl moiety (HOMO) and the lone-pair located at the nitrogen atom (HOMO-1) in the corresponding intermediate **INT-HDA** (Figure 4), which greatly hampers the subsequent ring-closure step.

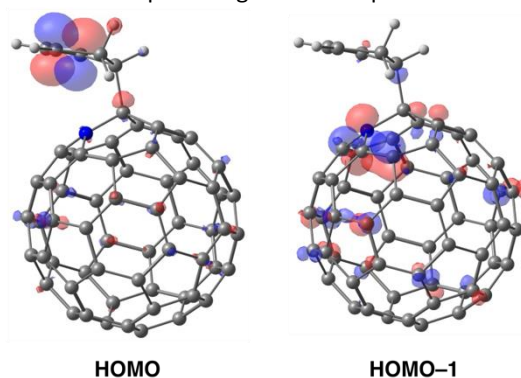


Fig. 4. Occupied molecular orbitals of intermediate **INT-HDA** for the cycloaddition reaction involving cyclopentadiene and $C_{59}N^-$ (isosurface value of 0.05 a.u.).

Although the computed LUMO energies qualitatively agrees with the observed reactivity trend (see above), the Activation Strain Model (ASM) of reactivity was applied next to quantitatively understand the origin of the different reactivity of these heterofullerenes. To this end, we compared the cycloaddition reactions involving the most reactive [6,6]-C-C

bonds of the parent neutral $C_{59}NH$,³⁸ $C_{59}N^+$ and $C_{59}N^-$ azafullerenes (i.e. (i.e. bonds 3, 4, and 2, respectively). Figure 5 shows the computed Activation Strain Diagrams (ASDs) for these processes from the corresponding initial reactant complexes up to the respective TSs along the IRC projected onto the shortest $C\cdots C$ bond forming distance. Not surprisingly, all systems exhibit rather similar ASDs in the sense that the interaction energy between the deformed reactants (measured by the ΔE_{int} term) remains constant or is even slightly destabilizing at the beginning of the process but becomes clearly stabilizing at the TS region. This behavior is also found not only in related Diels-Alder cycloadditions but also in completely different pericyclic reactions.³⁹ Closer inspection of the different ASDs in Figure 5 indicates that all systems require quite similar deformation energies (measured by the ΔE_{strain} term) to adopt the corresponding TS structure. Although the cationic system benefits from a slightly less destabilizing strain energy, the ΔE_{strain} term seems not decisive to govern the different reactivity of these species. At variance, the interaction energy between the reactants is clearly much stronger for the process involving $C_{59}N^+$ along the entire reaction coordinate than that computed for $C_{59}NH$ or $C_{59}N^-$. Indeed, the difference in the ΔE_{int} term roughly matches the difference in the computed total energy. For instance, at the same consistent $C\cdots C$ bond forming distance of 2.3 Å, $\Delta\Delta E_{\text{int}} = 10.4$ kcal/mol whereas $\Delta\Delta E = 11.5$ kcal/mol (for the processes involving $C_{59}N^+$ and $C_{59}NH$). Therefore, it can be concluded that the origin of the different Diels-Alder reactivity of the considered azafullerenes is found mainly in the interaction energy between the deformed reactants, which is greatly enhanced in the cationic system as compared to its neutral or anionic counterparts.

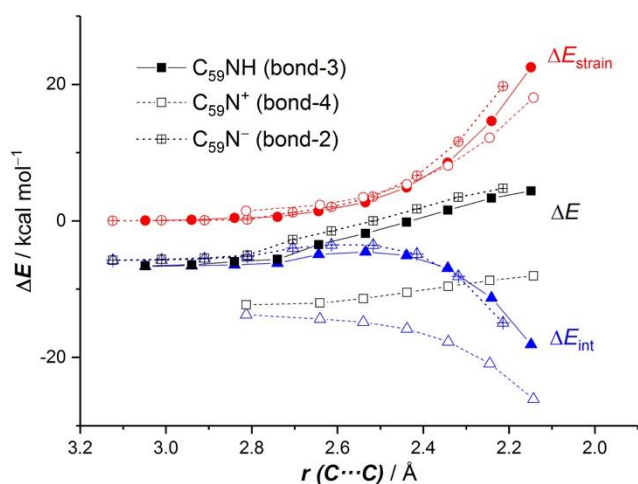


Fig. 5. Comparative activation-strain diagrams of the [4+2]-cycloaddition reactions between cyclopentadiene and $C_{59}NH$ (bond 3, solid lines), $C_{59}N^+$ (bond 3, dashed lines) and $C_{59}N^-$ (bond 2, dotted lines) along the reaction coordinate projected onto the forming $C\cdots C$ bond distance. All data have been computed at the BP86-D3/TZ2P+//RI-BP86-D3/def2-SVP level.

