

Analysis of Electron Delocalization in Aromatic Systems: Individual Molecular Orbital Contributions to *Para*-Delocalization Indexes (PDI)

Mireia Güell[†], Eduard Matito[†], Josep M. Luis[†], Jordi Poater[§] and Miquel Solà^{†,*}

Institut de Química Computacional and Departament de Química, Universitat de Girona, Campus de Montilivi, 17071 Girona, Catalonia, Spain, Afdeling Theoretische Chemie, Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands.

miquel.sola@udg.es

Abstract

Our research group has recently defined two new aromaticity indexes based on the analysis of electron delocalization in aromatic species using the quantum theory of atoms-in-molecules. One of these indexes is the *para*-delocalization index (PDI) that measures the electronic delocalization between *para*-related carbon atoms in six-membered rings. In this paper, we show that this index can be partitioned into individual molecular orbital contributions. We have applied this PDI decomposition to several polycyclic aromatic hydrocarbons showing that this partitioning provides new insight into the origin of aromaticity.

Keywords: Delocalization index, aromaticity, *para*-delocalization index (PDI), atoms-in-molecules (AIM), molecular orbital contributions, σ and π separation.

* To whom correspondence should be addressed. Phone: +34-972.418.912. Fax: +34-972.418.356.

[†] Institut de Química Computacional and Departament de Química, Universitat de Girona.

[§] Afdeling Theoretische Chemie, Vrije Universiteit.

1. Introduction

The concept of aromaticity is of central importance for the interpretation of molecular structure, stability, reactivity, and magnetic properties of many organic and inorganic compounds.^{1,2} Aromaticity is not an observable and consequently it has no precise quantitative definition and is not directly measurable experimentally. The imprecise nature of aromaticity has stimulated the quest for quantitative definitions, although nearly everyone would agree that there is not a well-established method to quantify the aromatic character of molecules yet. The evaluation of aromaticity is usually done indirectly by measuring some physicochemical property that reflects the aromatic character of molecules. Thus, most aromaticity indicators are based on the classical aromaticity criteria, namely, structural, magnetic, energetic, and reactivity-based measures.^{2,3} Undoubtedly, the origin of the aromatic properties is the cyclic delocalized distribution of π -electrons. For this reason, more recently, new ways to quantify the aromaticity based on the measure of electronic delocalization in aromatic molecules have been devised (for a recent review see reference 4). In particular, two new indexes based on the calculation of delocalization indexes (DIs) in the framework of the quantum theory of atoms-in-molecules (QTAIM) have been recently defined by some of us: the *para*-delocalization index (PDI)⁵ and the aromatic fluctuation index (FLU).⁶ In this context it is worth mentioning the work of Matta et al.⁷ who also attempted to construct an HOMA-like index⁸ from QTAIM by substituting the bond length by the total electron delocalization and also the use by Giambiagi et al.⁹ and Bultinck et al.¹⁰ of *n*-center electron DIs as descriptors of aromaticity.

In the continual drive to reach a wider understanding of aromaticity, some

aromaticity measures have been separated into their σ and π contributions in planar systems. This goal has been achieved for a series of indicators of aromaticity, namely, ring currents,¹⁵ nucleus-independent chemical shifts (NICS),^{16,17} electron localization function (ELF),¹⁸ and aromatic stabilization energies (ASE).¹⁹ Less common is the separation of aromaticity indexes into individual molecular orbital (MO) contributions in MO-based methods, although successful experiences have been reported for NICS^{17,20,21} and ring currents.²²⁻²⁵ The aim of the present work is to show that PDI can also be separated into individual MO contributions and, in the particular case of planar systems, into its σ and π contributions. Results for a series of polycyclic aromatic hydrocarbons (PAHs) are presented and compared when possible with results from MO-dissected NICS and ring currents.

2. Theoretical basis of the analysis

In 1996, Bader and coworkers²⁶ reported in a seminal work that the electron delocalization in benzene was greater for *para*-related carbon atoms (*para*-DI) than for *meta*-related ones (*meta*-DI). Later on, some of us⁵ defined the *para*-delocalization index (PDI) as the averaged of *para*-DI in six-membered rings (6-MRs) and used this index as a measure of local aromaticity. The PDI is a specific measure of local aromaticity for 6-MRs, where three *para*-related positions exist, namely, (1,4), (2,5), and (3,6). By definition, the PDI of a 6-MR is given by:

$$PDI = \frac{\delta(1,4) + \delta(2,5) + \delta(3,6)}{3}, \quad (1)$$

In Eq. (1), $\delta(A,B)$, the DI, is derived from the double integration of the exchange-correlation density over the atomic basins defined within the QTAIM theory:²⁷

$$\delta(A, B) = -2 \int_A \int_B \Gamma_{xc}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 . \quad (2)$$

The term $\delta(A, B)$ gives a quantitative measure of the number of electrons delocalized or shared between atomic basins A and B .

For closed-shell molecules and for single determinant wave functions, Eq. (2) is simplified to:²⁷

$$\delta(A, B) = 2 \sum_{i,j} S_{ij}(A) S_{ij}(B) , \quad (3)$$

where the summations run over all the occupied molecular spin-orbitals and $S_{ij}(A)$ is the overlap between occupied molecular spin-orbitals i and j over the basin of atom A .

