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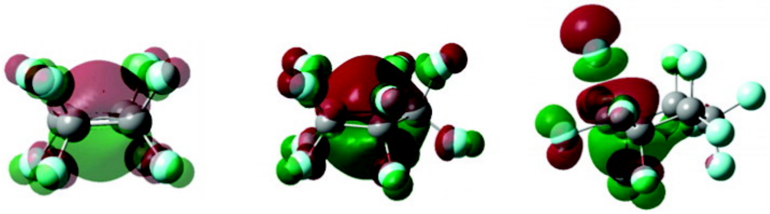

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The Peculiar Trend of Cyclic Perfluoroalkane Electron Affinities with Increasing Ring Size

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Abstract: The adiabatic electron affinities (AEAs), vertical electron affinities (VEAs), and vertical detachment energies (VDEs) of cyclic perfluoroalkanes, *c*-C_nF_{2n} ($n = 3-7$), and their monotrifluoromethyl derivatives were computed using various pure and hybrid density functionals with DZP++ (polarization and diffuse function augmented double-ζ) basis sets. The theoretical AEA of *c*-C_4F_8 at KMLYP/DZP++ is 0.70 eV, which exhibits satisfactory agreement with the 0.63 ± 0.05 eV experimental value. The nonzero-point-corrected AEA of *c*-C_4F_8 is predicted to be 0.41 eV at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory, which shows a slight deviation of 0.11 eV from the KMLYP estimated value of 0.52 eV for the same. With the zero-point correction from the MP2/6-311G(d) [Gallup, G. A. *Chem. Phys. Lett.* **2004**, *399*, 206] level of theory combined with the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ result, the most reliable estimate of AEA of *c*-C_4F_8 is 0.60 eV. *c*-$C_3F_6(-)$, *c*-$C_4F_8(-)$, and *c*-$C_5F_{10}(-)$ are unusual in preferring planar to near planar ring structures. The ZPE-corrected AEAs of *c*-C_nF_{2n} increase from $n = 3$ (0.24 eV) to $n = 5$ (0.77 eV), but then dramatically fall off to 0.40 eV for both $n = 6$ and $n = 7$. All of the other functionals predict the same trend. This is due to a change in the structural preference: C_s *c*-$C_6F_{12}(-)$ and C_1 *c*-$C_7F_{14}(-)$ are predicted to favor nonplanar rings, each with an exceptionally long C−F bond. (There also is a second, higher energy D_{3d} minimum for $C_6F_{12}(-)$.) The SOMOs as well as the spin density plots of the *c*-PFA radical anions reveal that the “extra” electron is largely localized on the unique F atoms in the larger $n = 6$ and $n = 7$ rings but is delocalized in the multiatom SOMOs of the three- to five-membered ring radical anions. The computed AEAs are much larger than the corresponding VEAs; the latter are not consistent with different functionals. The AEAs are substantially larger when a *c*-C_nF_{2n} fluorine is replaced by a $-CF_3$ group. This behavior is general; PFAs with tertiary C−F bonds have large AEAs. The VDEs for all the anions are substantial, ranging from 1.89 to 3.64 eV at the KMLYP/DZP++ level.

Introduction

The exceptional properties of perfluoroalkanes (PFAs) not only elicit scientific interest but also have led to multifarious industrial applications.[1,2] The attributes of chemical inertness, extreme hydrophobicity, thermal stability, low viscosity, and low dielectric constant make PFAs excellent candidates for lubricants, sealants, surfactants, oxygen carriers, anesthetics, and inert solvents.[3−9] The unusual solubility trend of PFAs has led to the emergence of a new field called “fluorous biphase chemistry”.[10] The concern of the present theoretical paper, the strong electron attaching properties of the PFAs, has also been exploited in tracer studies in atmospheric dispersion investigations.[11] The remarkable chemical inertness of PFAs arises from the unusually strong C−F bonds. Their chemical passivity has earned them the reputation of “immortal molecules”.[12] The notion of immortality is further corroborated by their unusually long lifetimes in the atmosphere. Given the fact that these molecules possess the notorious attributes of global warming potential, their long lifetimes could be of great concern.[13]

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Recently, Morris et al. have shown that electron attachment can reduce the lifetime of perfluorocyclobutane in the atmosphere from 3200 to 1400 years.[14]

