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# Origin of the Nonplanarity of Tetrafluoro Cyclobutadiene, $C_4F_4$

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Density functional theory as well as Møller-Plesset investigations has been carried out on tetrafluoro cyclobutadiene, $C_4F_4$, to explore the origin of its nonplanarity. Although Petersson et al. (Petersson, E. J.; Fanuele, J. C.; Nimlos, M. R.; Lemal, D. M.; Ellison, G. B.; Radziszewski, J. G. *J. Am. Chem. Soc.* **1997**, *119*, 11122−11123) had earlier predicted a nonplanar geometry of this compound on the basis of spectral and bond orbital analysis, the explanation of the same from a more fundamental point of view is still missing. In the present study, we provide a heuristic explanation for the origin of nonplanarity of $C_4F_4$. The two major driving forces behind this nonplanar geometry are the unusual aromaticity of this cyclic homoatomic $4\pi$ electron system and the second-order Jahn−Teller effect (SOJTE). These driving forces can well be explained by various energy and density parameters and also by nucleus-independent chemical shift (NICS) values. Aromaticity of a cyclic homoatomic $4\pi$ electron system is quite remarkable. The enhancement of $\pi$-delocalization as evidenced from molecular orbital analysis may be attributed to s-$p_\pi$ mixing in nonplanar $C_4F_4$.

## Introduction

The discovery of tetrafluoro cyclobutadiene, $C_4F_4$, highlights striking differences with its hydrocarbon analog, cyclobutadiene ($C_4H_4$). While $C_4H_4$ is planar, remarkably, its tetrafluoro derivative has nonplanar geometry. The first direct evidence for the existence of this compound was given by Petersson et al.[1] On the basis of the analysis of infrared spectrum and linear dichroism, they suggested a nonplanar geometry for $C_4F_4$. Moreover, they also took initiative to provide a theoretical justification of their findings only with the help of natural atomic orbital (NAO) and natural bond orbital (NBO) analysis. Albeit there have been a lot of novel and high-level investigations on cyclobutadiene[2−6] and some of its stable derivatives,[7−9] no theoretical investigations on the origin of nonplanarity of $C_4F_4$ have been performed.

In this work, we report a heuristic explanation on the origin of nonplanarity of this tetrafluoro derivative from a more fundamental point of view. In the present scenario, density functional theory (DFT) as well as Møller-Plesset perturbation (MP2)[10] techniques are called upon to unfold the mystery of $C_4F_4$. The investigation suggests that unusual aromaticity of nonplanar $C_4F_4$ in spite of its $4\pi$ electrons along with second-order Jahn−Teller effect (SOJTE)[11] are the major driving forces behind its nonplanarity. To provide an unequivocal description of the aforesaid stabilization mechanism, several factors such as nucleus-independent chemical shift (NICS), electron density ($\rho$), laplacian of electron density ($\nabla^2\rho$), current density, formation energy, molecular orbital analysis, $\sigma-\pi$ energy ($E_\sigma$ and $E_\pi$), and other energy parameters including electron correlation ($E_C$) have been taken into account. Remarkably, the highest occupied molecular orbital (HOMO) of nonplanar $C_4F_4$ provides a clear indication of $\pi$-delocalization around the ring carbons.

## Computational Details

All the calculations have been implemented in the GAUSSIAN 03 package.[12] The quantum chemical calculations performed here involve spin-restricted calculations under DFT and MP2 scheme except while calculating $E_\sigma$ (spin-polarized). Geometry of $C_4F_4$ has been optimized using B3LYP[13] type exchange-correlation functional and 6-311++G(d, p) basis set. The accuracy of the optimized structure is further confirmed by frequency calculations using the same functional and basis set. Optimizations have also been performed at MP2 level using 6-311++G(d,p) basis set. The NICS calculations are carried out using gauge-independent atomic orbital (giao) method whereas the density and the laplacian calculations have been performed by implementing cube = density and cube = laplacian keywords, respectively. The current density mappings and all the molecular orbital analyses have been done using proper checkpoint files.[14] For explicit calculation of the energy parameters of interest given in Figure 6, extralinks = l608 keyword is used. Both geometry optimizations and NICS calculations have also been performed on several relevant systems (see ref 14). All the above energy and density calculations are carried out within DFT scheme using the same basis set as in geometry optimization.

