Escherynes: Novel carbon allotropes with belt shapes

Ernesto Estrada [a,*], Yamil Simón-Manso [b]

[a] Department of Mathematics and Statistics, Institute of Complex Systems, University of Strathclyde, Glasgow G1 1XQ, UK
[b] Chemical and Biochemical Reference Data Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

ARTICLE INFO

ABSTRACT

A new family of belt-shaped carbon structures, called Escherynes, is theoretically proposed using the octadehydro annulene (ODA) skeleton as a building block. Several ODA rings are fused together and cyclized to form belt-structures. Two isomeric forms of the Escherynes are considered, Hückel and Möbius. We demonstrate that these compounds have thermodynamical and kinetic stabilities comparable to fullerenes. Density functional calculations of the structures revealed: (i) that Escherynes are relatively stable molecules, (ii) they have high affinity for lithium, (iii) large Möbius Escherynes (>60 atoms) are as stable as Hückel belts, and (iv) Möbius Escherynes display remarkable optical activity.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The discoveries of fullerenes [1], carbon nanotubes [2] and graphene [3] have increased dramatically the research interests on all-carbon materials [4,5]. Carbon-based materials have found applications in nanotechnology, materials science, electronics, optics and biotechnology, and occupy an important place in the development of emerging technologies [5–7]. In addition to their immense practical utility [5–7], a great motivation for the study of new carbon allotropes resides in the intrinsic molecular beauty [8] of these structures. It has been said that 'an impressive synthesis may be described as "beautiful" or "elegant" because of an appreciation of the molecule itself or the way it was created' [9]. Perhaps this has been the inspiration for the proposal of a few all-carbon materials with novel topologies, such as the metallic carbon [10], Haeckelites [11], and the recently proposed T-carbon compounds [12] among others. It is noteworthy that the structure of C_{60} fullerene was proposed as a theoretical 'conception' 15 years before its actual discovery [13,14]. Other beautiful and interesting structures that have captivated the imagination of chemists are the belt-shaped molecules [15]. Belt-shaped conjugated molecules can exist in two different configurations, namely twisted (Möbius) or untwisted (Hückel) belts. Recently, Guo et al. have shown that Möbius graphene strips with a zigzag edge behave as topological insulators [16]. Some fascinating belt-shaped conjugated molecules have been synthesized, such as the belt-shaped Möbius aromatic hydrocarbon reported by Ajami et al. [17], which confirms the theoretical predictions made by Heilbronner more than 40 years ago about the stability of Möbius twisted [4n]annulenes [18].

The search for new carbon allotropes and the search for new belt-shaped molecules constitute two of the basic pillars of the current work. The third pillar is the remarkable work developed in the area of acetylenic scaffolding [19–21], targeting exceptional molecular architectures and functional advanced materials. In this work we use the octadehydro[12]annulene (ODA) skeleton present in the fully planar π-conjugated per(silylethynylated)octadehydro[12]annulenes (PSOA) [22] as the basis for building new carbon allotropes. This work is structured as follows: Section 2, explains the basis of our molecular design for the new carbon allotropes. In Section 3 we provided a short overview of our computational methods and the strengths and limitations of our calculations. Section 4 shows the calculated properties, possible applications and the discussion of the results. Finally, Section 5 offers a brief conclusion.

2. Molecular design

We proceed by fusing together $m \geqslant 3$ ODA cycles forming a planar network as illustrated in Figure 1. Then by gluing together the ends of this strip we obtain the new carbon allotropes with belt-shapes of the Hückel type. We note that the Hückel isomer of C_{60} was depicted by Tykwinski et al. [23] as a challenging molecular target to be synthesized, and some precursors of it were already obtained in that work. Alternatively, we give a half twist to one of the cycles at the end of the planar network before fusing them in order to obtain Möbius versions of the carbon allotropes (see Figure 1). Using the building principles outlined in Figure 1 we construct the structures of the belt-shaped carbon allotropes, Hückel (H) isomers and their Möbius (M) versions, having 30 to 90 carbon atoms. The Möbius molecules designed in this Letter resemble some of the well-known pictures of the Dutch artist Escher who has been an inspirational artist for mathematicians and scientists.

