ORGANIC
LETTERS

2010
Vol. 12, No. 4
768−771

Why Are Perfluorocyclobutadiene and Some Other $(CF)_n{}^q$ Rings Non-Planar?

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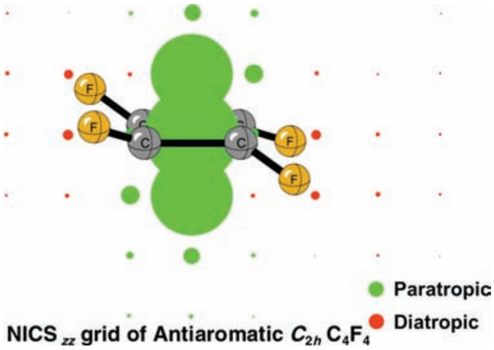
Received December 11, 2009

ABSTRACT



NICS$_{zz}$ grid of Antiaromatic C_{2h} C_4F_4

Although surprising, the nonplanarity of C_{2h} C_4F_4 is not unique. While C_6F_6 is planar, other members of the $(CF)_n$ family, for example, $C_5F_5{}^-$, $C_6F_6{}^-$, $C_7F_7{}^-$, and triplet $C_7F_7{}^-$ are not. C_{2h} C_4F_4 is not aromatic, as claimed (see above), but its antiaromaticity is reduced relative to the planar D_{2h} form due to decreased π antibonding and enhanced cross-ring π overlap. The nonplanar C_{2h} geometry also benefits from the relief of repulsive FC−CF bond eclipsing interactions.

Why is perfluorocyclobutadiene nonplanar?[1−4] Petersson et al.[1] first discovered the unexpected C_{2h} symmetry of C_4F_4, by observing a 595 cm^{-1} ring-puckering mode with negative dichroism in its vibrational spectrum; this would be IR inactive in D_{2h} symmetry. Their computed 11.6° out-of-plane angles of the C−F bonds (B3LYP/cc-pVDZ) result in substantial FCCF staggering across the single CC bonds (see Figure 1). The authors, noting the reminiscence to "the nonplanarity of the calculated structure of the perfluoroallyl radical"[5] attributed the nonplanarity of C_4F_4 to rehybridization,[1] "Electron withdrawal by the highly electronegative fluorines favors pyramidalization of the carbons by increasing the *p*-character of the C−F bonds, and this tendency is reinforced by the resulting attenuation of the cyclic conjugation in the π system." However, similar rehybridization occurs in perfluorobenzene (C_6F_6) and in perfluoroethylene (C_2F_4), but both have planar geometries.[6,7]

Could nonplanar C_4F_4 be aromatic? The remarkable conclusion "that aromaticity and the second-order Jahn-Teller effect (SOJTE)[8] are primarily responsible for the non-planarity of C_4F_4" was put forward by Seal and Chakrabarti (SC) in 2007 on the basis of extensive analyses of the effects of planarization on several energetic and magnetic properties.[2,4] SC interpreted the C_{2h} HOMO as showing "complete π-delocalization around the ring carbons." This was attributed to the mixing of *s* and p_π

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(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) Seal, P.; Chakrabarti, S. *J. Phys. Chem. A* **2007**, *111*, 715–718. The reported NICS(1)$_{zz}$ datum for C_{2h} C_4F_4 (ca. −2 ppm) is in error. Our recomputed values are +24.2 ppm (C_{2h} C_4F_4) and +33.1 ppm (D_{2h} C_4F_4).

(3) Koehler, F.; Herges, R.; Stanger, A. *J. Phys. Chem. A* **2007**, *111*, 5116–5118.

(4) Seal, P.; Chakrabarti, S. *J. Phys. Chem. A* **2007**, *111*, 5119–5121.

