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COMMENTS

Comment on “Origin of the Nonplanarity of Tetrafluoro Cyclobutadiene, C_4F_4”

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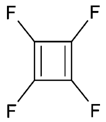
In a recent paper, Seal and Chakrabarti claim that the origin of the nonplanarity of tetrafluoro cyclobutadiene (**1**) is aromaticity and a second-order Jahn−Teller effect.[1]



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The claims for aromaticity rest on NICS(0) and NICS(1)$_{zz}$ values.[2] However, it had been shown that a single NICS value may fail in assigning aromaticity, and the NICS-scan method was introduced.[3] This was demonstrated specifically for derivatives of cyclopentadiene that were erroneously characterized as being aromatic or antiaromatic on the basis of single NICS values.[4] These investigations further revealed that simple NICS parameters may indicate diatropic and paratropic ring currents, but they do not necessarily signalize aromaticity or antiaromaticity, as evidently there are systems that show diatropic ring currents but are not aromatic.[4]

Aromaticity is one of the most useful concepts in chemistry even though it is not well defined and difficult to quantify. However, it is widely agreed that aromatic systems should exhibit diamagnetic ring currents (although their minimal strength is not well defined) and should be stable relative to nonaromatic reference systems. Reversely, antiaromatic systems exhibit paramagnetic ring currents and a destabilization relative to nonaromatic reference systems. Does **1** indeed exhibit the properties that allow its assignment as aromatic?

A NICS-scan of **1** (at GIAO-HF/6-311+G*//B3LYP/6-311++G**),[5] which is shown in Figure 1, clearly proves that the ring current is paratropic, and thus, **1** cannot be aromatic. The out-of-plane component is less positive than in unsubstituted cyclobutadiene,[6] suggesting a smaller paratropic ring current but certainly not a diatropic current, which an aromatic system should exhibit. The less positive values of the out-of-plane component and the negative isotropic values at short distances from the molecular plane result from the diamagnetic contribution of the lone pairs of the fluorine atoms (see below), but the cyclic conjugated π electrons show a NICS-scan shape which is typical for paratropic ring current.

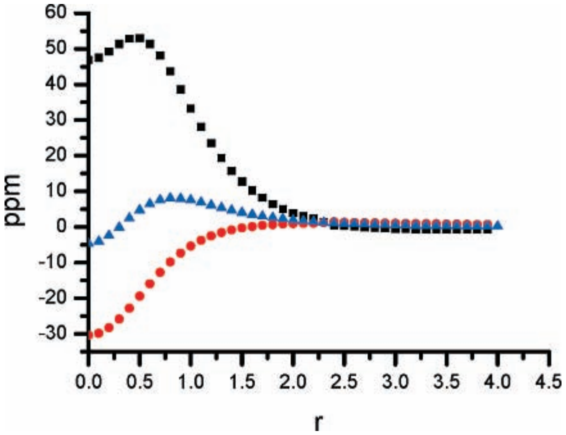

Figure 1. NICS values (ppm) as a function of distance (Å) from the molecular plane of tetrafluoro cyclobutadiene. ■, out-of-plane component. ●, in-plane component. ▲, isotropic.

Aromaticity should also be manifested in stability. The isodesmic and homodesmic equations, 1−4, measure the stability of **1** relatively to cyclobutadiene through different nonaromatic reference systems.[7] Regardless of the reference system, **1** does not show a special stability relative to cyclobutadiene. The bond separation energy equation, 5, even suggests destabilization relative to difluoro cyclobutadienes, which are certainly not aromatic.

Finally, it should be noted that the energy difference between planar and nonplanar **1** is only 2.05 kcal mol^{-1} (ZPE-corrected B3LYP/6-311++G** energies), where the planar form is a transition state (i.e., one imaginary frequency) between the two nonplanar structures. Certainly, this amount of energy is too small to claim that the antiaromatic planar **1** becomes aromatic upon deplanarization.

The ACID (anisotropy of the induced current density) scalar field is a measure of the density of delocalized electrons.[8] The ACID plots of cyclobutadiene and its tetrafluoro derivative **1** (Figure 2) indicate that the density of the delocalized π electrons in cyclobutadiene is considerably larger than that in its tetrafluoro derivative **1**. The current density vectors plotted on top of the ACID isosurface of cyclobutadiene define, as expected, a strong paratropic ring current (anticlockwise in Figure 3a) and, thus, prove its strong antiaromaticity. In **1** (Figure 2b), the ring current is weaker than that in the parent compound but still paratropic. Therefore, **1** is antiaromatic but less so than the parent cyclobutadiene. An examination of the ring currents that are induced by an in-plane magnetic field reveals why the isotropic NICS value of **1** is slightly negative. There are diatropic ring currents in cyclobutadiene, as well as in **1**, which are orthogonal to the π ring current, as can be observed in the in-plane component of the NICS-scan (Figure 1). The shielding effect of this diatropic current is overcompensated by the paratropic π current in cyclobutadiene; however, it is large enough to outmatch the much weaker paratropic ring current in the tetrafluoro derivative.

