

## Reply to “Comment on ‘Origin of the Nonplanarity of Tetrafluoro Cyclobutadiene, C<sub>4</sub>F<sub>4</sub>’”

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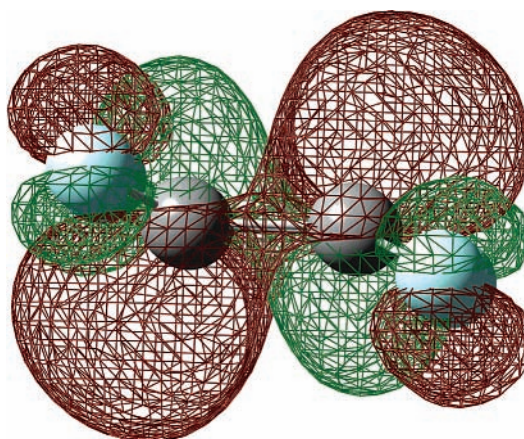
Aromaticity is a qualitative phenomenon which is of prime importance and is extensively used in the field of chemistry.<sup>1</sup> There are several criteria for assessing the aromatic behavior of a molecule, namely, energetic, structural, and magnetic criteria. Of these, the harmonic oscillator model of aromaticity (HOMA),<sup>2</sup> the nucleus-independent chemical shift (NICS),<sup>3</sup> ipso-centric current density mappings,<sup>4</sup>  $\sigma$ - $\pi$  separation,<sup>5</sup> the electron localization function (ELF),<sup>6</sup> anisotropy of the induced current density (ACID) mappings,<sup>7</sup> and formation energies are the ones widely used. In their paper, Koehler et al. have provided NICS scans, some stabilization schemes, and the ACID mappings to justify that C<sub>4</sub>F<sub>4</sub> is not aromatic in nature. However, they remain silent on several fundamental issues. These include molecular orbital analysis,  $\sigma$ - $\pi$  separation, kinetic energy variation, and net diamagnetic susceptibility. Moreover, a NBO analysis and the rehybridization concept, which are only mere consequences of some other factors, have been given as a probable reason for the nonplanar geometry of C<sub>4</sub>F<sub>4</sub>.

In the present study, from the analysis of the molecular orbitals (Figure 1), it is quite clear that the highest occupied molecular orbital (HOMO) of nonplanar C<sub>4</sub>F<sub>4</sub> is of neither a Hückel nor a Heilbronner Möbius type; rather, the nature is that of a non-Heilbronner Möbius type. For this kind of system, the NICS scans as well as the in-plane ACID mappings are not very authentic tools for predicting whether it is aromatic or not. Moreover, the ACID mappings are not very well established for Möbius systems and still remain an unresolved issue.

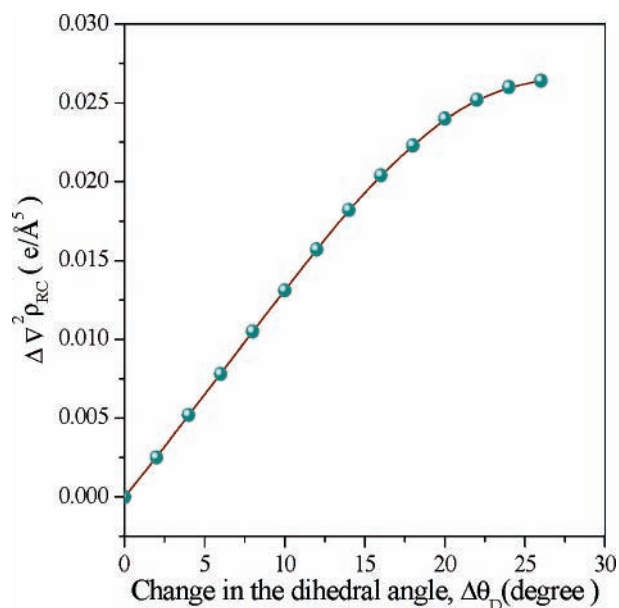
In our work,<sup>8</sup> we have not only confined ourselves to the NICS calculation but also provided some more fundamental energy and density parameters. These include  $\sigma$ - $\pi$  separation, formation energy analysis, analysis of the laplacian of electron density, and kinetic energy analysis. The net diamagnetic susceptibility has also been provided in the present reply in order to justify our prediction. All of these calculations are performed within density functional theory (DFT) and the Møller–Plesset perturbation (MP2) technique using the B3LYP/6-311++G-(d,p) method implemented in Gaussian 03.<sup>9</sup>

The formation energy analysis given in our work<sup>8</sup> supports the effective  $\pi$ -delocalization, which is shown in Figure 1. In explaining the stabilization energy gained due to an aromatic nature in a system, Koehler et al. have made use of some stabilization mechanism schemes. They have argued that C<sub>4</sub>F<sub>4</sub> does not show a special stability compared to that of its hydrocarbon analogue, cyclobutadiene (C<sub>4</sub>H<sub>4</sub>). The stabilization schemes given by Koehler et al. are problematic and not very fruitful for the assessment of special stability of C<sub>4</sub>F<sub>4</sub> relative to C<sub>4</sub>H<sub>4</sub>.