Chemical reactivity can be induced in PFAs through free electrons and reducing media. Seminal research by Tatlow and co-workers, as well as by Macnicol and Robertson, has shown that PFAs can be defluorinated by using reducing agents.[15,16] Macnicol and Robertson used an organic reductant, sodium benzenethiolate, to reduce trans-perfluorodecalin to $C_{10}(SPh)_{10}$.[16] Reductive defluorination of PFA proceeds through electron transfer from the electron-rich reagent to the PFA. In particular, it is now known that PFAs with tertiary C−F bonds are more prone to reduction.[17] Tertiary C−F bonds in PFAs have been implicated as the "Achilles heel", a potentially fatal feature toward chemical transformation in these unusually inert molecules.[17,18] Richmond and co-workers have shown that defluorination of perfluoromonomethylcyclohexane and perfluorodecalin can be achieved using organometallic nucleophiles at room temperature.[17b,c] Crabtree's group has made significant contributions in developing reagents and photosensitization techniques to defluorinate PFAs using various transition-metal-containing organometallic reagents.[17d−f] Reductive defluorination of saturated perfluoroalkanes has led to the emergence of the challenging frontier of "C−F bond activation in chemistry".[19] Though there are numerous reports on defluorination of PFAs possessing tertiary C−F bonds, reactions involving defluorination of PFAs devoid of tertiary C−F bonds are rare, indicating the lower propensity of PFAs without tertiary C−F bonds toward electron attachment. Richmond and co-workers have developed a Zr-based reagent which defluorinates perfluorocyclohexane, one of the very rare examples of reduction through electron transfer to a PFA sans the tertiary C−F bond.[20]

PFAs attach electrons excellently. Extensive experimental electron attachment studies have demonstrated that both cyclic and acyclic PFAs[21−47] bind low-energy electrons and can have positive electron affinities.[22−25,35−37] Cyclic PFAs are known to be better electron scavengers than their acyclic analogues.[48] The electron affinities of PFAs are crucial in determining their reactivity. Electron attachment to the PFAs in reducing environments forms radical anions; defluorination through fluoride ion loss follows.[15−19]

c-C_4F_8 (perfluorocyclobutane) has been the most thoroughly investigated cyclic PFA, both experimentally and theoretically. Electron attachment yields *c*-$C_4F_8^-$ over a wide range of electron energies below 200 meV.[32,45] Bound radical anion of *c*-C_4F_8 has been generated with γ-radiation at 130 K in a neopentane matrix and characterized by ESR spectroscopy.[49] Electron spin resonance studies confirm that the radical anion has a cyclic structure.[50] The experimentally estimated adiabatic electron affinity of *c*-C_4F_8 has been controversial. Miller and co-workers' 1994 rate constant measurements of electron attachment to *c*-C_4F_8 and subsequent equilibrium constant determination estimated the adiabatic electron affinity (AEA) to be 0.63 eV.[41] Later, Hiraoka et al. deduced a higher value, 1.05 ± 0.05 eV.[46] Recently, Miller and co-workers challenged Hiraoka et al.'s findings and confirmed that the AEA of *c*-C_4F_8 is 0.63 ± 0.05 eV.[47] Their G3(MP2) computations gave 0.59 eV. A similar value of 0.64 eV was suggested by Gallup based on ab initio MP2/6-311G(dps) computations.[51]

Our comprehensive recent study of the electron affinities of straight chain *n*-PFAs included an assessment of the AEA trend with increasing chain length.[52] The perfluorocycloalkanes (*c*-PFAs), *c*-C_nF_{2n}s, are known to possess better electron-scavenging properties than that of the straight chain PFAs.[48] Liebman, based on qualitative molecular orbital arguments, suggested over three decades ago that electron affinities of *c*-PFAs would be higher than their straight chain counterparts.[48] The bonding of *c*-PFAs depends on ring size. The angle strain is very large in the smaller rings and only diminishes in the

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larger rings. Hence, the nature of the C−C and C−F bonds in the small *c*-PFAs can be different from that of straight chain PFAs. These considerations encouraged the present computational exploration of the consequences of electron binding to *c*-PFAs: the patterns and trends in AEAs with increasing ring size and the unusual changes in geometries produced by electron attachment. Furthermore, electron attachment has been implicated as a primary process in the removal of perfluorocyclobutane, an atmospheric global warming gas. Electron affinity trends can provide insight about the vulnerability of PFAs, the potential global warming agents, to electron attachment and are likely to indicate which of these molecules will have smaller atmospheric lifetimes.

The extensive work on electron attachment of perfluorocarbons has revealed that perfluoromonomethylcycloalkanes, CF_3-*c*-PFA, with the general molecular formula $CF_3\text{-}c\text{-}C_nF_{2n-1}$, exhibit excellent electron-binding properties.[53−63] Like perfluoromonomethylcyclohexane, which has been investigated thoroughly,[53−57] CF_3-*c*-PFAs possess tertiary C−F bonds. Since acyclic PFAs with a tertiary C−F can have high adiabatic electron affinities,[52] we investigated the effects of $-CF_3$ substitution on the electron-binding properties of *c*-PFAs here.

Computational Methods

We computed energies, optimized structures, and harmonic vibrational frequencies using the GAUSSIAN 94 program[64] and the five generalized gradient approximation (GGA) exchange correlation functionals, BHLYP B3LYP, BLYP, BP86, and KMLYP, described briefly below:

B3LYP (as implemented in GAUSSIAN 94) is a hybrid of exact, “Hartree−Fock” exchange with local and gradient-corrected exchange and correlation terms, as proposed by Becke,[65] but with certain modifications to the correlation part. Instead of using the LSDA[66] and PW91[67] functional for local correlation, the B3LYP implementation[68] in GAUSSIAN 94 uses a mixture of LYP[69] and the VWN[70] correlation functional.