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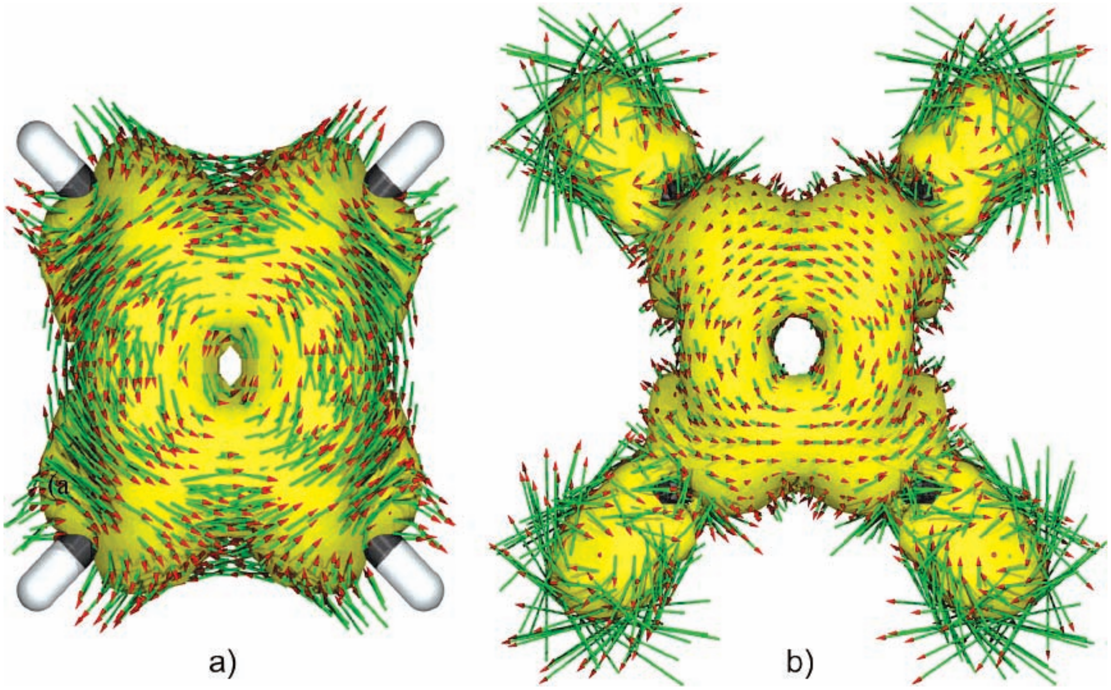
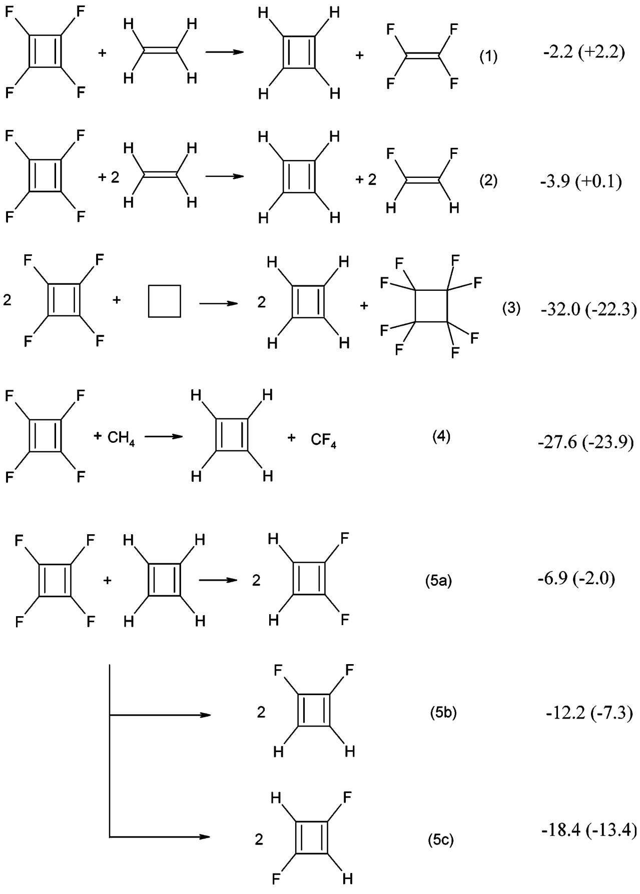