In molecules having a plane of symmetry, the orbitals can be classified as σ or π , depending on their symmetric or antisymmetric behavior with respect to reflection in the plane. Because the QTAIM partition of space preserves the symmetry of the system, the overlap integrals $S_{ij}(A)$ vanish when i and j belong to different sets, and consequently, the contributions of σ and π electrons to the DIs can be exactly separated. In this case it is also possible to define the π contribution to the PDI using the π component of the DIs between *para*-related carbon atoms in 6-MRs as:

$$PDI_{\pi} = \frac{\delta_{\pi}(1,4) + \delta_{\pi}(2,5) + \delta_{\pi}(3,6)}{3} . \quad (4)$$

Finally, Eq. (4) can also be written as:

$$\delta(A, B) = \sum_i 2 \sum_j S_{ij}(A) S_{ij}(B) = \sum_i \delta_i(A, B) , \quad (5)$$

where $\delta_i(A,B)$ gives the contribution of the i orbital to the total $\delta(A,B)$. Thus, for monodeterminantal wave functions, the DI can be separated into its individual MO contributions and, in particular, the PDI can also be split up into MO components as:

$$PDI_i = \frac{\delta_i(1,4) + \delta_i(2,5) + \delta_i(3,6)}{3} , \quad (6)$$

with:

$$PDI = \sum_i PDI_i = \sum_i \frac{\delta_i(1,4) + \delta_i(2,5) + \delta_i(3,6)}{3} . \quad (7)$$

One can also define analogously the $PDI_{\pi,i}$ as the contribution to PDI_{π} of the i π -orbital. While total $\delta(A,B)$ or $\delta_{\pi}(A,B)$ are always positive, the components $\delta_i(A,B)$ or $\delta_{\pi,i}(A,B)$ can be positive or negative depending on the overlaps between i and j orbitals in the basins of atoms A and B. $\delta_i(A,B)$ is negative when the two electrons occupying orbital i cause a greater localization of the rest of the electrons in the molecule, and, therefore produce a reduction in the total electronic delocalization.

3. Computational Details

Geometries of all PAHs in their ground states have been fully optimized with the hybrid density functional theory (DFT) B3LYP method²⁸ using the 6-311G(d,p) basis set by means of the Gaussian 03 program.²⁹ Integrations of DIs needed to calculate the PDIs have been performed using the AIMPAC collection of programs.³⁰ Calculation of these DIs at the DFT level of theory cannot be performed exactly³¹ because the electron-pair density is not available at this level of theory. As an approximation, we have used the Kohn-Sham orbitals obtained from DFT to calculate Hartree-Fock-like DIs using Eq. (5).³¹ The numerical accuracy of the AIM calculations has been assessed using two

criteria: i) The integration of the Laplacian of the electron density ($\nabla^2\rho(\mathbf{r})$) within an atomic basin must be close to zero; ii) The number of electrons in a molecule must be equal to the sum of all the electron populations of a molecule, and also equal to the sum of all the localization indices and half of the delocalization indices in the molecule.³² For all atomic calculations, integrated absolute values of $\nabla^2\rho(\mathbf{r})$ were always less than 0.001 a.u. For all molecules, errors in the calculated number of electrons were always less than 0.01 a.u.

4. Results and discussion

Scheme 1 depicts the eleven PAHs analyzed together with the labels assigned to each different ring. Table 1 contains the values of the PDI and PDI_π for all studied rings as well as all individual MO contributions to PDI_π which are certainly the most important contributions to the total PDI. The PDI_π contribution to the total PDI ranges from 90% in the most aromatic 6-MR (benzene) to 69% for the least aromatic 6-MR of indacene. The PDI_σ obtained as the difference between the total PDI and PDI_π has values that go from 0.010 e in benzene, pyracyclene, and acenaphthalene to 0.008 e in ring B of chrysene. So, the σ contribution to PDI is relatively small and, more importantly, it is quite constant for all PAHs studied and, therefore, the differences between PDI values come mainly from the PDI_π contribution. For this reason, the decomposition into individual MO contributions in Table 1 is only done for the PDI_π part of the PDI. The occupied π -orbitals of the eleven PAHs studied are depicted in Figure 1.

Scheme 1, Table 1, and Figure 1 here

For the archetypical aromatic molecule, benzene, it is found that the doubly degenerated e_{1g} HOMO orbitals are those that have a greater contribution to the PDI. The a_{2u} π -orbital has a negative contribution of -0.088 e. This means that the two electrons in a_{2u} MO reduce the delocalization between *para*-related carbon atoms in benzene. This can be understood by simple inspection of the a_{2u} and e_{1g} π -orbitals, which shows that the products $S_{a_{2u}e_{1g}}(C_1)S_{a_{2u}e_{1g}}(C_4)$, $S_{a_{2u}e_{1g}}(C_2)S_{a_{2u}e_{1g}}(C_5)$, and $S_{a_{2u}e_{1g}}(C_3)S_{a_{2u}e_{1g}}(C_6)$ involved in the $PDI_{\pi,a_{2u}}$ calculation are always negative or zero. Indeed, the product $S_{ij}(A)S_{ij}(B)$, being A and B *para* related carbon atoms in a 6-MR, is always negative or zero if the sum of total nodal planes in orbitals i and j gives an even number and positive or zero otherwise. Interestingly, when the two electrons from orbital a_{2u} are removed without reoptimizing the wave function, the PDI_{π} value becomes 0.375 e, which means that the aromaticity of benzene increases by removing these two electrons in the a_{2u} orbital according to PDI values.