BHLYP is another hybrid functional, which combines Becke’s “half-and-half” exchange functional,[71] which is a 50−50 hybrid of exact exchange and local spin density approximation, and the correlation part is described by the LYP functional.

BLYP uses Becke’s pure exchange functional[72] in conjunction to the LYP functional.[68]

BP86 combines Becke’s pure exchange functional[72] with Perdew’s P86[73,74] correlation correction.

KMLYP is a recently formulated hybrid functional,[75] which combines the HF exchange functional (E_x^H) and the Slater exchange functional (E_x^S). The description of correlation is provided by a combination of the LYP functional (E_c^{LYP}) and the correlation functional of Vosko, Wilk, and Nusair (E_c^{VWN}). The KMLYP energy functional may be expressed as

$$E = E_k + E_{ze} + E_{ee} + E_x^{\ S} + a(E_x^{\ H} - E_x^{\ S}) + b(E_c^{\ LYP} - E_c^{\ VWN}) + E_c^{\ VWN}$$

where E_k is Kohn−Sham kinetic energy functional; E_{ze} is the nuclear−electron Coulomb energy functional, and E_{ee} is the classical electron−electron Coulomb repulsion energy functional. The KMLYP parameters were $a = 0.557$ and $b = 0.448$.[75]

All computations employed double-ζ basis sets with polarization and diffuse functions. These DZP++ basis sets augmented the 1970 Huzinage−Dunning[76,77] contracted double-ζ basis sets for C and F with one set of five d-type polarization functions as well as with even tempered s- and p-type basis functions.[78] The latter were designed following Lee and Schaefer’s prescription:[78]

$$\alpha_{\text{diffuse}} = \frac{1}{2}\left(\frac{\alpha_1}{\alpha_2} + \frac{\alpha_2}{\alpha_3}\right)\alpha_1$$

where α_1, α_2, and α_3 are the three smallest Gaussian orbital exponents of s- and p-type primitive functions for a given atom ($\alpha_1 < \alpha_2 < \alpha_3$). The final DZP++ set contains 19 functions per C and F atom (10s6p1d/5s3p1d). This basis set had been employed earlier with pure and hybrid DFT methods in systematic calibration EA studies on a wide range of molecules.[79] The combination of the BLYP and B3LYP functionals with the DZP++ basis set reproduced experimental electron affinities with average errors of less than 0.15 eV. However, the BLYP, BP86, and B3LYP with the DZP++ basis set combination occasionally overestimate adiabatic electron affinities, especially when closed shell neutral saturated molecules give open shell anions on electron attachment.[80] However, Brinkmann and Schaefer have shown that the KMLYP/DZP++ level reproduces satisfactorily the adiabatic electron affinity of SF_6, a difficult example of this type.[80] In contrast, the B3LYP, BLYP, BP86, and BHLYP functionals, with the same DZP++ basis set, perform poorly in this respect. This suggests that the KMLYP/DZP++ level also may give the best results in the present study.

Restricted and unrestricted DFT methods were used for the neutral and the anionic species, respectively. All structures were optimized using analytic gradients with tight convergence criteria. The computed harmonic vibrational frequencies and zero-point energies were not scaled. Numerical integration was performed using the GAUSSIAN 94 default grid of 75 radial shells with 302 angular points per shell. Adiabatic (AEA) and vertical electronic affinities (VEA), as well as

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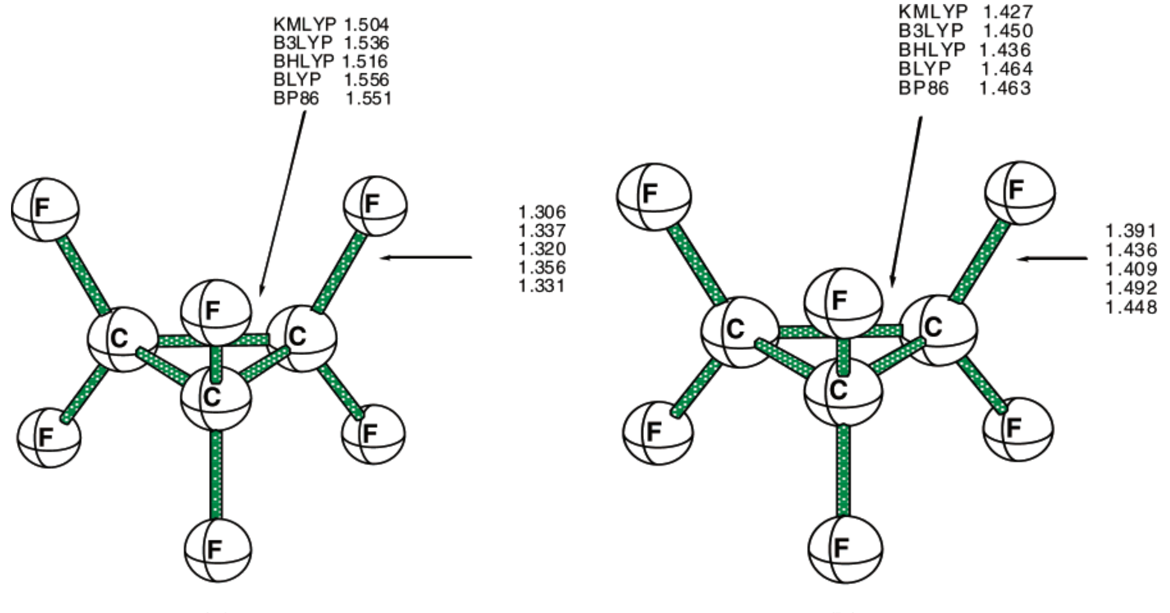