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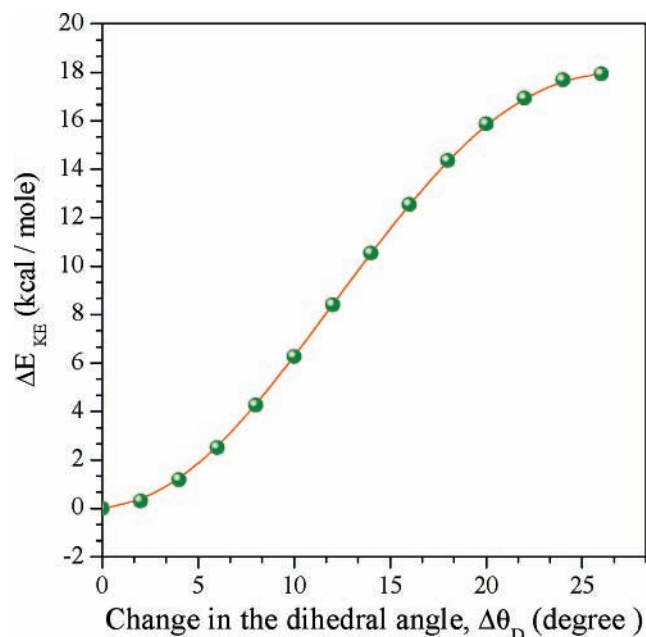
**Figure 1.** Highest occupied molecular orbital (HOMO) of nonplanar C<sub>4</sub>F<sub>4</sub> (a non-Heilbronner Möbius system)



**Figure 2.** Variation of change in the laplacian values against the change in the dihedral angle,  $\Delta\theta_D$ .

The laplacian of electron density calculated at the ring centroid (RC) ( $\nabla^2\rho_{RC}$ ),<sup>10</sup> being a measure of the inhomogeneity of the electron cloud in a system, gradually increases as one proceeds toward a planar geometry from a nonplanar one. Figure 2 depicts the change in the  $\nabla^2\rho_{RC}$  value,  $\Delta\nabla^2\rho_{RC}$ , with the change in the dihedral angle,  $\Delta\theta_D$ . The laplacian value for the most stable geometry (nonplanar C<sub>4</sub>F<sub>4</sub>) is set to zero, and the rest of the values are calibrated with respect to that one. The evolution of the HOMO of C<sub>4</sub>F<sub>4</sub> with the change in the dihedral angle (given in the Supporting Information file of our work<sup>8</sup>) further supports the analysis of the change in the laplacian of electron density.

From the knowledge of quantum mechanics, it is known that as delocalization increases, KE gradually decreases. The change in KE,<sup>11</sup>  $\Delta E_{KE}$ , against the change in the dihedral angle,  $\Delta\theta_D$ , is illustrated in Figure 3. The figure exemplifies a gradual stabilization in the KE as one proceeds toward a nonplanar geometry, revealing greater delocalization in nonplanar C<sub>4</sub>F<sub>4</sub>. As one approaches from a planar geometry to a nonplanar one, the evolution of the HOMO of C<sub>4</sub>F<sub>4</sub> (given in the Supporting



**Figure 3.** Variation of  $\Delta E_{KE}$  against the change in the dihedral angle,  $\Delta\theta_D$ .

**TABLE 1: The Net Diamagnetic Susceptibility,  $\chi$ , with the Change in the Dihedral Angle,  $\Delta\theta_D$**

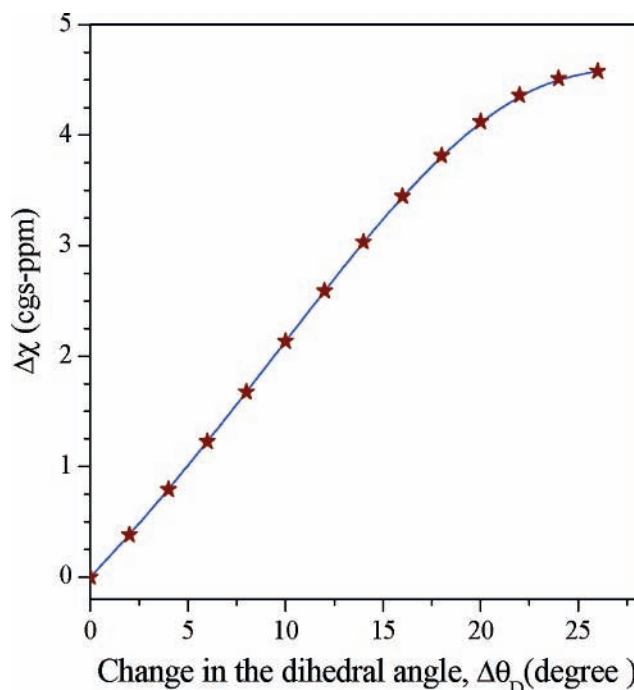
change in the dihedral angle, $\Delta\theta_D$ (degree)	net diamagnetic susceptibility, $\chi$ (cgs-ppm)
0 (nonplanar)	-43.3552
2	-42.9726
4	-42.5624
6	-42.1291
8	-41.6789
10	-41.2203
12	-40.7638
14	-40.3219
16	-39.9091
18	-39.5408
20	-39.2320
22	-38.9956
24	-38.8418
26 (planar)	-38.7762