## Results and Discussion

Although the geometry of $C_4F_4$ has been optimized using both B3LYP type exchange-correlation functional and MP2 technique, the former geometry is presented in Figure 1 since it outperforms the latter one.[14] A side view of $C_4F_4$ is given in Figure 1b to clearly indicate the nonplanarity of this tetrafluoro derivative. A bond length alteration (BLA) of 0.21 Å (1.54 Å − 1.33 Å) is observed for the nonplanar geometry while that of planar geometry is 0.27 Å (1.59 Å − 1.32 Å).

The molecular orbital analysis, particularly the HOMO of tetrafluoro cyclobutadiene as given in Figure 2a, exemplifies complete $\pi$-delocalization around the ring carbons whereas the

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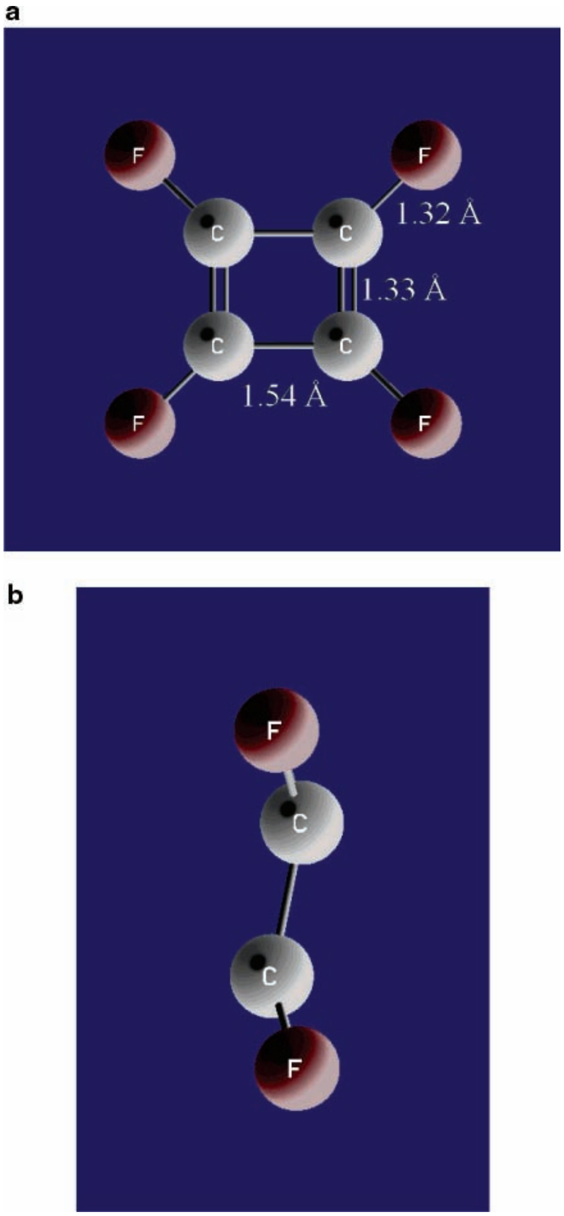

**Figure 1.** B3LYP optimized geometry of $C_4F_4$ showing (a) bond lengths reported in Å and (b) a side view clearly showing nonplanarity.

HOMO of its hydrocarbon analog, $C_4H_4$ (Figure 2b), has its lobes centered only on the C═C double-bonded carbon atoms. The effective delocalization in nonplanar geometry is further justifiedby the formation energy analysis.[14] The formation energy can be represented as

$$\Delta E_F = E_F\,(C_nX_n) - \frac{n}{2}E_F(C_2X_2)$$

where $n$ is the number of atoms and X = H and F in this case. While negative formation energy (−57.456 kcal/mol) is observed for nonplanar $C_4F_4$, its hydrocarbon analogue, $C_4H_4$, has a positive value (2.446 kcal/mol). This is a clear indication of the stabilization of $C_4F_4$ due to resonance. As a consequence, natural inquisition strives one to face the challenging question of whether or not $C_4F_4$ in the nonplanar configuration is aromatic.