(a) (b)

Figure 1. Optimized molecular geometries of (a) neutral c-C_3F_6 (D_{3h} symmetry) and (b) anionic n-$C_3F_6^-$ (D_{3h} symmetry). All bond lengths reported are in angstroms.

the vertical detachment energies (VDE) were computed as follows:

AEA = Energy (optimized neutral) − Energy (optimized radical anion)

VEA = Energy (optimized neutral) − Energy (radical anion at the neutral geometry)

VDE = Energy (neutral at radical anion optimized geometry) − Energy (optimized anion)

Total spin densities, computed as the density difference between the α and β electrons, reveal the extent of the unpaired electron delocalization in the radical anions.

$$\rho^s(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})$$

Conflicting experimental and theoretical results regarding the AEAs of c-C_4F_8 has led us to use sophisticated ab initio correlated methods to reliably provide a reliable estimate of AEA of c-C_4F_8. For c-C_4F_8, nonzero-point-corrected AEAs were evaluated using ab initio methods. For the closed shell neutral molecule, restricted second-order Moller−Plesset perturbation theory (MP2) with frozen core was used in conjunction with Dunning augmented correlated consistent triple-ζ quality basis (aug-cc-pVTZ)[81] to optimize the molecular geometries. Unrestricted open shell MP2 with frozen core was used to optimize the anionic molecular geometry using aug-cc-pVTZ basis sets. Single-point total energies were computed employing coupled cluster with single and double excitations, and with perturbative estimation of the connected triple excitations [CCSD(T)][82a−c] for sophisticated treatment for dynamic electron correlation on the MP2-optimized molecular geometries of the anion and the neutral to obtain reliable theoretical estimate of nonzero-point-corrected AEA of c-C_4F_8 and to evaluate the performance of the several DFT functionals in predicting AEAs for cyclic PFAs. For all the correlated methods, the 1s orbitals of C and F were frozen.

Results and Discussion

A. Neutral Perfluorocycloalkanes and Their Radical Anions (*c*-PFAs). The neutral and anion molecular geometries of the c-PFAs, C_nF_{2n} ($n = 3-7$, Figures 1−5), were optimized with five pure and hybrid density functional methods. The AEAs of the c-PFAs computed using the different functionals are summarized in Table 2, and the B3LYP AEAs of the c-PFAs are compared with the AEAs of their linear chain counterparts in Table 3. AEAs computed by constraining the geometries of the c-PFA and their anions to D_{nh} symmetry are summarized in Table 4. The spin density plots of all the radical anions studied are shown in Figures 6 and 13. The singly occupied molecular orbitals (SOMOs) for the anions of c-C_3F_6, c-C_4F_8, c-C_5F_{10}, and c-C_6F_{12} are shown in Figure 7. The adiabatic electron affinities of CF_3-c-C_nF_{2n-1} ($n = 3-6$) are listed in Table 7.

The structures of the neutral c-PFAs parallel those of their hydrocarbon counterparts. All the functionals gave similar geometries. The planarization energies of the c-PFAs ranged from 0 to 64 kcal/mol at the KMLYP/DZP++ level of theory (see Table 1). c-C_3F_6 favors D_{3h} symmetry, but D_{4h} c-C_4F_8 is the transition structure for interconversion of the degenerate D_{2d} minima.[47] Two conformations of the c-C_5F_{10} five-membered perfluoroalkane ring, the C_s envelope, and the C_2 half-chair form have almost identical energies (within 0.01 kcal/mol at B3LYP/DZP++). While C_2 c-C_5F_{10} was the minimum at all levels, the C_s geometry had only a very small imaginary frequency (8i cm^{-1} at B3LYP/DZP++). Planar D_{5h} c-C_5F_{10} had a degenerate set of imaginary frequencies (22i cm^{-1}) and was 4.5 kcal/mol higher in energy at the same level. Perfluorocyclohexane, c-C_6F_{12}, prefers the chair cyclohexane conformation (D_{3d} symmetry). The most stable conformation of the seven-membered perfluorocycloheptane ring has C_2 symmetry (Figure 5a).