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10.1021/ol902866n

orbitals and "is responsible for the aromatic nature of C_4F_4." For nonplanar C_{2h} C_4F_4, SC reported a diamagnetic −7.2 ppm isotropic NICS(0)[9] (in the ring center) and −2.1 ppm $NICS(1)_{zz}$[10] (for the *zz* tensor component, perpendicular to the ring plane, 1 Å above the ring center). These negative (i.e., "aromatic", diatropic) values contrasted with the positive (i.e., "antiaromatic", paramagnetic) +3.5 NICS(0) and +1.3 ppm $NICS(1)_{zz}$ data corresponding to the D_{2h} form. (As we document below, SC's NICS evidence for the aromaticity of the C_{2h} form was misinterpreted and even erroneous.)

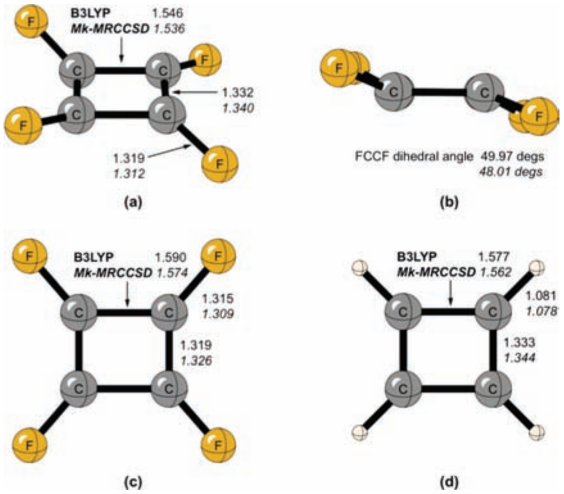

Figure 1. Geometries of C_{2h} C_4F_4 (a−b), D_{2h} C_4F_4 (c), and cyclobutadiene (d), computed at B3LYP/6-311+G** and Mk-MRCCSD/cc-PVTZ (in italics). Both Figure 1 as well as the TOC graphic are prepared by HFSmol.[11]

SC's aromaticity claim was challenged by Koehler, Herges, and Stanger (KHS) shortly afterward based on "energetic considerations, NICS-scans, and ACID analyses."[3] According to KHS's refutation, C_4F_4 failed to show any special stability relative to CBD energetically, and its $NICS_{zz}$ scan only revealed weakened paratropicity compared to cyclobutadiene. Thus, according to KHS, C_4F_4 is not aromatic, but at most only might be somewhat less antiaromatic than CBD.[3] KHS suggested that F electron withdrawal in C_{2h} C_4F_4 was more effective than in planar D_{2h} C_4F_4 (due to greater *p* character in the CF bond hybridization). This reduced the "destabilizing interaction between the two double bonds" to a greater extent and favored the nonplanar C_{2h} form.

However, KHS[3] did not remark on the startling discrepancy between their ca. +32 ppm $NICS(1)_{zz}$ value for D_{2h} C_4F_4, and SC's +1.3 ppm value (−2.1 ppm for C_{2h} C_4F_4).[2] Our computed PW91/IGLOIII $NICS(1)_{zz}$ data for D_{2h} (+33.1 ppm) and C_{2h} (+24.2 ppm) C_4F_4 (see Table 1) supports KHS's data. SC mistook an in-plane (*xx*, *yy*) tensor component of the isotropic NICS for the perpendicular (*zz*) tensor component analyses (as explained in ref 12).

Table 1. GIAO-Nucleus Independent Chemical Shifts (NICS) Data for D_{2h} and C_{2h} C_4F_4 and Cyclobutadiene (CBD) (Computed at PW91/IGLOIII//B3LYP/6-311+G**), All Units Are in ppm

NICS data	C_{2h} C_4F_4	D_{2h} C_4F_4	D_{2h} CBD
NICS(0)	−7.3	−4.3	+26.4
NICS(1)	+5.1	+9.1	+17.7
$NICS(0)_{zz}$	+47.5	+48.3	+108.6
$NICS(1)_{zz}$	+24.2	+33.1	+54.6
$NICS(0)_{\pi zz}$	+30.6	+41.0	+58.3
$NICS(1)_{\pi zz}$	+26.6	+35.9	+51.33