* Corresponding author. Fax: +44 0 141 548 3345.
E-mail address: ernesto.estrada@strath.ac.uk (E. Estrada).
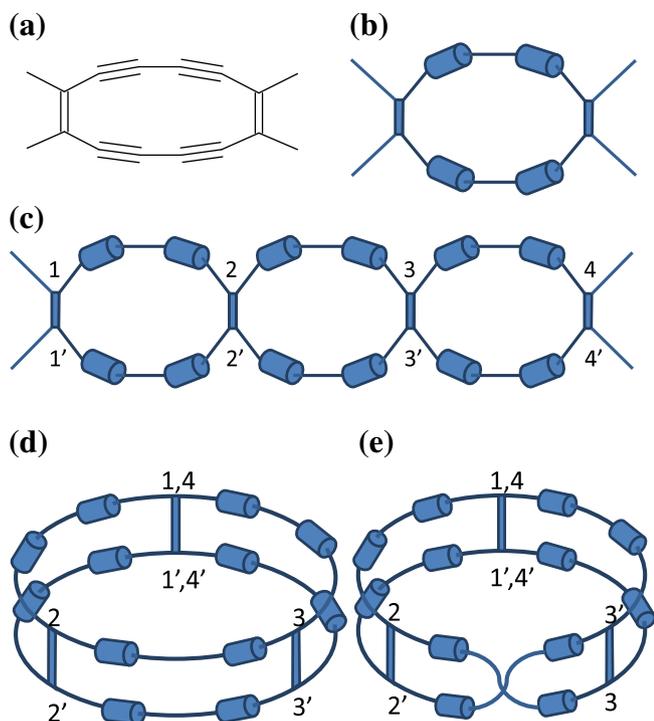
Figure 1. Illustration of the structures of ODA acetylenic scaffolding of Diederich (a) and its pictorial representation in which double bonds are replaced by vertical bars and triples bonds by solid cylinders (b). Trimeric structure (c) used to illustrate the formation of belt-shapes Escherynes with Hückel (d) and Möbius (e) belt shapes.

Consequently, we propose to name this new family of molecules as 'Escherynes'.

3. Computational method

We employ first-principles methods based on the density functional theory (DFT) throughout this work, in particular the very well-known hybrid B3LYP model. It combines several desirable characteristics, such as favorable scaling behavior with system size, good energies, correlated wave function, etc. Regarding these calculations, it is worth mentioning that B3LYP has been reported as being biased in favor of cumulenic over acetylenic structures [24]. However, the energy differences between both structures are very small and the results still remain controversial (see Ref. [25] for further details).

We optimize all structures presented in this Letter using the program GAUSSIAN09 [26] at the B3LYP/3−21G∗ computational level. Frequency calculations at the same computational level were used to check that the optimal structures were true minima. Binding energies calculations include basis set superposition error (BSSE) carried out with the counterpoise method. The binding energy is defined as $BE = [nE(atom) − E_{total}(molecule)]/n$ where $E_{total}(molecule)$ is the total energy of the molecule, e.g., Escheryne or fullerene, and $E(atom)$ is the average energy of a free carbon atom obtained with the basis set of the molecule. The input geometries for fullerenes, C_{60} and C_{70} are I_h and D_{5h}, respectively, but no symmetry constraints are used for the optimization.

4. Results and discussion

In Figure 2 we plot the binding energies (BE) per atom for the H and M isomers relative to fullerenes of the same number of carbon atoms. (Although, fullerenes are structurally very different to belts, they are also the most stable form of carbon molecules experimen-
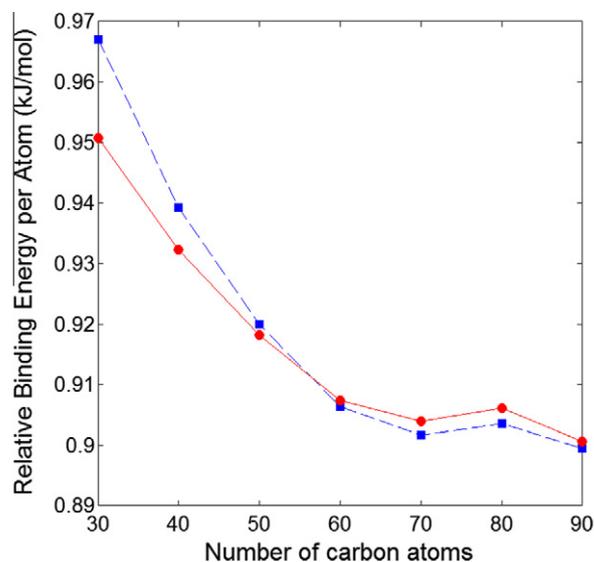
Figure 2. Binding energies per atom (kJ/mol) relative to those of analogous fullerenes for the Möbius (full circles) and Hückel (full squares) belt-shaped structures as a function of the number of carbon atoms in the belt.