The pure functionals, BLYP and BP86, which generally predict longer C−C and C−F bonds than the B3LYP, KMLYP,

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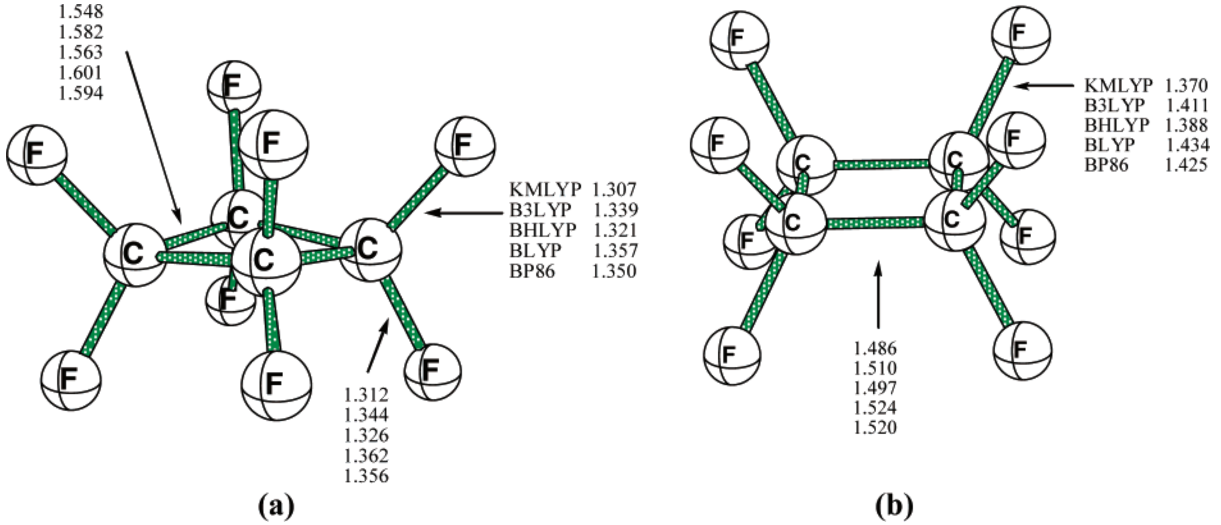

Figure 2. Optimized molecular geometries of (a) neutral c-C_4F_8 (D_{2d} symmetry) and (b) anionic c-$C_4F_8^-$ (D_{4h} symmetry). All bond lengths reported are in angstroms.

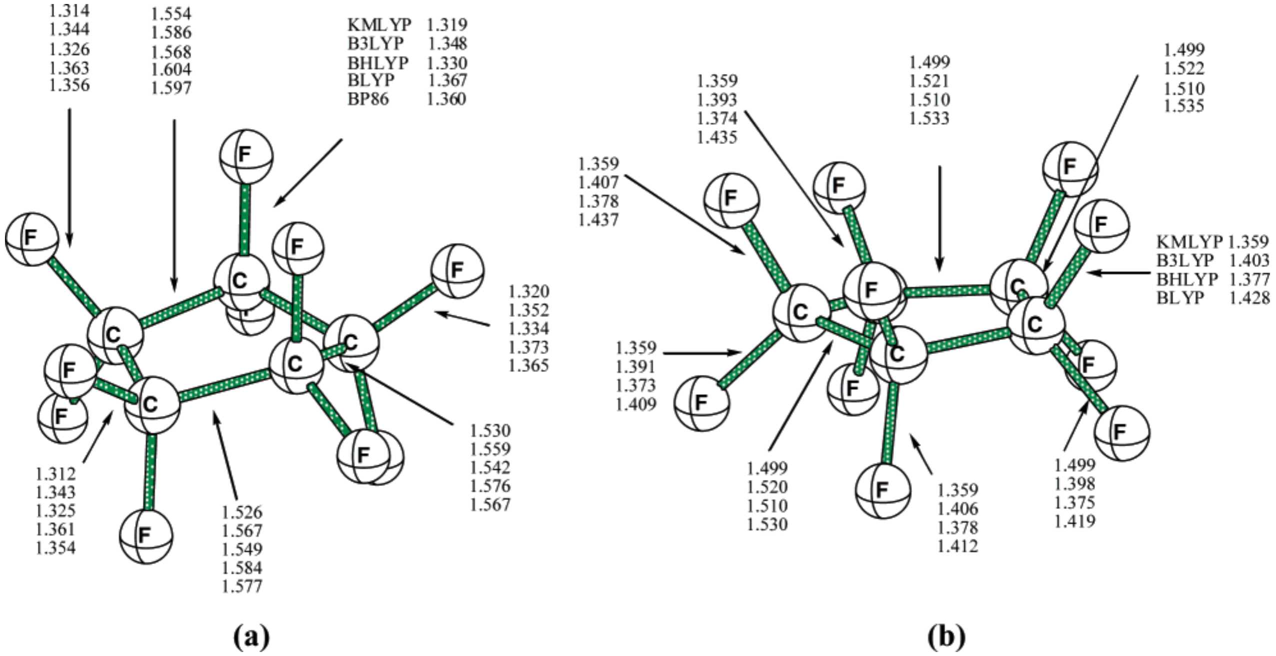

Figure 3. Optimized molecular geometries of (a) neutral c-C_5F_{10} (C_2 symmetry) and (b) anionic c-$C_5F_{10}^-$ (C_s symmetry). All bond lengths reported are in angstroms.