Our result for benzene is totally in line with those derived from the analysis of the individual MO contributions to ring currents and dissected-MO NICS. As shown by Steiner and Fowler, an occupied-to-unoccupied $e_{1g}(\text{HOMO}) \rightarrow e_{2u}(\text{LUMO})$ translationally allowed transition gives the main diamagnetic contribution to the diatropic ring of benzene.²³⁻²⁵ According to this results only the four electrons of the two e_{1g} π -orbitals contribute significantly to the ring current.^{23,24} As to the NICS studies, although the NICS(0) value of the a_{2u} MO is more negative than that of the two e_{1g} π -orbitals,¹⁷ the opposite is true for NICS_{zz}(0) (the zz tensor component of the isotropic

NICS(0)).²¹ Since the ring current density in aromatic compounds is more related to NICS_{zz}(0) than to NICS(0) itself,³³ the conclusion from NICS studies is also that the e_{1g} π -orbitals are the main responsible of the aromatic behavior in benzene.²¹

In the naphthalene π -system again only the four electrons in the two highest-lying a_u(HOMO) and b_{1u}(HOMO-1) make significant contributions to the total diamagnetic ring current.²⁴ These two orbitals also give important individual MOs contributions to PDI, but in our case the orbital that contributes the most to the PDI is the b_{3g}(HOMO-2) owing to the large and positive $S_{a_u b_{3g}}(C_1)S_{a_u b_{3g}}(C_4)$ term. Thus, the three highest-lying MOs of naphthalene contribute positively to the PDI, while the two lowest-lying π -orbitals have negative contributions, especially the b_{1u}(HOMO-7). Thus, like in benzene, the π -orbital with a unique nodal plane (the molecular plane) is the one that reduces more significantly the PDI value.

Similarly, for the A ring of anthracene and phenanthrene, the four highest-lying occupied π -orbitals are those that contribute more to the PDI, while involvement of the three lowest-lying π -orbitals is negative or close to zero. Contributions of the four highest-lying occupied π -orbitals to the PDI of phenanthrene are larger, in general, than to anthracene as expected from the large aromatic character of ring A in phenanthrene.¹³ For the B ring of anthracene the a_u(HOMO-2) has a negative contribution, while the b_{2g}(HOMO-8) has a positive non-negligible role in the π -*para* electronic delocalization. For tetracene and chrysene, the six highest-lying MOs are those that contribute more to the PDI of both rings A and B, while the three lowest-lying π -orbitals have a negative contribution, with the only exception of the b_{2g}(HOMO-4) and b_{1u}(HOMO-9) orbitals for the ring B of tetracene that have small negative and positive contributions to PDI,

respectively.

As indicated by other aromaticity indexes,³⁴ PDI gives also the largest aromaticity to the most external rings A of pyrene and coronene. For these A rings, the largest contributions to PDI come from the six and seven highest-lying occupied π -orbitals, respectively. In particular, for the ring A of pyrene, the large value assigned to the $a_u(\text{HOMO}-3)$ π -orbital comes mainly from its interaction with the $b_{3g}(\text{HOMO})$. Interestingly, for the less aromatic ring B of pyrene and coronene, the contributions from the b_{3g} and e_{2u} HOMO orbitals, respectively, to the PDI values are negative. Indeed, for coronene, we find, unexpectedly, that the pair of degenerate e_{2u} HOMOs does not have an important participation to the PDIs of rings A and B. This result is in not in line with the orbital contributions to the current density analysis carried out by Steiner and Fowler in coronene. These authors found that both the inner and outer circulations in coronene come mainly from the four electrons in the degenerate e_{2u} HOMO.²⁴

Acenaphthalene results from the addition of a fused 5-MR to naphthalene, while a further addition of a 5-MR leads to pyracylene. 5-MR addition decreases the aromaticity of the 6-MRs when going from naphthalene to acenaphthalene, and from this to pyracylene.¹² Similarly to that found for most 6-MRs, the main contributions to the PDI of the 6-MRs in acenaphthalene originate from the highest-lying π -orbitals ($b_1(\text{HOMO}, \text{HOMO}-2, \text{HOMO}-3)$ and $a_2(\text{HOMO}-1)$). For pyracylene, the most important individual MO contributors to PDI are the $b_{2g}(\text{HOMO}$ and $\text{HOMO}-8)$ π -orbitals and especially the near-degenerate $b_{1u}(\text{HOMO}-1)$ and $a_u(\text{HOMO}-2)$ π -MOs. This is consistent with the fact that the electrons placed in these two latter orbitals are the main

responsible for the diamagnetic electronic circulation around the perimeter of the naphthalenic unit, according to Steiner and Fowler.²⁴ Finally, for indacene, with two 5-MRs and only one 6-MR, the aromaticity of the 6-MR is rather low and the main contributions to PDI come from the b_{2g} orbitals, specially owing to the positive overlap between orbitals b_{3g} (HOMO-3) and b_{2g} (HOMO). MO-dissected ring currents also show that the origin of the paratropic ring current of the 6-MR in indacene lies basically in the b_{2g} (HOMO) \rightarrow b_{1g} (LUMO) transition.

4. Conclusions

In this work, we have decomposed the *para*-delocalization index of local aromaticity into its individual molecular orbital components for a series of PAHs. In general, we have found the lowest-lying π -MOs contribute negatively to the PDI_π and the total PDI, while the highest-lying π -MOs are those that increase more the π -electronic delocalization between *para*-related C atoms. In this sense, those orbitals with a larger number of nodal planes usually have a larger contribution to the *para*-electronic delocalization than those with a few nodal planes. Indeed, for all systems studied, the π -orbital with a unique nodal plane (the molecular plane) negatively contributes to the PDI, and in most cases this π -orbital is the one that reduces more significantly the PDI value.