According to the computed LUMO energies, the crucial role of the interaction energy in these processes can be initially ascribed to the different occupied-unoccupied orbital interactions in these systems. To check this hypothesis, we

further decomposed the ΔE_{int} term along the reaction coordinate into its different physical components by means of the Energy Decomposition Analysis (EDA) method. As graphically shown in Figure 6, the orbital interactions between the deformed reactants (measured by ΔE_{orb}) are rather similar for all systems and are even slightly weaker for the reaction involving the most reactive $C_{59}N^+$ azafullerene. Therefore, it becomes clear that the ΔE_{orb} term is not at all controlling the enhanced Diels-Alder reactivity of $C_{59}N^+$ as compared to $C_{59}NH$ or $C_{59}N^-$. A similar scenario is found when comparing the electrostatic interactions (ΔV_{elstat}) or the dispersion interactions (ΔE_{disp}), which are nearly identical for all the systems along the entire reaction coordinate. Differently, the process involving the cationic $C_{59}N^+$ azafullerene benefits from a significant decrease in the Pauli repulsion term (ΔE_{Pauli}), which becomes less destabilizing particularly at the TS region. The significance of the Pauli repulsion in these transformations becomes evident when comparing the difference in this term between $C_{59}N^+$ and $C_{59}NH$ or $C_{59}N^-$, $\Delta\Delta E_{\text{Pauli}} = 14.3$ and 19.7 kcal/mol (for $C_{59}NH$ and $C_{59}N^-$, respectively, at the same consistent $C\cdots C$ bond forming distance of 2.3 Å), which is fully consistent with the observed reactivity trend.

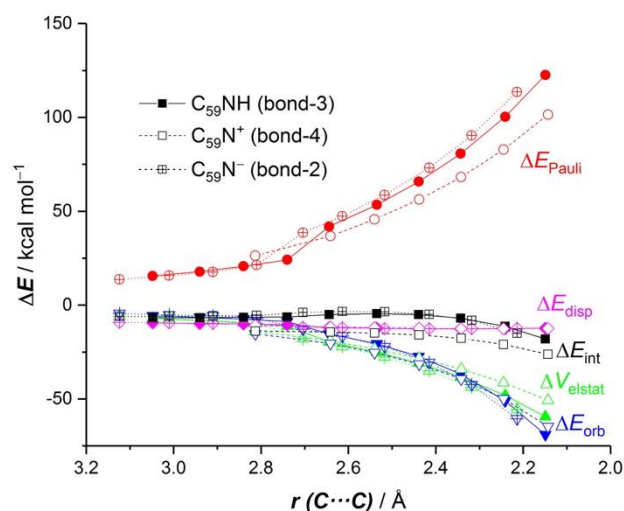


Fig. 6. Comparative energy decomposition analysis of the [4+2]-cycloaddition reactions between cyclopentadiene and $C_{59}NH$ (bond 3, solid lines), $C_{59}N^+$ (bond 3, dashed lines) and $C_{59}N^-$ (bond 2, dotted lines) along the reaction coordinate projected onto the forming $C\cdots C$ bond distance. All data have been computed at the BP86-D3/TZ2P+//RI-BP86-D3/def2-SVP level.

Despite the process involving the bond-2 of $C_{59}N^+$ is not preferred from a thermodynamic point of view over the process involving bond-4 ($\Delta\Delta E_{\text{R}} = 1.7$ kcal/mol, see Table 1), it occurs with a rather similar activation barrier ($\Delta\Delta E = 0.1$ kcal/mol). For this reason, we also compared the Diels-Alder reactions for $C_{59}N^+$ and $C_{59}N^-$ occurring at the analogous bond-2 by means of the ASM/EDA method. Once again, it was found that the interaction energy is clearly much stronger for the process involving $C_{59}N^+$ along the entire reaction coordinate as a result of a less destabilizing Pauli repulsion between the reactants (see Figures S4 and S5 in the E.S.I.). In addition, for this particular

transformation, the orbital interaction term (ΔE_{orb}) also favours the process involving the cationic azafullerene.