In their rebuttal,[4] SC also did not comment on this $NICS(1)_{zz}$ discrepancy with KHS but plotted changes in diamagnetic susceptibility, kinetic energy, and nucleus-electron interaction energy in going from D_{2h} to C_{2h} C_4F_4. Although this evidence only indicates general trends, it was interpreted as supporting their original[2] "prediction of the aromatic behavior" of C_{2h} C_4F_4. Their claimed 18 kcal/mol decrease in kinetic energy upon puckering was interpreted to reveal "greater delocalization in non-planar C_4F_4."

Petersson, et al.'s[1] original rehybridization argument seemed reasonable superficially. Thus, the $Csp^{1.94}$ hybridization of the CBD C−H bonds (close to sp^2) contrasts with the $Csp^{2.59}$ hybridization of the C_{2h} C_4F_4 C−F bonds (close to sp^3) (PW91/IGLOIII NLMO[13] data). But this difference does not explain the nonplanarity of C_4F_4 satisfactorily since sp^3 hydridization does not necessarily favor local pyramidal geometries. Especially when highly electronegative F substituents are present, geometry and hybridization based on the ratio of localized orbital occupancies (NLMO) do not have a simple relationship,[14] e.g., the carbon in tetrahedral CF_4 ($sp^{2.33}$) is roughly sp^2 rather than sp^3 hybridized.[15] The C−F bonds of the antiaromatic fluorocyclobutadiene ($sp^{2.80}$), 1,4-difluorocyclobutadiene ($sp^{2.73}$), 1,3-difluorocyclobutadiene ($sp^{2.68}$), and 1,2-difluorocyclobutadiene ($sp^{2.67}$), have even more *p* character than C_{2h} ($sp^{2.59}$) and D_{2h} ($sp^{2.51}$) C_4F_4, but only trifluorocyclobutadiene ($sp^{2.58}$, $sp^{2.60}$, and $sp^{2.64}$) is very slightly nonplanar.

Our definitive multireference coupled cluster computations (Mk-MRCCSD/cc-PVTZ)[16] find that the D_{2h} C_4F_4 transition structure is only 2.0 kcal/mol higher in energy than the C_{2h} minimum (this confirms KHS's[3] 2.05 kcal/mol difference at B3LYP/6-311+G*). The energy required to deform the D_{2h} C_4H_4 minimum into a simulated C_4F_4-like C_{2h} C_4H_4 geometry was estimated by fixing

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(8) The possibility of having a second order Jahn-Teller effect (SOJTE) in C_4F_4 is unlikely. The D_{2h} HOMO-LUMO gap is not small at all (ca. 0.15 a.u., HOMO energy −0.22361 a.u.), at C_{2h} it is 0.13 a.u. (HOMO energy −0.24001 a.u.). Moreover, the SOJTE requirement (see Pearson, R. G. *Proc. Natl. Acad. Sci.* **1975**, *72*, 2104–2106) is not met: the HOMO (a_g) and LUMO (b_g) orbitals of C_{2h} C_4F_4 do not have the same symmetry Seal and Chakrabarti's original argument stating that there is "a manifestation of the electron-phonon or vibronic coupling" in C_4F_4, based on the dominating "attractive" $E_{(n-e)}$ in C_{2h} C_4F_4, is not direct evidence for SOTJE.

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(10) Corminboeuf, C.; Heine, T.; Seifert, G.; Schleyer, P. v. R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 273–276.

(11) Wheeler S. E. *HFSmol*; University of Georgia: Athens, GA, 2008.

(12) SC's erroneous "$NICS(1)_{zz}$" value for C_{2h} C_4F_4 (−2.1 ppm) corresponds to the in-plane $NICS(1)_{yy}$ (−1.4 ppm) in our PW91/IGLOIII computation ($NICS(1)_{xx}$ = −7.6 ppm). Although *zz* is the conventional out-of-plane designation, it does not always represent the perpendicular tensor component in the NICS output, since the "*xx*, *yy*, and *zz*" assignment depends on the orientation of the molecule.