Acknowledgments

Financial help has been furnished by the Spanish MEC Project No. CTQ2005-08797-C02-01/BQU and by the catalan Departament d'Universitats, Recerca i Societat de la Informació (DURSI) through project No. 2005SGR-00238. M.G. and E.M. thank the MEC for the doctoral fellowships no. AP-2004-4775 and AP2002-0581, respectively. J.P. also acknowledges the DURSI for the postdoctoral fellowship 2004BE00028. We also thank the Centre de Supercomputació de Catalunya (CESCA) for partial funding of computer time.

References

- (1) P. v. R. Schleyer, *Chem. Rev. (Washington, D. C.)*, 2001, **101**, 1115-1118; P. v. R. Schleyer, *Chem. Rev. (Washington, D. C.)*, 2005, **105**, 3433-3435; V. I. Minkin, M. N. Glukhovtsev and B. Y. Simkin, in *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; John Wiley & Sons: New York, 1994; P. J. Garrat, in *Aromaticity*; John Wiley & Sons: New York, 1986; A. T. Balaban, *Pure & Appl. Chem.*, 1980, **52**, 1409-1429; D. Lloyd, *J. Chem. Inf. Comp. Sci.*, 1996, **36**, 442-447.
- (2) T. M. Krygowski, M. K. Cyrański, Z. Czarnocki, G. Häfelfinger and A. R. Katritzky, *Tetrahedron*, 2000, **56**, 1783-1796.
- (3) A. R. Katritzky, P. Barczynski, G. Musumarra, D. Pisano and M. Szafran, *J. Am. Chem. Soc.*, 1989, **111**, 7-15.
- (4) J. Poater, M. Duran, M. Solà and B. Silvi, *Chem. Rev.*, 2005, **105**, 3911-3947.
- (5) J. Poater, X. Fradera, M. Duran and M. Solà, *Chem. Eur. J.*, 2003, **9**, 400-406.
- (6) E. Matito, M. Duran and M. Solà, *J. Chem. Phys.*, 2005, **122**, 014109.
- (7) C. F. Matta and J. Hernández-Trujillo, *J. Phys. Chem. A*, 2003, **107**, 7496-7504; C. F. Matta and J. Hernández-Trujillo, *J. Phys. Chem. A*, 2005, **109**, 10798-10798.
- (8) J. Kruszewski and T. M. Krygowski, *Tetrahedron Lett.*, 1972, **13**, 3839-3842; T. M. Krygowski, *J. Chem. Inf. Comp. Sci.*, 1993, **33**, 70-78.
- (9) M. Giambiagi, M. S. de Giambiagi, C. D. dos Santos and A. P. de Figueiredo, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3381-3392; C. G. Bollini, M. Giambiagi, M. S. Giambiagi and A. P. Figueiredo, *J. Math. Chem.*, 2000, **28**, 71-81.
- (10) P. Bultinck, R. Ponec and S. Van Damme, *J. Phys. Org. Chem.*, 2005, **18**, 706-718.
- (11) J. Poater, I. García-Cruz, F. Illas and M. Solà, *Phys. Chem. Chem. Phys.*, 2004, **6**, 314-318; G. Portella, J. Poater, J. M. Bofill, P. Alemany and M. Solà, *J. Org. Chem.*, 2005, **70**, 4560-4560; E. Matito, J. Poater, M. Duran and M. Solà, *J. Mol. Struct. (Theochem)*, 2005, **727**, 165-171; J. Poater, J. M. Bofill, P. Alemany and M. Solà, *J. Org. Chem.*, 2006, **71**, 1700-1702.
- (12) J. Poater, M. Solà, R. G. Viglione and R. Zanasi, *J. Org. Chem.*, 2004, **69**, 7537-7542.