and BHLYP hybrid functionals, performed less well in reproducing the only experimentally known geometry (for c-C_4F_8). The electron diffraction C−C (1.566 ± 0.008 Å) and C−F (1.333 ± 0.002 Å) bond lengths[83] are reproduced best at BHLYP level (see Figure 2). The KMLYP and B3LYP C−C bond lengths also are satisfactory, while those given at BLYP and BP86 are too long. The experimental ring puckering angle in c-C_4F_8, 17.5°, is not reproduced well, even by the hybrid functionals (10.6° at KMLYP, 9.5° at B3LYP, and 7.5° at BHLYP); the pure functional puckering angles are even smaller (Figure 2).

B. *c*-PFA Radical Anions. Remarkable changes in all the *c*-PFA geometries result after electron attachment. In general, the C−C bonds shorten and the C−F bonds lengthen. These changes are quite uniform in the three-, four-, and five-membered ring *c*-PFA radical anions, where the extra electron occupies a high symmetry SOMO with C−C bonding but with C−F antibonding character. Consequently, the C−C bond length in the c-$C_3F_6^-$ D_{3h} minimum, 1.436 Å at BHLYP/DZP++ (Figure 1b), is much shorter than that (1.516 Å) in the corresponding neutral. The C−F bond lengths are opposite: much longer (1.409 Å) in c-$C_3F_6^-$ versus 1.320 Å in neutral c-C_3F_6 (also at BHLYP/DZP++).

The neutral c-C_4F_8 and the c-$C_4F_8^-$ anion exhibit the same C−C and C−F bond length relationships (Figure 2), but there is a further significant difference. While c-C_4F_8 favors a puckered D_{2d} geometry, the c-$C_4F_8^-$ anion prefers D_{4h} symmetry with all the functionals as well as at MP2.[47,51] The higher, planar

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[83] Chang, C. H.; Porter, R. F.; Bauer, S. H. *J. Mol. Struct.* **1971**, *7*, 89.

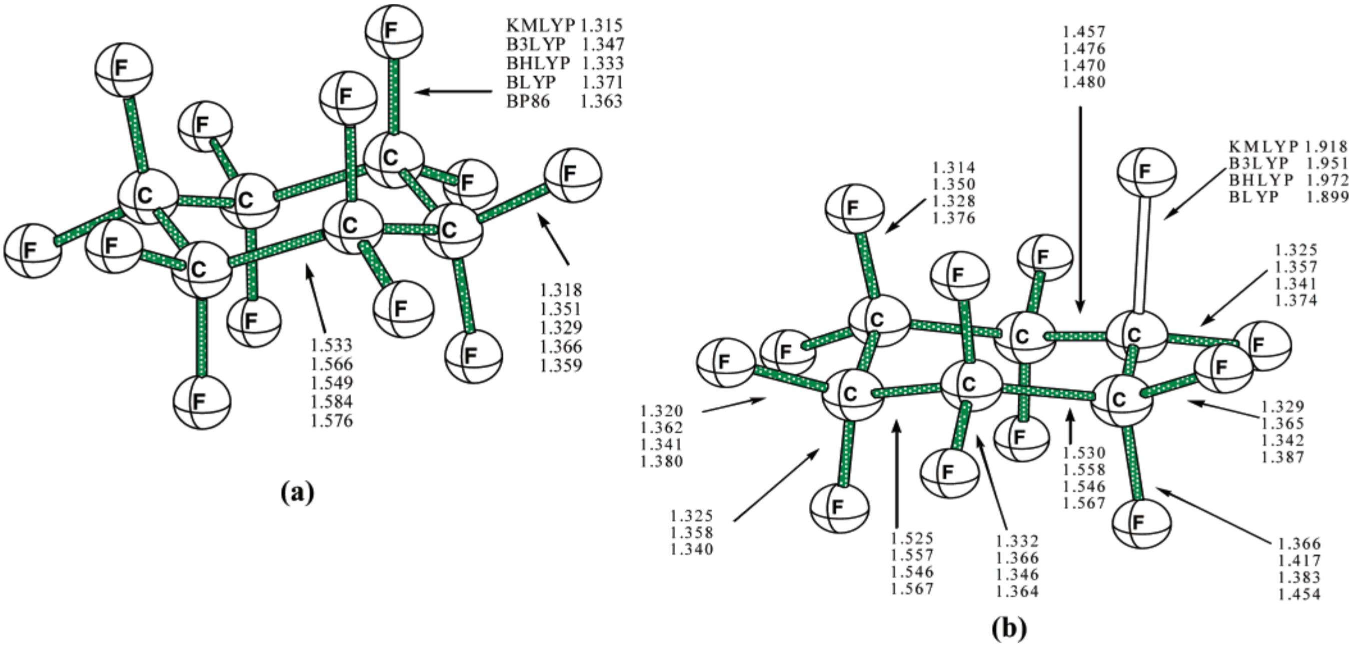

Figure 4. Optimized molecular geometries of (a) neutral c-C_6F_{12} (D_{3d} symmetry) and (b) anionic c-$C_6F_{12}^-$ (C_s symmetry). All bond lengths reported are in angstroms.

symmetry facilitates more effective delocalization of the odd electron to all the fluorines simultaneously. Other cyclic PFA radical anions tend toward planar or more nearly planar geometries (see Table 1).