Of the several criterions used for assessing aromaticity[15−17] in a molecule, magnetic criterions are the ones that are closely related because of their dependence on the induced ring currents associated with cyclic electron delocalization. NICS is one of

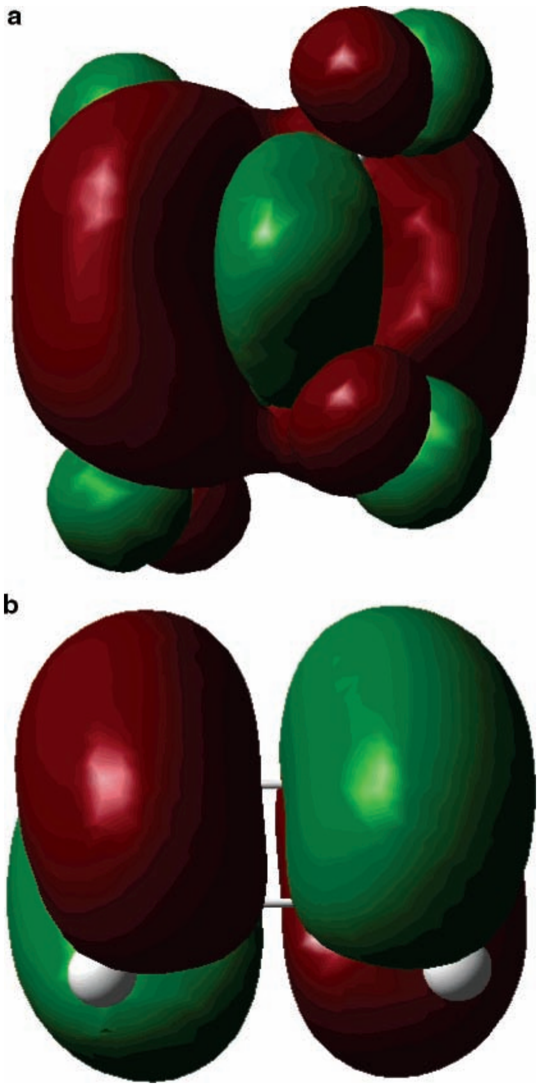

**Figure 2.** Highest occupied molecular orbital (HOMO) of (a) nonplanar $C_4F_4$ showing complete $\pi$-delocalization around the ring carbons and (b) planar $C_4H_4$.

the ways that has gained a lot of importance owing to its easy computability after its introduction by Schyleyer et al.[18] It is computed as negative magnetic shielding at some selected points in space as for example, at the ring centroid (RC). Albeit a BLA of 0.21 Å (1.54 Å − 1.33 Å) is observed for nonplanar geometry, a high negative NICS value at RC indicates the presence of substantial degree of aromaticity in $C_4F_4$.

To elucidate the aromatic character of nonplanar $C_4F_4$, a thorough study on NICS, current density, $\rho$, and $\nabla^2\rho$ along with the various energy parameters of interest has been performed by changing the dihedral angle ($\theta_D$), i.e., approaching from the optimized nonplanar geometry ($\Delta\theta_D = 0°$) to a planar one. All the values have been given in a tabular form.[14] Figure 3 depicts the variation of NICS(0) calculated at RC against $\Delta\theta_D$. Apart from the usual NICS(0), more convincing NICS$(1)_{zz}$ (the $zz$ component of the magnetic shielding tensor calculated at 1 Å above RC)[16] has also been calculated and is shown in Figure 3 along with NICS(0). Both the values follow an increasing trend as one approaches a planar geometry. This elucidates aromatic behavior in nonplanar $C_4F_4$ and justifies our prediction about the origin of its nonplanarity. Moreover, the NICS$(1)_{zz}$ values also support our view that aromaticity in $C_4F_4$ comes from $\pi$-electrons. The effect of incorporation of fluorine in cyclobutadiene results in a significant change in the NICS(0) (33.6458