- (13) G. Portella, J. Poater, J. M. Bofill, P. Alemany and M. Solà, *J. Org. Chem.*, 2005, **70**, 2509-2521.
- (14) A. R. Katritzky, M. Karelson, S. Sild, T. M. Krygowski and K. Jug, *J. Org. Chem.*, 1998, **63**, 5228-5231; K. Jug and A. M. Köster, *J. Phys. Org. Chem.*, 1991, **4**, 163-169; A. R. Katritzky, K. Jug and D. C. Oniciu, *Chem. Rev. (Washington, D. C.)*, 2001, **101**, 1421-1449; T. M. Krygowski and M. K. Cyrański, *Chem. Rev. (Washington, D. C.)*, 2001, **101**, 1385-1419; M. K. Cyrański, T. M. Krygowski, A. R. Katritzky and P. v. R. Schleyer, *J. Org. Chem.*, 2002, **67**, 1333-1338.
- (15) E. Steiner and P. W. Fowler, *Int. J. Quantum Chem.*, 1996, **60**, 609-616; E. Steiner, P. W. Fowler and L. W. Jenneskens, *Angew. Chem. Int. Ed.*, 2001, **40**, 362-266; E. Steiner, P. W. Fowler, L. W. Jenneskens and R. W. A. Havenith, *Eur. J. Org. Chem.*, 2002, 163-169.
- (16) P. v. R. Schleyer, H. J. Jiao, N. J. R. van Eikema Hommes, V. G. Malkin and O. L. Malkina, *J. Am. Chem. Soc.*, 1997, **119**, 12669-12670; P. v. R. Schleyer, M. Manoharan, Z. X. Wang, B. Kiran, H. J. Jiao, R. Puchta and N. J. R. van Eikema Hommes, *Org. Lett.*, 2001, **3**, 2465-2468.
- (17) T. Heine, P. V. Schleyer, C. Corminboeuf, G. Seifert, R. Reviakine and J. Weber, *J. Phys. Chem. A*, 2003, **107**, 6470-6475.
- (18) J. C. Santos, W. Tiznado, R. Contreras and P. Fuentealba, *J. Chem. Phys.*, 2004, **120**, 1670-1673; J. C. Santos, J. Andres, A. Aizman and P. Fuentealba, *J. Chem. Theor. Comput.*, 2005, **1**, 83-86.
- (19) G. Hohlneicher, L. Packschies and J. Weber, *ChemPhysChem*, 2005, **6**, 2541-2551.
- (20) R. B. King, T. Heine, C. Corminboeuf and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 2004, **126**, 430-431.
- (21) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842-3888.
- (22) E. Steiner, P. W. Fowler and R. W. A. Havenith, *J. Phys. Chem. A*, 2002, **106**, 7048-7056; E. Steiner, P. W. Fowler, R. G. Viglione and R. Zanasi, *Chem. Phys. Lett.*, 2002, **355**, 471-477; A. Soncini, E. Steiner, P. W. Fowler, R. W. A. Havenith and L. W. Jenneskens, *Chem. Eur. J.*, 2003, **9**, 2974-2981; P. W. Fowler, C. W. Rees and A. Soncini, *J. Am. Chem. Soc.*, 2004, **126**, 11202-11212.
- (23) E. Steiner and P. W. Fowler, *Chem. Commun.*, 2001, 2220-2221.
- (24) E. Steiner and P. W. Fowler, *J. Phys. Chem. A*, 2001, **105**, 9553-9562.

- (25) A. Soncini, P. W. Fowler and F. Zerbetto, *Chem. Phys. Lett.*, 2005, **405**, 136-141.
- (26) R. F. W. Bader, A. Streitwieser, A. Neuhaus, K. E. Laidig and P. Speers, *J. Am. Chem. Soc.*, 1996, **118**, 4959-4965.
- (27) X. Fradera, M. A. Austen and R. F. W. Bader, *J. Phys. Chem. A*, 1999, **103**, 304-314.
- (28) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789; P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627.
- (29) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople; Gaussian 03, Revision C.01 ed.; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (30) F. W. Biegler-König, R. F. W. Bader and T.-H. Tang, *J. Comput. Chem.*, 1982, **3**, 317 (<http://www.chemistry.mcmaster.ca/aimpac/>).
- (31) J. Poater, M. Solà, M. Duran and X. Fradera, *Theor. Chem. Acc.*, 2002, **107**, 362-371.
- (32) X. Fradera, J. Poater, S. Simon, M. Duran and M. Solà, *Theor. Chem. Acc.*, 2002, **108**, 214-224.
- (33) C. Corminboeuf, T. Heine, G. Seifert, P. v. R. Schleyer and J. Weber, *Phys. Chem. Chem. Phys.*, 2004, **6**, 273-276.
- (34) M. Güell, J. Poater, J. M. Luis, O. MÓ, M. Yáñez and M. Solà, *ChemPhysChem*, 2005, **6**, 2552-2561.

Figure Captions

Scheme 1. Schematic representation of the molecules studied together with ring labels.

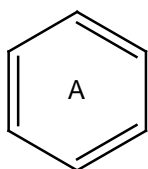
Figure 1. Occupied π molecular orbitals of (a) benzene, (b) naphthalene, (c) anthracene, (d) phenanthrene, (e) tetracene, (f) chrysene, (g) pyrene, (h) coronene, (i) acenaphthalene, (j) pyracylene, and (k) indacene. Isosurface values are -0.05 and 0.05 a.u. The z-axis contains energies in hartrees.

Table 1. PDI and PDI $_{\pi}$ for all studied rings as well as all individual molecular orbital contributions to PDI $_{\pi}$. Units are electrons.

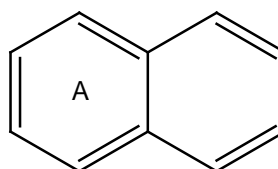
Molecule	Symmetry	Label	Orbitals	PDI contributions	
				A	B
Benzene	D _{6h}	M1	a _{2u} (17)	-0,0880	
			e _{1g} (20,21)	0,1813	
			PDI $_{\pi}$	0,0933	
			PDI	0,1034	
Naphthalene	D _{2h}	M2	b _{1u} (27)	-0,0445	
			b _{2g} (31)	-0,0120	
			b _{3g} (32)	0,0459	
			b _{1u} (33)	0,0452	
			a _u (34)	0,0311	
			PDI $_{\pi}$	0,0656	
			PDI	0,0749	
Anthracene	D _{2h}	M3	b _{1u} (36)	-0,0210	-0,0450
			b _{2g} (39)	-0,0327	0,0153
			b _{1u} (43)	0,0103	-0,0183
			b _{3g} (44)	0,0213	0,0480
			a _u (45)	0,0390	-0,0087
			b _{2g} (46)	0,0273	0,0293
			b _{3g} (47)	0,0113	0,0347
			PDI $_{\pi}$	0,0557	0,0553
			PDI	0,0655	0,0652
Phenanthrene	C _{2v}	M4	b ₁ (36)	-0,0273	-0,0347
			a ₂ (40)	-0,0353	0,0127
			b ₁ (43)	0,0070	0,0050
			b ₁ (44)	0,0347	0,0110
			a ₂ (45)	0,0367	0,0140
			a ₂ (46)	0,0350	0,0133
			b ₁ (47)	0,0210	0,0157
			PDI $_{\pi}$	0,0717	0,0370
			PDI	0,0812	0,0465