tally known and the best reference molecules to test the thermodynamic stability.) It can be seen that both H and M isomer series have binding energies which are larger, but of comparable magnitude, to those of the corresponding fullerenes. The smallest H structures are more stable than the M structures. However, when the number of carbon atoms is 60 there is a transition in the relative stability of H and M structures. From this point on, M isomers seems to be more stable than the H isomers. A large calculation, recommended by a reviewer, on the H and M structures of 130 atoms (not shown in Figure 2) shows that the crossing of the H and M binding energies in Figure 2 has no physical meaning. The basis set was rather small to draw a definite conclusion about the relative stability of the H and M isomers and the calculations are too expensive to repeat it with a bigger basis set. However, we can assure that the energies are very close for structures with more than 60 atoms. In fact, for the isomers of 130 atoms the H-structure (BE = 576.3 kJ/mol) is slightly more stable than the M-structure (573.2 kJ/mol). Table 1 shows the bond distances for the Escherynes with 60 atoms following the bond description of Figure 1a. The typical distances reported for single, double and triple bonds are about 154, 134, and 120 pm, respectively. Thus, the bond structure for both isomers seems to be more delocalized than the simple scheme shown in Figure 1a.

If we consider the 'wire' formed by the single and triple bonds only (C—C≡C—C≡C—C) we can observe a larger bond-length and bond-order equalizations in this region of Escherynes than in that of PSOA. This effect indicates a large electronic conjugation along this wire in Escherynes, which is particularly pronounced in the M isomers. In this case, the double bonds perpendicular to

Table 1
Bond distances (pm) for the Escherynes with 60 carbon atoms. (The assignment of single, double and triple bonds follows the bond description of Figure 1a for ODA.)

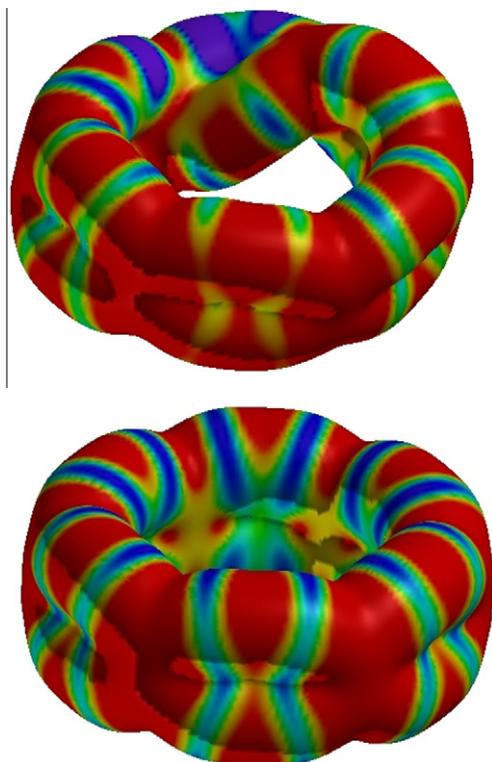| Molecule	Bond distances (pm)[a]		
	C—C	C=C	C≡C
C_{60} (Hückel)	133 (12)	146 (6)	123 (24)
	139 (24)		
C_{60} (Möbius)	131 (12)	154 (6)	(24)
	136 (24)		

[a] B3lYP/3−21 g calculations.

Table 2
Energy difference (kJ/mol) between the lowest and highest molecular orbital (HOMO–LUMO gap) for Esherynes and Fullerenes with different number of atoms.

No. of atoms	HOMO–LUMO Gap (kJ/mol)		
	Hückel	Möbius	Fullerene
30	104.3	147.3	64.6
40	158.8	123.7	147.4
50	77.2	104.3	158.6
60	99.9	111.8	294.8
70	60.2	69.3	270.5
80	79.8	67.8	54.1
90	66.4	55.7	167.8

this wire increase 10% their bond length respect to that in ODA, transforming them into single bonds. Both types of single bonds (=C—C≡ and ≡C—C≡) are shortened by 4%, while the triple bonds are enlarged in the same proportion. These effects make these molecules electronically more stable and more flexible, which contribute to their global thermodynamic stability as reflected by their BEs.