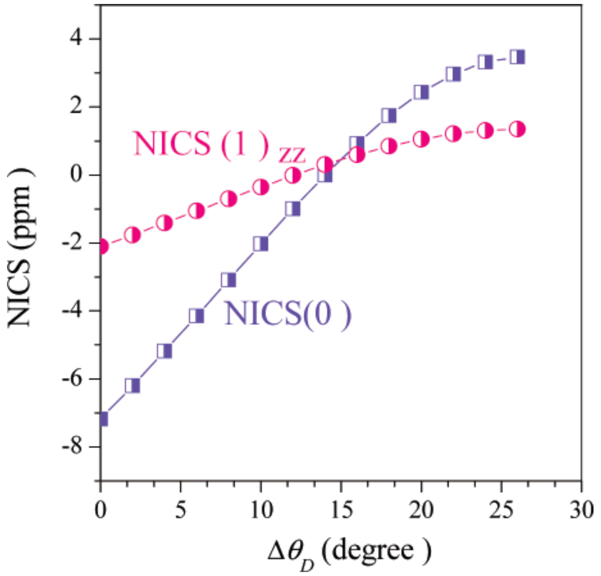

**Figure 3.** Variation of NICS(0) and NICS(1)$_{zz}$ against change in the dihedral angle, $\Delta\theta_D$.

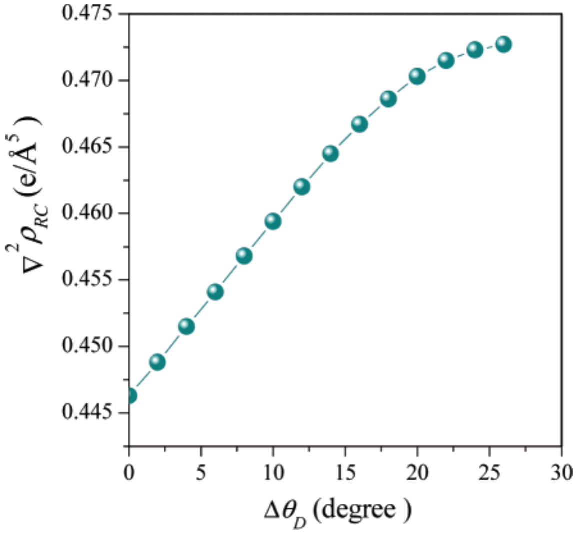

**Figure 4.** Variation of $\nabla^2\rho_{RC}$ against change in the dihedral angle, $\Delta\theta_D$.

ppm)[14] values. On the other hand, the incorporation of six fluorine atoms in benzene results in a change of 10.2233 ppm.[14] The Mulliken charge analysis[14] reveals that charge transfer from carbon (C) to fluorine (F) atoms in nonplanar $C_4F_4$ is much less than that in $C_6F_6$. Thus, the large change observed in the NICS(0) values of $C_4F_4$ compared to $C_6F_6$ may be attributed to the chair-like nonplanar arrangement of the F atoms in $C_4F_4$.

As we proceed from a nonplanar geometry ($\Delta\theta_D = 0°$) to a planar one, the charge transfer from carbon to fluorine increases as evident from Mulliken charge analysis[14] which results in gradual decrease of $\rho$ at RC. Likewise, on increasing $\Delta\theta_D$, the effective $\pi$-delocalization in the ring gradually decreases (this is evident from the evolution of HOMO of $C_4F_4$ with change in $\theta_D$[14]**)** that leads to inhomogenity of the electron cloud in the system, or in other words, the system is electronically more and more homogeneous as we approach nonplanar geometry. This inhomogenity is a consequence of an increase in $\nabla^2\rho$ value. Figure 4 reflects the variation of this $\nabla^2\rho$ calculated at RC against $\Delta\theta_D$. It follows similar trend as that of the NICS values, i.e., it increases with increase in $\Delta\theta_D$.