Tetracene	D _{2h}	M5	b _{1u} (46)	-0,0112	-0,0315
			b _{2g} (48)	-0,0262	-0,0042
			b _{1u} (51)	-0,0151	0,0018
			b _{3g} (55)	0,0114	0,0344
			b _{2g} (56)	0,0154	-0,0080
			a _u (57)	0,0292	0,0088
			b _{1u} (58)	0,0191	0,0212
			b _{3g} (59)	0,0253	0,0050
			a _u (60)	0,0040	0,0252
			PDI _π	0,0519	0,0527
PDI	0,0611	0,0614			
Chrysene	C _{2h}	M6	a _u (45)	-0,0158	-0,0296
			b _g (48)	-0,0332	-0,0011
			a _u (52)	-0,0126	-0,0005
			b _g (55)	0,0062	0,0124
			a _u (56)	0,0265	0,0178
			b _g (57)	0,0313	0,0068
			b _g (58)	0,0306	0,0044
			a _u (59)	0,0260	0,0165
			a _u (60)	0,0106	0,0173
			PDI _π	0,0697	0,0439
PDI	0,0791	0,0521			
Pyrene	D _{2h}	M7	b _{1u} (39)	-0,0236	-0,0254
			b _{2g} (45)	-0,0327	0,0111
			b _{3g} (46)	0,0132	-0,0057
			b _{1u} (49)	0,0155	-0,0082
			a _u (50)	0,0338	0,0113
			b _{1u} (51)	0,0047	0,0391
			b _{2g} (52)	0,0291	0,0155
			b _{3g} (53)	0,0199	-0,0031
			PDI _π	0,0600	0,0346
			PDI	0,0691	0,0435

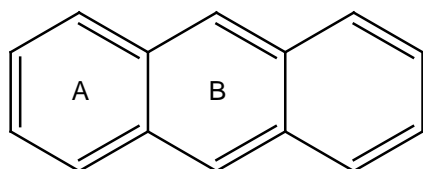
Coronene	D _{6h}	M8	a _{2u} (55)	-0,0144	-0,0234
			e _{1g} (61,62)	0,0196	0,0216
			e _{2u} (68,69)	0,0058	-0,0054
			a _{2u} (72)	0,0125	-0,0147
			b _{1g} (73)	0,0004	0,0000
			b _{2g} (74)	0,0162	0,0029
			e _{1g} (75,76)	0,0255	0,0514
			e _{2u} (77,78)	0,0177	-0,0092
			PDI _π	0,0441	0,0233
PDI	0,0531	0,0318			
Acenaphthalene	C _{2v}	M9	b ₁ (30)	-0,0358	
			a ₂ (35)	-0,0112	
			b ₁ (37)	0,0189	
			b ₁ (38)	0,0409	
			a ₂ (39)	0,0277	
			b ₁ (40)	0,0198	
			PDI _π	0,0604	
			PDI	0,0701	
Pyracylene	D _{2h}	M10	b _{1u} (34)	-0,0353	
			b _{2g} (38)	0,0226	
			b _{3g} (41)	-0,0109	
			b _{1u} (43)	-0,0063	
			a _u (44)	0,0257	
			b _{1u} (45)	0,0412	
			b _{2g} (46)	0,0208	
			PDI _π	0,0577	
PDI	0,0678				
Indacene	D _{2h}	M11	b _{1u} (29)	-0,0269	
			b _{2g} (35)	0,0165	
			b _{3g} (37)	0,0253	
			b _{1u} (38)	-0,0071	
			a _u (39)	-0,0121	
			b _{2g} (40)	0,0251	
			PDI _π	0,0208	
PDI	0,0303				