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all angles to those of C_{2h} C_4F_4 and then optimizing the CC and CH bond lengths. The 6.4 kcal/mol higher energy results largely from angle strain of the puckered CH's.

But what is responsible for the nonplanarity of C_4F_4? Is C_{2h} C_4F_4 really aromatic? Why do some perfluorinated rings, for example, C_4F_4, favor nonplanar geometries, whereas others, for example, C_6F_6, are planar?

Planar C_4F_4 differs markedly from CBD and the partially fluorinated cyclobutadienes in having four repulsive eclipsed vicinal F•••F interactions around the ring. The data in Figure 2 show that this repulsion destabilizes D_{2h} C_4F_4 by +22.7 kcal/mol (eq 2) relative to four C_4FH_3 fluorocyclobutadienes! The Figure 2 data also agrees with KHS's conclusion that fluorine substitution disfavors C_4F_4 versus C_4H_4 energetically. However, this steric repulsion between the two single C−C bond FC−CF's is partially relieved in nonplanar C_{2h} C_4F_4.

Since fluorocyclobutadiene C_4FH_3 is not destabilized relative to CBD (see Figure 2, eq 1), the energetic effect of FC−CH and HC−CH eclipsing are about the same. As expected from energetic additivity (see Figure 2), the overall FC−CF repulsion is only half as large in trifluorocyclobutadiene (+11.7 kcal/mol, see eq 3); it is less for 1,2- (+7.0 kcal/mol, eq 4) as well as 1,4- (+4.2 kcal/mol, eq 5) difluorocyclobutadiene, and is negligible for 1,3-difluorocyclobutadiene (−0.4 kcal/mol, eq 6) since there are no eclipsed FC−CF's.

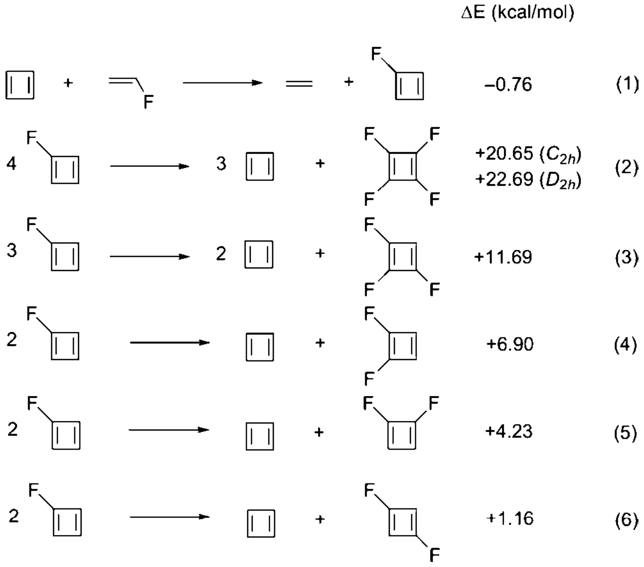

Figure 2. Homodesmotic evaluations of the vicinal FCCF repulsion in fluorinated cyclobutadienes (B3LYP/6-311+G** + ZPE data). Note that the additivity relationships: (4) + (5) ≈ (3) and 2(4) + 2(5) ≈ (2, D_{2h}) reveal no special energetic effects.

Similarly, due to the effect of the two vicinal FC−CF repulsions involving the central C−F, the perfluoroallyl radical favors a nonplanar geometry,[5] even though the 1,1,3,3-tetrafluoroallyl radical is planar. Tetra-tert-butyl cyclobutadiene[17] and tetranitrocyclobutadiene[2] also are nonplanar because of their very bulky substituents. Despite having larger Cl atoms, the C_4Cl_4 minimum is planar (D_{2h} symmetry) as the ClC−CCl Cl's are much further apart (3.867 Å) than the FC−CF F's in D_{2h} C_4F_4 (3.313 Å) (at B3LYP/6-311+G*). However, the triplet C_4Cl_4 minimum is slightly nonplanar (C_{2h} symmetry) (the data for C_4Cl_4 and $C_{20}H_{36}$ are provided in the Supporting Information).