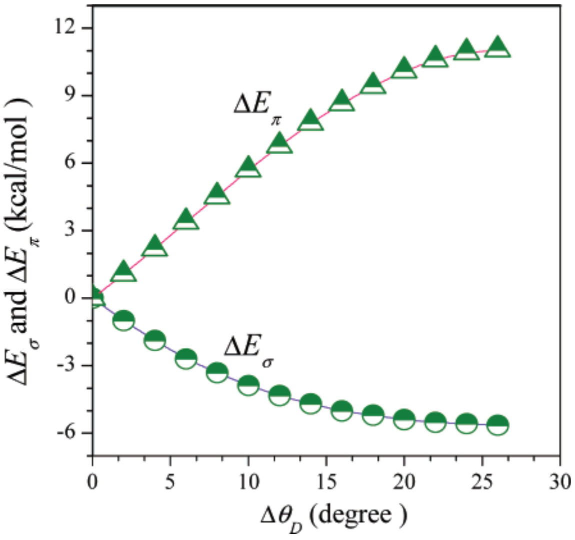

**Figure 5.** Variation of $\Delta E_\sigma$ and $\Delta E_\pi$ against change in the dihedral angle, $\Delta\theta_D$.

The analysis of the $\sigma-\pi$ energy is also one of the major factors in determining aromaticity in a molecule. In the present study since the molecule is nonplanar, we follow the high-spin method of $\sigma-\pi$ separation.[19] In this method, the $\pi$ energy, $E_\pi$, is calculated using the relation, $E_\pi = E_{GS} - E_{HS}$, where $E_{GS}$ is the ground-state energy and $E_{HS}$ is the energy of the high-spin (H.S.) state with quintet spin multiplicity (in case of $4\pi$ electronic system, $C_4F_4$). $E_{HS}$ actually represents the energy of the $\sigma$ frame, $E_\sigma$, with some exchange repulsions. A vivid description for the calculation of $\sigma-\pi$ energies is given in ref 14. Figure 5 illustrates the dependence of $\Delta E_\sigma$ and $\Delta E_\pi$ on the structural changes. $\Delta E_{GS}$ and $\Delta E_\sigma$ is calculated by setting the corresponding energies of the most stable structure (nonplanar geometry) to zero and the rest of the values are calibrated with respect to those. On the other hand, $\Delta E_\pi$ is calculated using the relation, $\Delta E_\pi = \Delta E_{GS} - \Delta E_\sigma$. It is evident from Figure 5 that as $\Delta\theta_D$ becomes smaller, the $\Delta E_\sigma$ value gradually increases whereas a reverse trend is observed for $\Delta E_\pi$ value. Earlier, Petersson et al.[1] have suggested pyramidalization of the carbon atoms of $C_4F_4$ resulting in the attenuation of the cyclic conjugation in the $\pi$ system. Remarkably, the present study predicts an opposite trend (as evident from the NICS, current density, $\rho$, and $\nabla^2\rho$ values and also from the molecular orbital analysis,[14] particularly HOMO of nonplanar $C_4F_4$). Instead of an attenuation, maximum $\pi$-delocalization has been observed in the nonplanar geometry. The enhancement of this delocalization may be attributed because of the mixing of s orbitals (4.505%) with $p_\pi$ orbitals (95.355%) and is responsible for the aromatic nature of $C_4F_4$.[14]

Apart from the $\sigma-\pi$ energies, there are several other energy parameters which are essential in explaining the origin of the nonplanar geometry of our compound of interest, $C_4F_4$. These are kinetic enegy ($E_{KE}$), nucleus−electron interaction energy ($E_{n-e}$), electron−electron repulsion energy ($E_{e-e}$), nucleus−nucleus interaction energy ($E_{n-n}$), exchange energy ($E_X$), and correlation energy ($E_C$). It has been observed while extracting the value for different energy parameters that the B3LYP results, particularly, $E_{KE}$ and $E_C$ values, do not follow a definite trend. However, the MP2 calculations done on the B3LYP optimized geometry give us quite satisfactory results.[14] The relevant changes in stabilization ($\Delta E_S$) and destabilization ($\Delta E_{DS}$) energies shown in Figure 6 are the MP2 results.