The analysis of the frontier molecular orbitals (MO) of the H Escheryne C_{60} shows that there are very narrow peaks near to the highest occupied molecular orbital (HOMO). The symmetry-breaking in the M structure yields a set of nondegenerated orbitals and broadening of the frontier MO peaks with frontier orbitals more delocalized in the region opposite to the twist. The gap between the HOMO and lowest unoccupied MO (LUMO) has been widely used as a criterion of kinetic stability of organic molecules in general and of carbon allotropes in particular [27]. A relatively large HOMO–LUMO gap implies high kinetic stability due to the difficulties for adding new electrons to a high energy LUMO as well as to extract electrons from a low energy HOMO. As a consequence,

activated complexes with compounds having very large HOMO–LUMO gaps are quite difficult to form. Using a weighted HOMO–LUMO gap [28] as a criterion of kinetic stability we have found that Escherynes with 40 (M), 50, 60, 70 and 90 atoms are kinetically more reactive than similar fullerenes (see Table 2).

For C_{30} and C_{80} both types of Escherynes are kinetically more stable than the corresponding fullerenes. In general, H isomers are kinetically more stable if the number of carbon atoms is 40, 60 or 80. In the case of M structures it can be seen that C_{60} is kinetically the most stable molecule and it is even more stable than the H analogous. The previous analysis of the thermodynamic and kinetic stability of Escherynes makes these molecules tick in most of the boxes required for them to be viable in a chemical lab.

Although we are far from guessing all possible applications of the new belt-shaped molecules designed in this Letter we can foresee some of them. In particular, the new molecules can act as host–guest interaction materials based on π stacking or electrostatic forces. We have built the electrostatic potential maps (EPM) for C_{60} Escherynes by mapping the potential onto the electron density surface (0.002 e/bohr3) evaluated at B3LYP//6–31G∗ level. According to the EPM for the C_{60} Escherynes (see Figure 3) we can infer a high affinity for alkali metals in the case of both types of Escherynes. Our calculations indicate a strong interaction of Li atoms with Escheryne molecules. This kind of 'lithium storage' complexes has been previously reported for carbon molecules with different remarkable applications [29,30]. Complexes between fullerenes and other alkali metals – 'fullerides' – have also been reported as superconductor materials [31]. The $LiC_{60}(H)$ and $LiC_{60}(M)$ com-
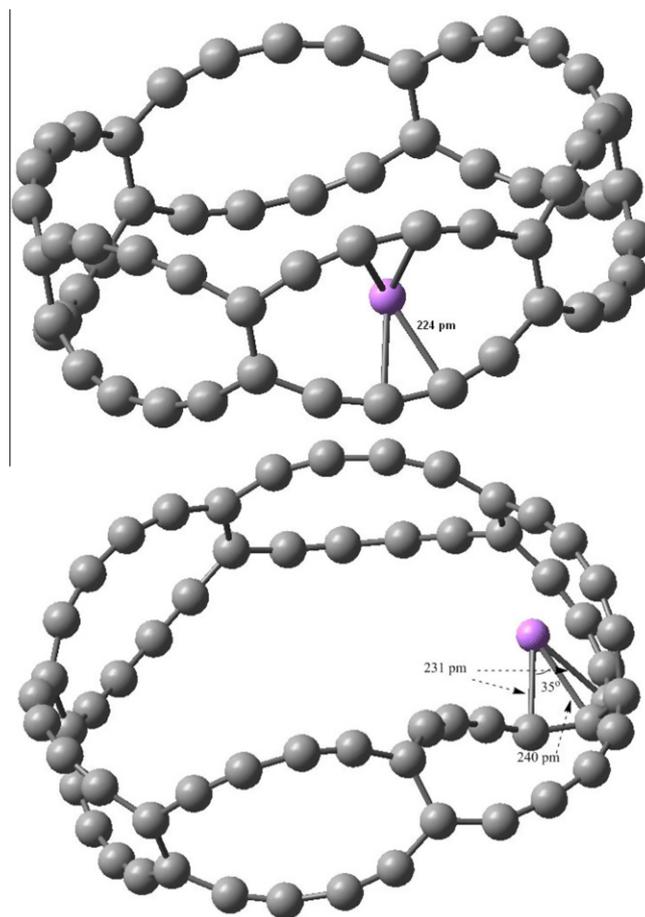