Compared to its D_{2h} transition state, we agree that C_{2h} C_4F_4 benefits from having somewhat better molecular orbital features. As noted by SC,[2,4] the twisting of the HOMO in C_{2h} C_4F_4 decreases its unfavorable π antibonding cross-ring interaction and increases the overlap between the π lobes of the same sign. However, SC's suggestion that aromatic character results is exaggerated; we agree with KHS that the effect only reduces antiaromaticity somewhat.

The alleviation of vicinal FC−CF repulsion, accompanied by decreased antibonding character of the HOMO (note the significantly shortened CC single bond in C_{2h} C_4F_4, from 1.590 Å to 1.546 Å, see Figure 1), results in a more compact carbon ring framework in C_{2h} C_4F_4. Hence, the nonplanar C_4F_4 has greater nuclear−nuclear (nn)/electron−electron (ee) repulsion but even greater nuclear-electron (ne) attraction than the planar D_{2h} form (see Table S2 in the Supporting Information). Nevertheless, these energy component analyses give only limited insight to the origin of C_4F_4 puckering, as they reflect the energy lowering associated with all geometric changes in the molecule, which are not indentifiable individually. We find that the kinetic energy change going from C_{2h} to D_{2h} C_4F_4 is only 0.01 kcal/mol (see Table S2 in the Supporting Information), in contrast to SC's report of 18 kcal/mol (this discrepancy is explained in ref 18).

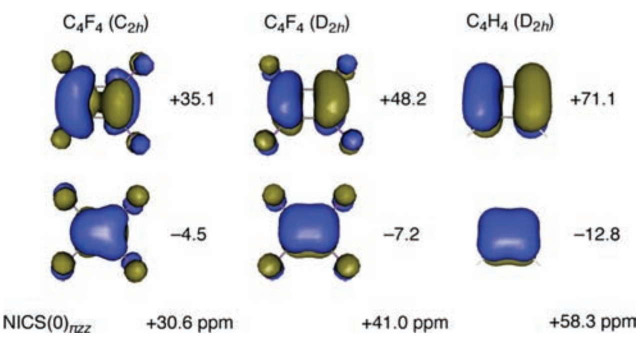

Figure 3. NICS$_{zz}$ data for the π MO's of C_4F_4 (C_{2h} and D_{2h}) and cyclobutadiene (CBD) and their total NICS(0)$_{\pi zz}$ values. All canonical molecular orbital (CMO) NICS data were computed at the PW91/IGLOIII level.

SC's conclusion that C_{2h} C_4F_4 is aromatic also was supported misleadingly by the small negative isotropic C_{2h} C_4F_4 NICS(0) value (−7.3 ppm) (see Table 1), as well as their erroneous NICS(1)$_{zz}$ and D_{2h} NICS(0) data.[2,10] Canonical molecular orbital (CMO) analyses NICS(0)$_{\pi zz}$[19,20] evaluate the diatropicity/

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(17) Balci, M.; McKee, M. L.; Schleyer, P. v. R. *J. Phys. Chem.* **2000**, *104*, 1246–1255.