KMLYP predicts a planar D_{5h} structure for the c-$C_5F_{10}^-$ radical anion. This illustrates a trend in the performance of DFT, as all the other functionals favor C_s symmetry to a small extent energetically. The deviation of the radical anion geometry from D_{5h} symmetry increases with the decreasing percentage of exact exchange in the functional employed. Thus, the pure BP86 and BLYP functionals predict the largest degree of ring puckering. However, all the c-$C_5F_{10}^-$ radical anion structures exhibit C−C bond shortening and C−F bond lengthening relative to the neutral molecule.

The c-$C_6F_{12}^-$ radical anion is unique in this cyclic set in having two low-lying minima, which differ significantly in their geometries and electronic structures. Both isomers, one with D_{3d} and the other with C_s symmetry, are predicted by all hybrid functionals (except BP86, which only gives the D_{3d} form). The D_{3d} radical anion isomer has the same point group as its neutral precursor, c-C_6F_{12}, but there are significant differences in the geometrical parameters. The c-$C_6F_{12}^-$ axial C−F bonds are lengthened more than the equatorial C−F bonds (by 0.020 Å at BHLYP/DZP++, see Figure S1 in the Supporting Information), the C−C bonds are shortened, and the ring is flattened.

The D_{3d} c-$C_6F_{12}^-$ structure marks the transition from the smaller planar D_{nh} or nearly planar rings facilitating optimum delocalization of the odd electron in the c-PFA radical anions to the larger highly nonplanar rings, where angle strain reduction is more important energetically than evenly distributed electron delocalization.

The relative energies of the two c-$C_6F_{12}^-$ minima depend on the theoretical method. The second, C_s isomer is 9.8, 6.8, 3.5, and 0.13 kcal/mol lower in energy that the D_{3d} form at the KMLYP/DZP++, BHLYP/DZP++, B3LYP/DZP++, and BLYP/DZP++ levels, respectively. D_{3d} c-$C_6F_{12}^-$ is the only minimum with pure BP86 functional.

The second c-$C_6F_{12}^-$ (C_s) radical anion isomer and the only c-$C_7F_{14}^-$ minimum (with C_1 symmetry) have a pronounced structural feature not present in the smaller radical anion rings: a single, exceptionally long C−F bond. In C_s c-$C_6F_{12}^-$, this is one of the C−F axial bonds ($r = 1.972$ Å at BHLYP/DZP++). The distorted C_s c-$C_6F_{12}^-$ structure may be considered to be either as an intermediate leading to the separated perfluorocyclohexyl radical and the fluoride anion, $C_6F_{11}^{\bullet} + F^-$ or as a complex between the two. This complexation energy is 42 kcal/mol at B3LYP/DZP++. The alternative dissociation energy of c-$C_6F_{12}^-$ into $C_6F_{11}^-$ and $F^{\bullet}$ is 50 kcal/mol. The straight chain perfluoroalkane radical anions, n-$C_nF_{2n+2}^-$, also have one extraordinarily long C−F bond on a carbon in the middle of the chain.[52] In general, the C−C bonds associated with the carbon bearing the long C−F bond are shorter ($r_{CC} = 1.470$ Å for c-$C_6F_{12}^-$ (C_s) at BHLYP/DZP++) than the other C−C bonds. Only the C−F bonds *anti-periplanar* to the exceptionally long C−F bond in c-$C_6F_{12}^-$ (C_s) are lengthened relative to the other C−F bonds. This can be explained on the basis of negative hyperconjugation, as has been discussed in our earlier work[52] (also see Figure S2 in Supporting Information). That the odd electron occupies a rather localized SOMO also is shown clearly by the spin density plots in Figure 6 (compare Figure 6d with Figure 6a−c for the smaller rings).

Like C_s c-$C_6F_{12}^-$, the sole c-$C_7F_{14}^-$ radical anion minimum (C_1, Figure 5b) has a remarkably long C−F bond, $r = 1.982$ Å at BHLYP/DZP++. The other structural features of the C_s c-$C_6F_{12}^-$ and c-$C_7F_{14}^-$ radical anions are quite similar (see Figures 4 and 5) also to those of straight chain n-PFA$^-$ radical anions.[52] This implies that the larger (but not the smaller) PFA rings actually behave like the straight chain PFAs after electron attachment.