Figure 3. Mapping of the electrostatic potentials of the C_{60} isomers (red: positive, blue: negative) onto the electron density surfaces (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Figure 4. Illustration of the complexes formed between H (top) and M (bottom) C_{60} Escherynes with Li atom and some of the geometric parameters of the complexes.
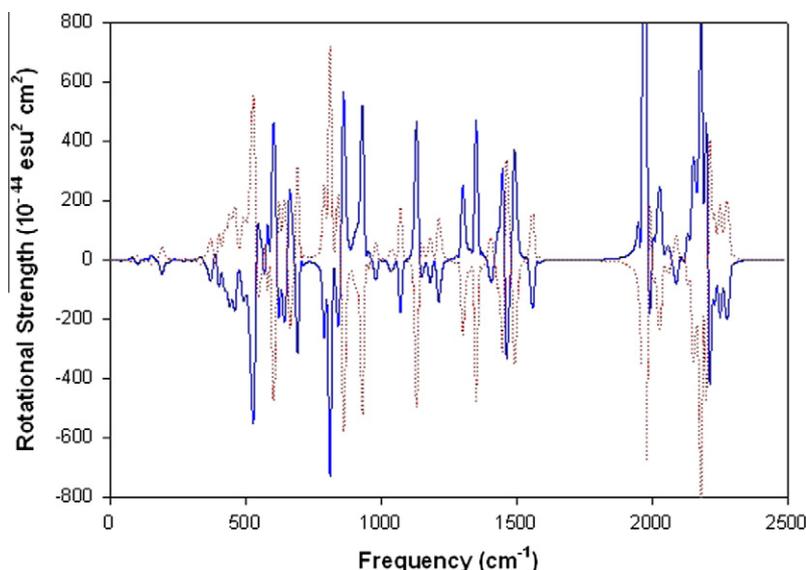
Figure 5. Vibrational circular dichroism spectra of the two enantiomers of C_{60} Escheryne with Möbius topology.

plexes have BE equal to 2.95 and 3.10 eV, respectively, which indicates that these complexes are significantly more stable than the one formed by C_{60} fullerene and Li, which has a BE = 1.52 eV [32]. In $LiC_{60}(H)$ the Li atom is positioned at the center of the interior side (endohedral doping) of the ODA rings at 224 pm from the carbon atoms (see Figure 4). Other complexes of the type Li_nC_{60} can also be formed but they have not been considered here. In $LiC_{60}(M)$ the metal is positioned on the twist at 231 pm from the closest carbon atom (see Figure 4) also forming an endohedral complex. The closest C–Li distance found by Chandrakumar and Ghosh [32] in similar calculations for fullerene-Li complexes is 226.8 pm, which is very similar to the ones reported here.

We can infer the existence of both diamagnetic and paramagnetic ring currents in the belts of Escheryne molecules. The H structures could be seen as 'gigantic' benzene rings [33], which suggest an enhanced diamagnetism due to the huge area available for the current loop of the π electrons. On the other hand, it has been predicted for M cyclacenes that the twist travels around the belt inducing a magnetic current [34], which could also be expected to take place in the case of the M Escheryne isomers.

An interesting characteristic of M strips is that they can display topological chirality. In order to investigate the optical activity of M Escherynes we have conducted first-principle calculations of the circular dichroism (CD) spectra of the C_{60} Escherynes. CD is a chiroptical technique that measures the optical activity of chiral compounds by detecting differences in absorbance between right and left circularly polarized light. We used the optimized geometries to evaluate the optical rotations $[\alpha]_D$ and the vibrational CD spectra. Our calculations show no optical activity for H C_{60} isomer ($[\alpha]_D$ = −4.84 degrees $[dm \times g/cm^3]^{-1}$), but a remarkable one for the chiral M C_{60} Escheryne isomers ($[\alpha]_D$ = −12453.56 degrees $[dm \times g/cm^3]^{-1}$). Figure 5 shows the vibrational CD spectra of both enantiomers, where it can be seen that the M structure exhibits a strong optical activity. The symmetry observed in these spectra is the result of the lack of much conformational flexibility in the enantiomeric forms of M C_{60} Escherynes. It must be noticed that this optical activity can be modulated by varying the number of twists in the M bands.

It has been remarked that the first step in any synthesis is to identify a target structure on the basis of the mechanical, optical or binding properties of the compound in question [35]. In this work we have completed this research cycle by identifying Esche-

ryne structures which are stable and display remarkable electronic, magnetic and optical properties. Further retrosynthetic analysis may identify the best routes for their synthesis. We are confident that the current development in acetylenic chemistry is enough for targeting these compounds in a wet lab. Work is in progress on many reasonable extensions of this letter, such as the design and calculation of Esheryne structures with width greater than 1 and some interesting 3D structures. It includes also the re-parametrization of an effective semi-empirical method for computing the band structure of Escherynes and their derivatives.