Figure 2. ACID isosurface of cyclobutadiene D_{2h} (a) and tetrafluoro cyclobutadiene **1** C_{2h} (b). The isosurface values are 0.05, the current density vectors are plotted onto the isosurfaces, the length of the green arrows is proportional to the absolute value of the current density at the origin of the arrow, and the magnetic field vectors are orthogonal with respect to the molecular plane in (a) and orthogonal with respect to the plane defined by the four fluorine atoms in (b). The ring currents in (a) as well as in (b) are paratropic (anticlockwise); hence, both species are antiaromatic. The density of delocalized π electrons and the ring currents are larger in cyclobutadiene (a) as compared to those in the tetrafluoro derivative (b). Nevertheless, both structures are π antiaromatic.



The conclusion that can be drawn from the above analysis is straightforward and more general; aromaticity always gives rise to a diatropic ring current, which usually gives rise to a negative NICS. However, the reverse statement is not necessarily true. A negative NICS value can also be induced by local currents. Hence, the use of single NICS values as a proof for aromaticity may lead to wrong assignments.

What is, then, the reason for the nonplanarity of the title compound? First, it should be noted that, due to the small energy difference between planar and nonplanar **1** (see above), the effects must either be subtle or they are the result of a delicate balance between opposing factors. Nonetheless, a NBO[9]-based explanation is offered here.

Fluorine, being an electronegative substituent, decreases bond curvatures,[10] thus forcing a stronger rehybridization on the bound carbon. Indeed, in cyclobutadiene, the lobes which form the short bonds are $sp^{1.64}$ hybridized, whereas in the planar **1**, the hybridization is $sp^{1.31}$. In the optimized **1**, this hybridization is $sp^{1.62}$. The electronegativity of a carbon atom depends on its hybridization so that the less p character it has, the more electronegative it is. The hybrids of carbon in the C−F bonds are also different, $sp^{2.85}$ and $sp^{2.74}$ in the planar and optimized **1**, respectively. This means that in the nonplanar form, the fluorine atom can attract more electron density from the carbon and reduce the destabilizing interaction between the two double bonds. Indeed, the NBO charges on the fluorine atoms are −0.299 and −0.304 in the planar and optimized **1**, respectively. Thus, the reason behind the nonplanarity of the title compound has to do with the rehybridization that is caused by the electronegative substituents. Note that NBO analysis also shows other and much larger effects, such as the better interaction between the π bonds as donors and the C−F bonds and F atoms as acceptors in the nonplanar form, but these are completely cancelled by the interactions of the lone pairs as donors and the C═C π^* species as acceptors, which are stronger by the same amount in the planar form.

In summary, energetic considerations, NICS-scans, and ACID analyses prove that **1** is not aromatic, as is claimed in the paper.[1]

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References and Notes

(1) Seal, P.; Chakrabarti, S. *J. Phys. Chem. A* **2007**, *111*, 715.

(2) For a comprehensive review about NICS, see: Chen, Z.; Chaitanya, S.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.

(3) Stanger, A. *J. Org. Chem.* **2006**, *71*, 883.

(4) Stanger, A. *Chem.—Eur. J.* **2006**, *12*, 2745.

(5) (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004. (b) All of the molecules underwent a full geometry optimization at the B3LYP/6−311++G** theoretical level and analytical frequencies calculations for ensuring a minimum ($N_{\mathrm{imag}} = 0$) and for obtaining ZPE corrections.

(6) For reference NICS-scan plots of aromatic and antiaromatic systems, see references 3 and 4.

(7) Reported are the ZPE-corrected energy and $\Delta H^0{}_{298}$ in parentheses in kcal mol^{-1}.

(8) Geuenich, D.; Hess, K.; Koehler, F.; Herges, R. *Chem. Rev.* **2005**, *105*, 3758.

(9) Gaussian NBO Version 3.1 was used. See. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899 and references therein.

(10) (a) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800. (b) Stanger, A. *J. Am. Chem. Soc.* **1998**, *120*, 12034. (c) Stanger, A.; Tkachenko, E. *J. Comput. Chem.* **2001**, *22*, 1377.