All the energy parameters of interest for the nonplanar geometry are set to zero and the same for other geometries are calibrated with respect to those values. In the inset of Figure 6, the net stabilization curve is shown which is taken to be the

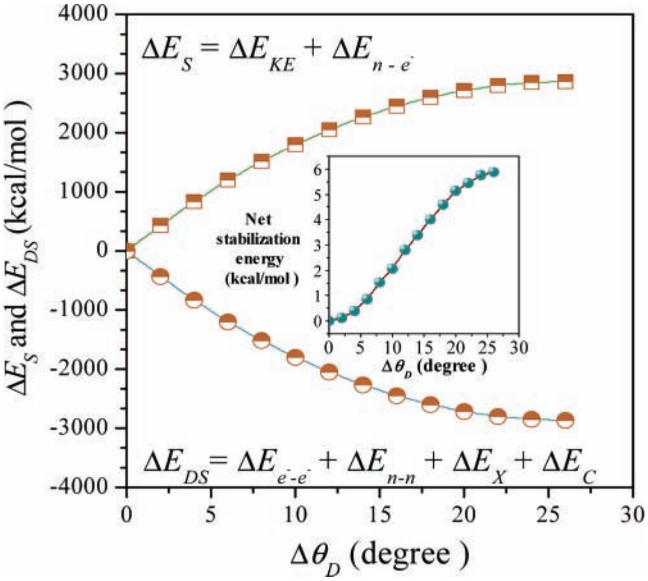

**Figure 6.** Variation of $\Delta E_S$ ($\Delta E_S = \Delta E_{KE} + \Delta E_{n-e}$) and $\Delta E_{DS}$ ($\Delta E_{DS} = \Delta E_{e-e} + \Delta E_{n-n} + \Delta E_X + \Delta E_C$) against $\Delta\theta_D$ (change in the dihedral angle). Inset: Variation of net stabilization energy against $\Delta\theta_D$.

difference between the stabilization and destabilization energies. The curve quite clearly suggests favoring of the nonplanar geometry ($\Delta\theta_D = 0°$) over the planar one. While the combined effect of $\Delta E_{KE}$ and $\Delta E_{n-e}$ stabilizes the nonplanar geometry, the effect of the rest destabilizes it. The variation of kinetic energy clearly suggests the presence of strong $\pi$ delocalization in the nonplanar $C_4F_4$. Among the energy parameters, the nucleus−electron interaction energy ($E_{n-e}$) plays the dominant role in stabilizing the nonplanar geometry. This interaction energy is a manifestation of the electron−phonon or vibronic coupling. It is well-known that SOJTE is a consequence of vibronic coupling when a system has filled shell electronic configuration, and it leads to a structure with a broken symmetry. Figure 6 quite clearly depicts the role of electron−phonon or vibronic coupling in stabilizing the nonplanar geometry with a lower symmetry ($D_{2h}$ to $C_{2h}$). Normally, SOJTE leads to bond length alteration in homoatomic four-membered ring systems.[20] In the present study, apart from bond length alteration in $C_4$ moiety of $C_4F_4$, the molecule also suffers a loss in symmetry ($D_{2h}$ to $C_{2h}$) because of SOJTE induced chair-like conformation of the fluorine atoms.

## Conclusion

In the present state of the art, we conclude that aromaticity and SOJTE are primarily responsible for the nonplanarity of $C_4F_4$. Aromaticity of a cyclic homoatomic $4\pi$ electron system is quite remarkable. The energy and density values support this unusual aromaticity in $C_4F_4$. The NICS and laplacian values follow an increasing trend as one approaches a planar geometry. A similar trend is also observed in $\Delta E_\pi$ values while the trend is reversed for $\Delta E_\sigma$ values. This justifies the aromatic behavior of $C_4F_4$ which acts as a driving force behind the nonplanary of this tetrafluoro derivative. Among the other energy parameters of interest, $\Delta E_{KE}$ and $\Delta E_{n-e}$ stabilizes the nonplanar geometry. The variation of kinetic energy suggests the presence of strong $\pi$ delocalization in nonplanar $C_4F_4$ and the variation of $E_{n-e}$ which finally results in SOJTE favoring the nonplanar geometry of $C_4F_4$. From the molecular orbital analyses, enhancement of $\pi$-delocalization can well be predicted as one proceeds toward a nonplanar geometry of $C_4F_4$ which may be attributed to s−$p_\pi$ mixing. These findings are quite fascinating in explaining the stabilization mechanism of $C_4F_4$.