5. Conclusion

In this Letter we report the conception of a new family of carbon allotropes: *Escherynes*. Our *ab initio* calculations reveal: (i) that Escherynes are relatively stable molecules, (ii) they form 'lithium storage' complexes more stable than similar complexes formed by fullerenes, (iii) large Escherynes (>60 atoms) with Möbius structure are as stable as normal belt structures and (iv) Möbius Escherynes display remarkable optical activity.

Acknowledgements

References

[1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.E. Curl, R.E. Smalley, Nature 318 (1985) 162.
[2] S. Iijima, Nature 354 (1991) 56.
[3] K.S. Novoselov, A. Geim, S.V. Morozov, D. Jian, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science 306 (2004) 666.
[4] M. Terrones, H. Terrones, Phil. Trans. R. Soc. Lond. A 361 (2003) 2789.
[5] A. Hirsch, Nature Mat. 9 (2010) 868.
[6] J. Opatkiewicz, M.C. LeMieux, Z. Bao, ACS Nano 4 (2010) 2975.
[7] A.H.C. Neto, Mater. Today 13 (2010) 12.
[8] R. Hoffmann, Am. Sci. 76 (1988) 389.
[9] Beauties of synthesis. How to excite an organic chemist. Nature 2006, 443 (2006) 1.
[10] R. Hoffmann, T. Hughbanks, M. Kertész, J. Amer. Chem. Soc. 105 (1983) 4831.
[11] H. Terrones, M. Terrones, E. Hernández, N. Grobert, J.-C. Charlier, P.J. Ajayan, Phys. Rev. Lett. 84 (2000) 17169.

[12] X.-L. Sheng, Q.-B. Yan, F. Ye, Q.-R. Zheng, G. Su, Phys. Rev. Lett. 106 (2011) 155703.
[13] E. Osawa, Kagaku (Kyoto) 25 (1970) 854.
[14] R.E. Curl, R.E. Smalley, H.W. Kroto, S. O'Brien, J.R. Heath, J. Mol. Graph. Model. 19 (2001) 185.
[15] R. Herges, Chem. Rev. 106 (2006) 482042.
[16] Z.L. Guo, Z.R. Gong, H. Dong, C.P. Sun, Phys. Rev. B 80 (2009) 195310.
[17] D. Ajami, O. Oeckler, A. Simon, R. Herges, Nature 426 (2003) 819.
[18] E. Heilbronner, Tetrahedron Lett. 1964 (1923) 29.
[19] F. Diederich, Chem. Comm. (2001) 219.
[20] F. Diederich, M. Kivala, Adv. Mater. 22 (2010) 803.
[21] U.H.F. Bunz, Y. Rubin, Y. Tobe, Chem. Soc. Rev. 28 (1999) 107.
[22] J. Anthony, C.B. Knobler, F. Diederich, Angew. Chem. Int. Ed. 32 (1993) 406.
[23] R.R. Tykwinski, F. Diederich, V. Gramlich, P. Seiler, Helv. Chim. Acta 79 (1996) 634.
[24] D. Plattner, K.N. Houk, J. Am. Chem. Soc. 117 (1995) 4405.
[25] S. Arulmozhiraja, T. Ohno, J. Chem. Phys. 128 (2008) 114301.
[26] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
[27] P. Fowler, Nature 350 (1991) 20.
[28] J. Aihara, Theor. Chem. Acc. 102 (1999) 134.
[29] N.A. Kaskhedikar, J. Maier, Adv. Mater. 21 (2009) 2664.
[30] A. V. Zabula, A. S. Filatov, S. N. Spisak, A. Yu. Rogachev, R. A. Petrukhina, *Science* 333 (2011) 1008.
[31] O. Gunnarsson, Rev. Mod. Phys. 69 (1997) 575.
[32] K.R.S. Chandrakumar, S.K. Ghosh, Nano Lett. 8 (2008) 13.
[33] J.A.N.F. Gomes, Chem. Rev. 101 (2001) 1349.
[34] M.C. dos Santos, F. Alvarez, Chem. Phys. Lett. 471 (2009) 276.
[35] N.M. Jenny, M. Mayor, T.R. Eaton, Eur. J. Org. Chem. (2011) 4965.