(18) Kinetic energy components are very sensitive to molecular geometries (whether or not they are fully relaxed). SC reported a 18 kcal/mol kinetic energy change in going from C_{2h} to D_{2h} C_4F_4 at MP2/6-311+G*//B3LYP/6-311+G* and 8.5 kcal/mol at B3LYP/6-311+G*. These values are artifacts of computing the energetic components at geometries which were optimized at different levels (see SITable S2 and S3). In contrast, our recomputations give 2.14 kcal/mol at MP2/6-311+G*//MP2/6-311+G* (in our SI) and only 0.01 kcal/mol at B3LYP/6-311+G*//B3LYP/6-311+G* (see page 3). There is no kinetic energy difference!

paratropicity of planar as well as nonplanar molecules accurately and are more soundly based than other NICS based indicies, as only contributions perpendicular to the ring plane (*zz*) of the relevant CMO's are included. Thus, both C_{2h} (NICS(0)$_{\pi zz}$ = +30.6 ppm, at PW91/IGLOIII, *zz* is the tensor component perpendicular to the plane of the carbon ring) and D_{2h} (+41.0 ppm) C_4F_4 are clearly antiaromatic (NICS(0)$_{\pi zz}$ = +58.3 ppm for CBD, at the same level) (see Figure 3). Similar to nonplanar C_4F_4, the 4 π electrons $C_3H_3^-$ also has puckered CH bonds and reduced antiaromaticity (NICS(0)$_{\pi zz}$ = +30.4 ppm).

As recognized in 1997[21] and emphasized many times since,[19] isotropic NICS (an average of the *xx*, *yy*, and *zz* tensor contributions)[9] are seriously contaminated by contributions of the in-plane *xx* and *yy* tensor components, especially at the centers of small rings. Only the perpendicular *zz* tensor components are related to aromaticity in such cases, but these may not dominate. Specifically, the diatropicity of the *in-plane* NICS(0)$_{xx}$ (−39.0 ppm and −21.0 ppm) and NICS(0)$_{yy}$ (−19.1 ppm and −40.3 ppm) tensor components in C_{2h} and D_{2h} C_4F_4, respectively, overwhelm the paratropicity of the more relevant NICS(0)$_{zz}$ (+47.5 ppm and +48.3 ppm) contributions (see Table 1). Isotropic NICS(1)[19, 21] data (at points 1 Å above the ring center) alleviate this problem somewhat. Indeed, the NICS(1) values for both C_{2h} (+5.1 ppm) and D_{2h} (+9.1 ppm) C_4F_4 are *positive* (see Table 1), indicating weak antibonding (paratropic) character. When only the perpendicular tensor component is considered, both NICS(0)$_{zz}$ and NICS(1)$_{zz}$ are positive for C_{2h} and D_{2h} C_4F_4 (+24.2 ppm and +33.1 ppm, respectively; Table 1). The NICS$_{zz}$ scans of KHS provide similar information, but the NICS(0)$_{\pi zz}$ data in Table 1 and Figure 3 are definitive, as only the π MO contributions are included (note the NICS$_{\pi zz}$ grid, TOC graphic).

The smaller NICS(0)$_{\pi zz}$ value of *planar* D_{2h} C_4F_4 (+41.0 ppm) than D_{2h} CBD (+58.3 ppm) is due to the significant differences in their CC bond lengths (see Figure 1). The NICS(0)$_{\pi zz}$ value of CBD is reduced from +58.3 to +49.2 ppm when the D_{2h} C_4F_4 CC bond lengths are imposed. Hence, at least part of the reduced antiaromaticity in D_{2h} C_4F_4, compared to CBD, can be attributed to the increase in CC bond length alternation due to fluorine substitution.[22]

Therefore, C_4F_4 is nonplanar due to the alleviation of the vicinal FC−CF eclipsing strain at the single CC bonds and to partial relief of antiaromaticity. The nonplanarity of C_4F_4 is not unique.

Nonplanar geometries are favored by $C_5F_5^-$ (6 π) $C_6F_6^-$ (7 π),[24] $C_7F_7^-$ (7 π), $C_7F_7^-$ (8 π, triplet), and $C_8F_8^{2-}$ (10 π), even though their $(CH)_n^q$ counterparts are planar (see Figure 4). Other perfluorinated rings have planar geometries, i.e. $C_5F_5^+$ (4 π electrons), $C_5F_5^-$ (5 π), $C_6F_6^-$ (5 π),[23] C_6F_6 (6 π), and $C_7F_7^+$ (6 π). In general, fluorinated anions tend to be nonplanar (as in CF_3^-), but cations favor planarity (as in CF_3^+). Larger perfluorinated rings have smaller F•••F distances, but also much shorter CC "single bond" lengths (less than 1.48 Å for all perfluorinated five, six, and seven membered ring species, compared to 1.590 Å in C_4F_4); larger CC bond orders resist FCCF twisting. Vicinal FC−CF repulsion is relieved by puckering more easily in antiaromatic species, while nonplanarity is resisted, for example, by C_6F_6, due to aromaticity reduction.