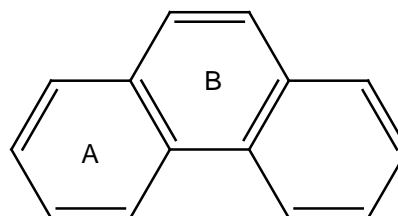
M1: Benzene



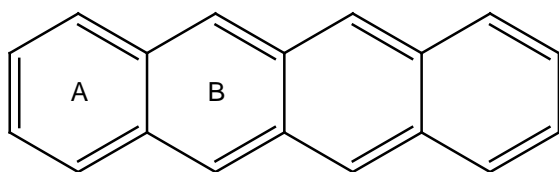
M2: Naphthalene



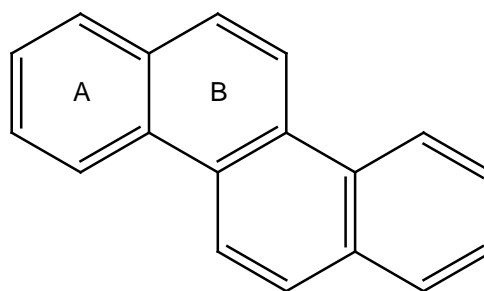
M3: Anthracene



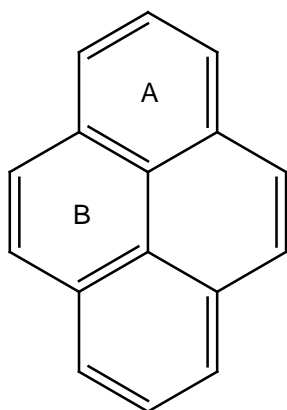
M4: Phenanthrene



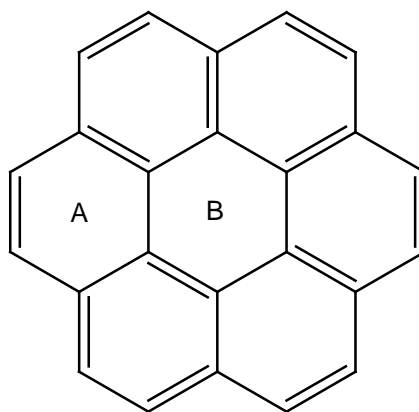
M5: Tetracene



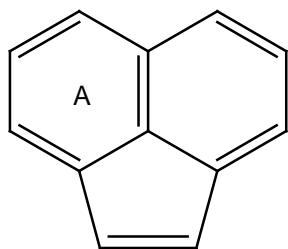
M6: Chrysene



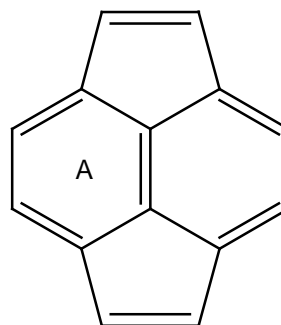
M7: Pyrene



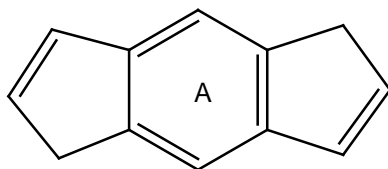