The more destabilizing Pauli repulsion in C_{59}NH and in the isoelectronic C_{59}N^- azafullerene results from closed-shell electronic repulsion between the HOMO of the diene (a doubly occupied π -molecular orbital) and the HOMO of the azafullerene (a π -molecular orbital involving the $\text{C}=\text{N}$ bond, see Figure 7). In contrast, the latter orbital is empty in C_{59}N^+ (and in the isoelectronic C_{60} fullerene) and therefore, such an unfavorable closed-shells interaction is not possible. Therefore, the presence of these two additional electrons in C_{59}NH and C_{59}N^- induce a significant electronic repulsion with the diene which is translated into a more destabilizing Pauli repulsion. As a consequence, the total diene-dienophile interaction becomes much weaker which ultimately results into the computed lower reactivity of these systems as compared to the cationic C_{59}N^+ (or the parent C_{60}). Interestingly, whereas the increase in the energy barrier in C_{59}N^- and $\text{Cl}^-@C_{60}$ with respect to C_{60} is similar for the analogous Diels-Alder cycloaddition reaction with cyclopentadiene, the physical reasons behind the observed decrease of reactivity are completely different. An increased Pauli repulsion explains the lower reactivity of C_{59}N^- as compared to C_{60} , while for the endohedral $\text{Cl}^-@C_{60}$ fullerene, the significantly weaker $\pi(\text{diene}) \rightarrow \pi^*(\text{fullerene})$ orbital interaction is responsible for its lower reactivity.^{18c} A similar control of the reactivity by the Pauli repulsion between closed-shells was also found in the slightly related inverse-electron demand Diels-Alder cycloadditions involving heteroaromatic azadienes⁴⁰ and in other completely different processes such as acetylene trimerization⁴¹ or $\text{S}_{\text{N}}2$ reactions.⁴²

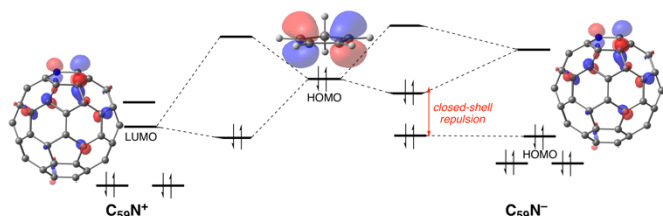


Fig. 7. Schematic molecular orbital correlation diagrams for the cycloaddition reactions between cyclopentadiene and C_{59}N^+ (left) and C_{59}N^- (right).

Conclusions

Similar to the process involving the parent C_{59}NH or C_{60} , the Diels-Alder cycloaddition reactions between cyclopentadiene and C_{59}N^+ or C_{59}N^- proceed concertedly through synchronous transition states. (ii) However, significant differences in both the reactivity and regioselectivity are found. For instance, whereas the cycloaddition involving C_{59}N^+ or C_{59}NH occurs in a [6,6]-C-C bond belonging to the six-membered ring where the nitrogen atom is present, the preferred cycloaddition occurs at a completely different C-C bond for C_{59}N^- . (iii) The following Diels-Alder reactivity trend is found: C_{59}N^+ ($\Delta E^\ddagger = 4.2$ kcal/mol) > C_{60} ($\Delta E^\ddagger = 5.2$ kcal/mol) > C_{59}NH ($\Delta E^\ddagger = 8.0$ kcal/mol) > C_{59}N^- ($\Delta E^\ddagger = 10.5$ kcal/mol). (iv) Although this reactivity trend qualitatively agrees with the corresponding LUMO energies, it is found that

the frontier molecular orbital interactions do not control the different reactivity of these systems. (v) Compared to C_{59}NH or C_{59}N^- , the cationic C_{59}N^+ azafullerene benefits from a much stronger interaction between the deformed reactants along the entire reaction coordinate. This enhanced interaction mainly derives from a significant decrease of the Pauli repulsion in this particular system. Indeed, the presence of the two additional electrons in C_{59}NH and C_{59}N^- as compared to C_{59}N^+ induces a significant electronic repulsion between closed-shells, which is translated into a much weaker interaction that ultimately results into the computed lower reactivity of these systems.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