Consequently, it is remarkable that the aromatic $C_5F_5^-$, despite having six π electrons, is nonplanar. We attribute this to the pyramidalizing effect of its negative charge. The D_{5h} geometry of $C_5F_5^-$ (NICS(0)$_{\pi zz}$ = −24.3 ppm) is a second order (E_1'') "monkey" saddle point on the potential energy surface involved in the stereomutation of the nearly isoenergetic dienylic C_s (NICS(0)$_{\pi zz}$ = −15.9 ppm) and allylic C_2 (NICS(0)$_{\pi zz}$ = −16.6 ppm) minima. Both these minima have small planarizing energies (ca. 0.7 kcal/mol) to the D_{5h} form, and are connected through a C_1 transition state (NICS(0)$_{\pi zz}$ = −16.6 ppm). All $C_5F_5^-$ forms are aromatic, the nonplanar ones slightly less so. In contrast, the $C_5F_5^+$, despite having 4 π electrons, has a planar minimum due to its positive charge. The 5 π electron $C_5F_5^-$ also is planar.

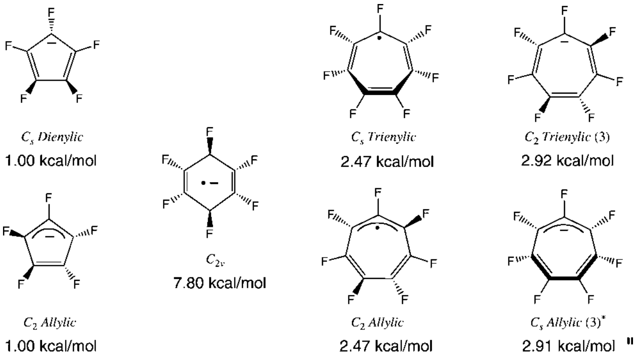

Figure 4. Planarization energies for nonplanar $(CF)_n^q$ species (at B3LYP/6-311+G*) with planar hydrocarbon analogs. *The allylic $C_7H_7^-$ triplet (C_s) has one negligible imaginary frequency (−4.86 cm^{-1}).

We conclude that C_4F_4 prefers C_{2h} instead of D_{2h} symmetry for two reasons: reduced antiaromaticity due to the less unfavorable π overlap across the ring and reduced vicinal FC−CF repulsions. Such repulsions tend to deplanarize perfluorinated $(CF)_n$ rings, but obviously not their hydrocarbon (or less fluorinated) analogs. Nonplanar $(CF)_n$ rings only have small planarizing energies since planar geometries maximize π delocalization. In view of *the delicate balance between opposing factors*[3] exemplified by the behavior of a broader set of neutral and charged $(CF)_n$ rings, the nonplanarity of C_4F_4 is not "*special*" at all.

Acknowledgment. We gratefully acknowledge financial support from NSF Grant CHE-0716718 (P.v.R.S.). This work also was supported in Mainz by the Deutsche Forschungsgemeinschaft (GA 370/5-1) and by the Fonds der Chemischen Industrie (F.A.E.).

Supporting Information Available: The complete Gaussian reference, computed energetic components for C_{2h} and D_{2h} C_4F_4, total energies of the various $(CF)_n^q$ and $(CH)_n^q$ species and Cartesian coordinates for C_4F_4, $C_5F_5^-$, C_4Cl_4, and tetra-tert-butyl cyclobutadiene are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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