M8: Coronene



M9: Acenaphthalene



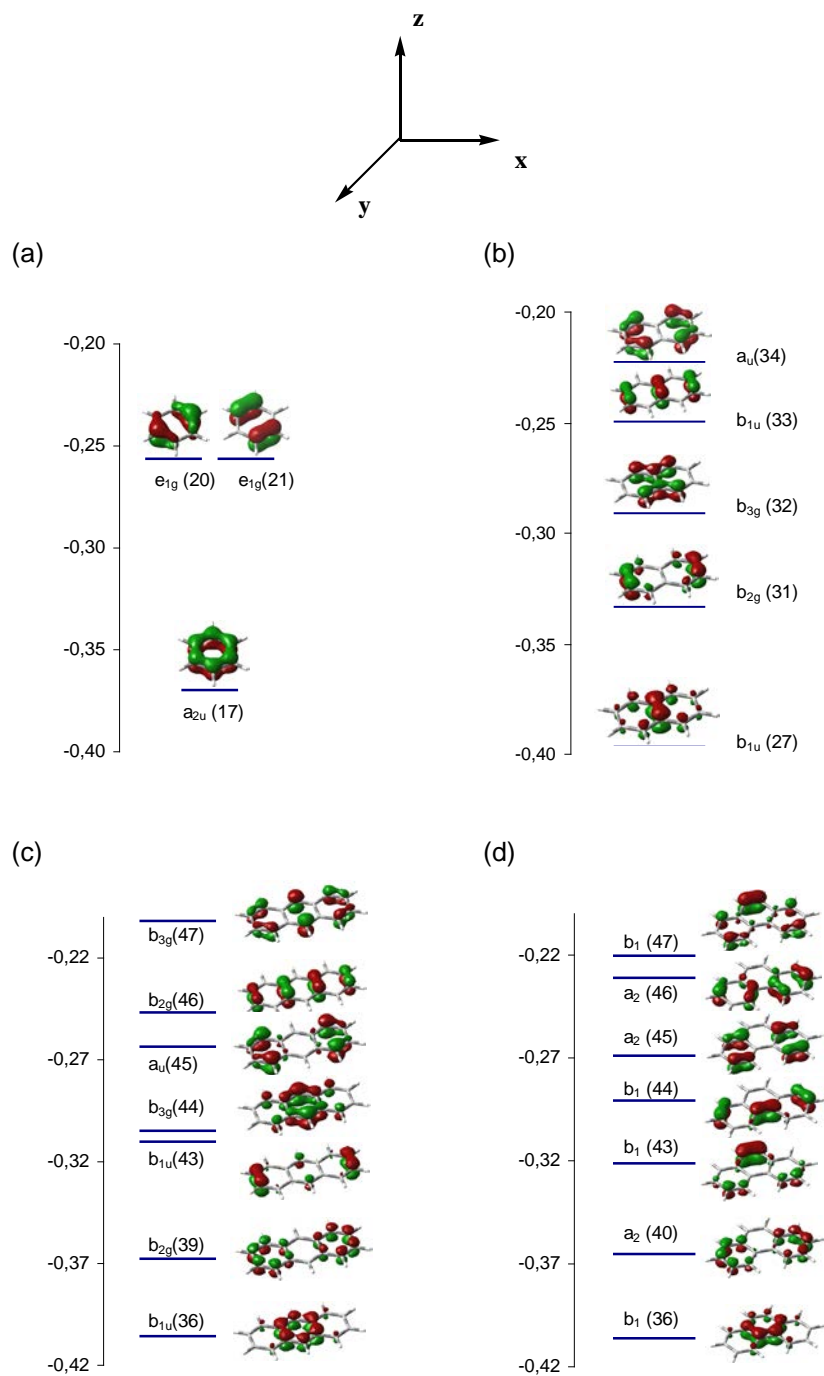
M10: Pyracylene



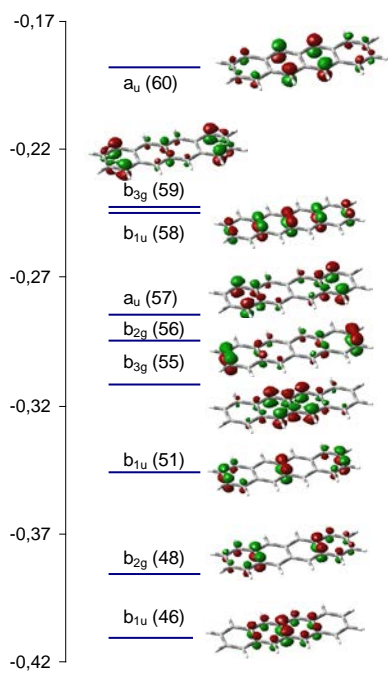
M11: Indacene

SCHEME 1

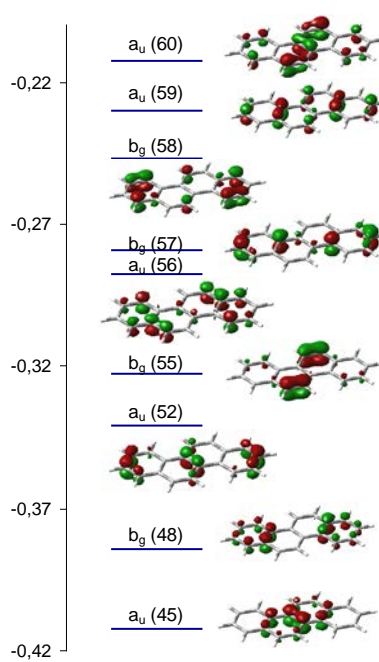
Figure 1.



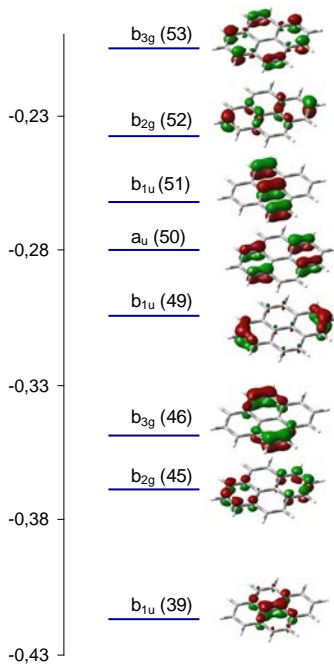
(e)



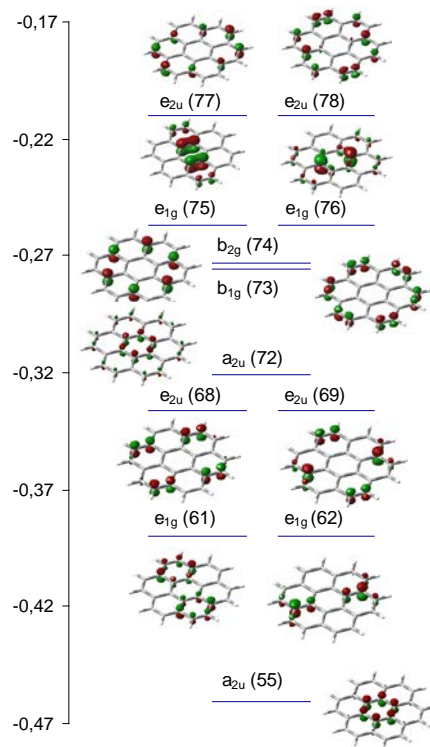
(f)



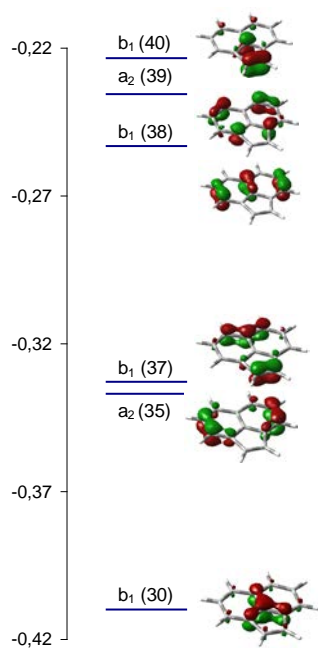
(g)



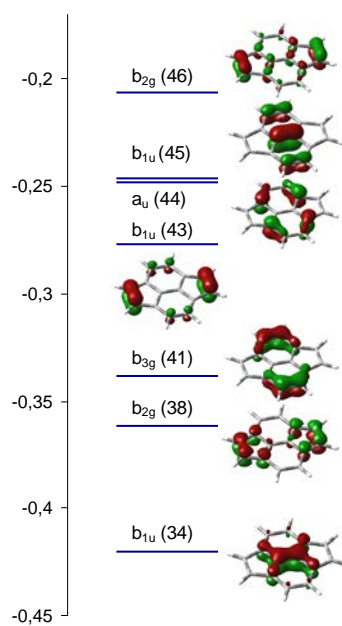
(h)



(i)



(j)



(k)