Information file of ref 8) suggests that the delocalization is cyclic, which is consistent with the change in KE. Like the laplacian value, the value of KE for the most stable geometry is set to zero, and the rest are calibrated with respect to that one.

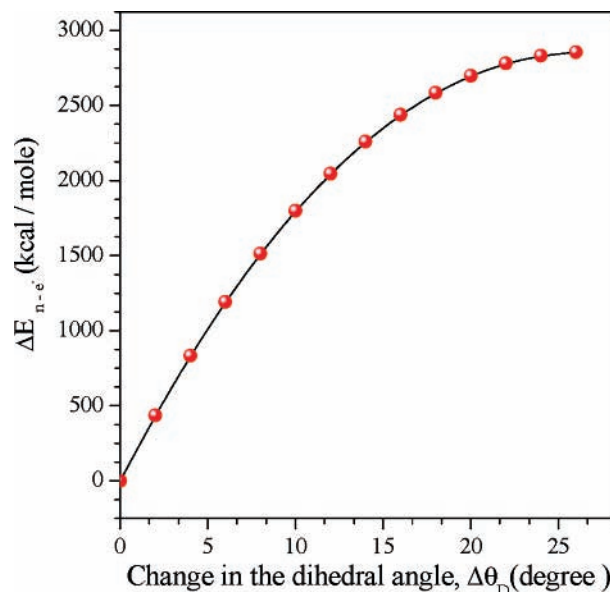
Another important probe for evaluating any aromatic behavior in a system is the net magnetic susceptibility. In  $C_4F_4$ , the net diamagnetic susceptibility<sup>12</sup> ( $\chi$ , which is defined as the net contribution from the diamagnetic and paramagnetic susceptibility tensors) becomes more and more negative as we move toward a nonplanar geometry (see Table 1). The change in the value of net diamagnetic susceptibility,  $\Delta\chi$ , with the change in the dihedral angle,  $\Delta\theta_D$ , is given in Figure 4.

Apart from the above-mentioned energy and density calculations,  $\sigma$ - $\pi$  separation<sup>5,13</sup> is also a very important and useful criterion for describing aromatic behavior in a system. In our work,<sup>8</sup> it has been clearly illustrated that as one approaches a planar geometry, there is a gradual  $\pi$ -destabilization which corroborates well with the other calculations of the paper<sup>8</sup> and also with the above-mentioned analysis in the present reply.

In their comment, Koehler et al. have pointed out that due to the strong electron-withdrawing effect of fluorine (F) atoms in



**Figure 4.** Variation of  $\Delta\chi$  against the change in the dihedral angle,  $\Delta\theta_D$ .



**Figure 5.** Variation of  $\Delta E_{n-e}$  against the change in the dihedral angle,  $\Delta\theta_D$ .

$C_4F_4$ , rehybridization takes place, leading to more bond curvature. They have also provided some natural bond orbital (NBO) analysis to explain the nonplanarity of  $C_4F_4$ . This NBO analysis and the concept of rehybridization are only mere consequences of some other factors. We strongly believe that a second-order Jahn–Teller effect is conceptually more fundamental than the arguments of Koehler et al. Figure 5 shows the variation of the change in the nucleus–electron interaction energy,<sup>11</sup>  $\Delta E_{n-e}$ , against the change in the dihedral angle,  $\Delta\theta_D$ . The  $E_{n-e}$  of the most stable geometry is set to zero, and the rest of the energy values are then calibrated with respect to that one. Figure 5 shows a difference of about 2800 kcal in the  $\Delta E_{n-e}$  value of the planar and nonplanar geometries. Such an appreciable change in the nucleus–electron interaction energies

clearly indicates that SOJTE plays the most crucial role in the symmetry breaking process ( $D_{2h}$  to  $C_{2h}$ ).

In conclusion, we believe that our prediction of the aromatic behavior of  $C_4F_4$  is correct. Moreover, the second-order Jahn–Teller effect plays a dominant role behind the nonplanar geometry of the tetrafluoro derivative,  $C_4F_4$ .

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- (10) The laplacian of the electron density is calculated using the keyword cube = laplacian.
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