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**Supporting Information Available:** Optimized coordinates of $C_4F_4$ (nonplanar and planar) and $C_4H_4$, IR spectrum of $C_4F_4$, formation energies, molecular orbital plots, evolution of HOMO of $C_4F_4$ with change in dihedral angle, current density mappings, all the NICS, density and laplacian values, Mulliken charge analysis, analysis of $\sigma-\pi$ energy separation, NBO analysis, all the energy parameters of interests, full Gaussian reference, and some concomitant properties of various other systems studied. This material is available free of charge via the Internet at http://pubs.acs.org

## References and Notes

(1) Petersson, E. J; Fanuele, J. C.; Nimlos, M. R.; Lemal, D. M.; Ellison, G. B.; Radziszewski, J. G. *J. Am. Chem. Soc.* **1997**, *119*, 11122−11123.

(2) Fattahi, A.; Lis, L.; Tian, Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 4984−4988.

(3) Maksić, M. E-; Vazdar, M.; Barbatti, M.; Lischka, H.; Maksi'c, Z. B. *J. Chem. Phys.* **2006**, *125*, 064310−064318.

(4) Gath, S.; Gleiter, R.; Schaller, R. J.; Rominger, F. *Organometallics* **2004**, *23*, 1116−1121.

(5) Kovačević, B.; Barić, D.; Maksić, Z. B.; Müller, T. *J. Phys. Chem. A* **2004**, *108*, 9126−9133.

(6) Lee, V. Y.; Takanashi, K.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 4758−4759.

(7) Fattahi, A.; Lis, L.; Kass, S. R. *J. Am. Chem. Soc.* **2005**, *127*, 13065−13069.

(8) *(8) Balsi, M.; McKee, M. L.; Schleyer, P. v. R. J. Phys. Chem. A* **2000**, *104*, 1246−1255.

(9) (a) Maier, G.; Alzerrecca, A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1015−1016. (b) Masamune, S.; Nakamura, N.; Suda, M.; Ona, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481−8483.

(10) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503.

(11) Sen, S.; Seal, P.; Chakrabarti, S. *Phys. Rev. B* **2006**, *73*, 245401−245404.

(12) Frisch, M. J.; et al. *GAUSSIAN 03*; Gaussian Inc.: Pittsburgh, PA, 2003 (see the Supporting Information for the complete reference).

(13) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377. (b) Lee, C.; Wang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(14) See Suppporting Information.

(15) (a) Lloyd, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 442−447. (b) Krygowski, T. M.; Cyrański, M. K.; Czarnocki, Z.; Häfelinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783−1796. (c) Krygowski, T. M.; Cyrański, M. K. *Chem. Rev.* **2001**, *101*, 1385−1420. (d) Special Issue on Aromaticity, *Phys. Chem. Chem. Phys.* **2004**, *2*. (e) Lazzeretti, P. *Phys. Chem. Chem. Phys.* **2004**, *6*, 217−223. (f) Santos, J. C.; Tiznado, W.; Contreras, R.; Fuentealba, P. *J. Chem. Phys.* **2004**, *120*, 1670−1673. (g) Rzepa, H. S. *Chem. Rev.* **2005**, *105*, 3697−3715. (h) Kertesz, M.; Choi, C. H.; Yang, S. *Chem. Rev.* **2005**, *105*, 3448−3481. (i) Rehaman, A.; Datta, A.; Mallajosyula, S. S.; Pati, S. K. *J. Chem. Theory Comput.* **2006**, *2*, 30−36.

(16) Shaidaei, H. F. B.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863−866.

(17) (a) Takanashi, K.; Lee, V. Y.; Matsuno, T.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2005**, *127*, 5768−5769. (b) Mesbah, W.; Prasang, C.; Hofmann, M.; Geiseler, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1717−1719.

(18) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v E. *J. Am. Chem. Soc.* **1996**, *118*, 6317−6318.

(19) Jug, K.; Hiberty, P. C.; Shaik, S. *Chem. Rev.* **2001**, *101*, 1477−1500.

(20) Datta, A.; Pati, S. K. *J. Chem. Theory Comput.* **2005**, *1*, 824−826.