This curious dichotomy between the structures of the smaller and the larger c-PFA radical anions is due to competition between two effects. (a) The enhanced stabilization due to delocalization of the "extra electron" over the entire molecule. This delocalization is possible only in planar, nearly planar, or

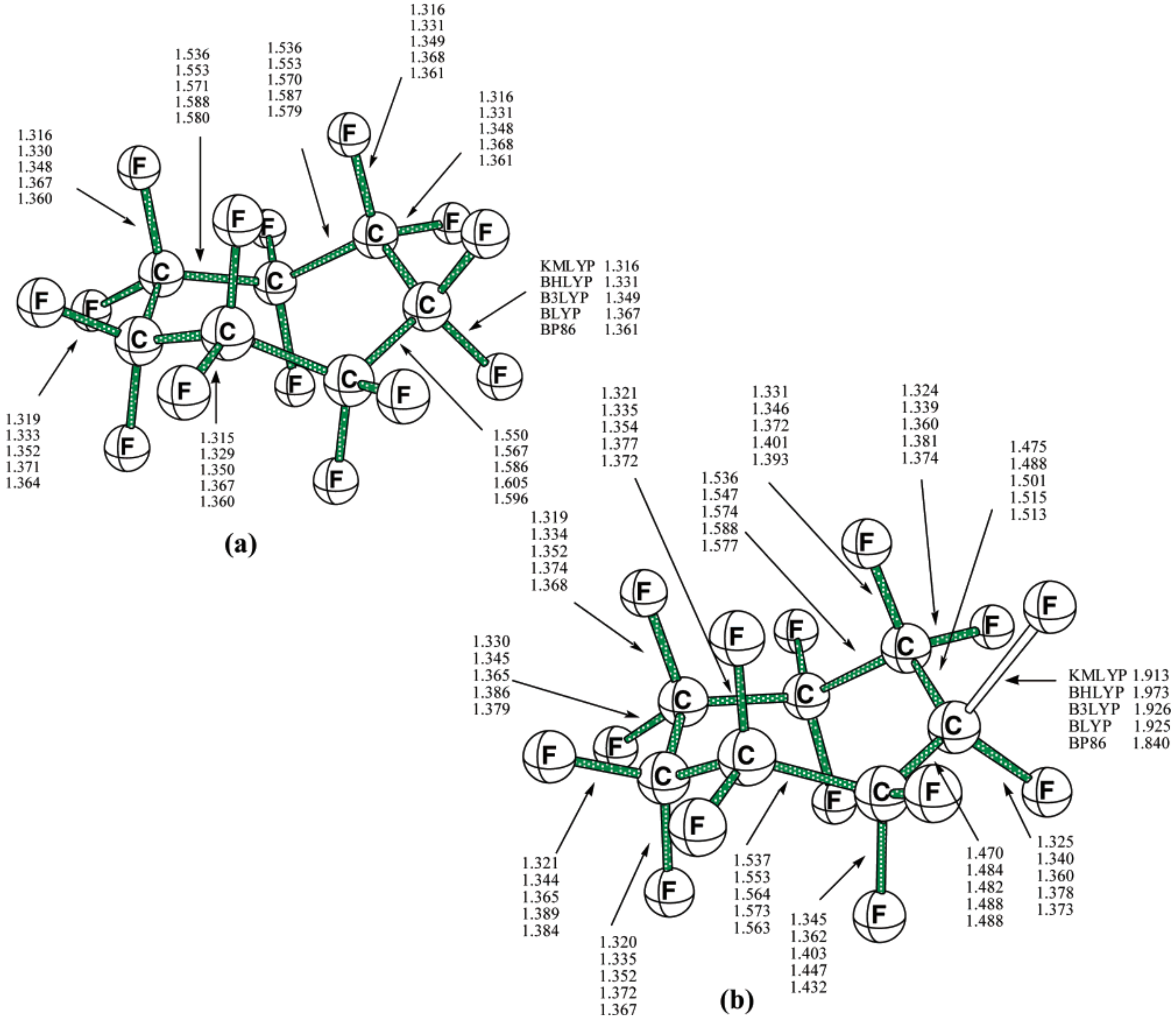

Figure 5. Optimized molecular geometries of (a) neutral $c\text{-}C_7F_{14}$ (C_2 symmetry) and (b) anionic $c\text{-}C_6F_{12}^-$ (C_1 symmetry). All bond lengths reported are in angstroms.

Table 1. Planarization Energies (in kcal/mol) Computed as the Difference between the Energy of the *c*-PFA Species in D_{nh} Symmetry and the Energy of the Same Species in Its Most Favorable Conformational Minimum

species	planarization energies at B3LYP/DZP++ (kcal/mol)	planarization energies at KMLYP/DZP++ (kcal/mol)
$c\text{-}C_3F_6$	0.0 (planar minimum)	0.0 (planar minimum)
$c\text{-}C_4F_8$	0.10	0.21
$c\text{-}C_5F_{10}$	4.54	5.16
$c\text{-}C_6F_{12}$	28.47	31.12
$c\text{-}C_7F_{14}$	58.23	64.06
$c\text{-}C_3F_6^-$	0.0 (planar minimum)	0.0 (planar minimum)
$c\text{-}C_4F_8^-$	0.0 (planar minimum)	0.0 (planar minimum)
$c\text{-}C_5F_{10}^-$	0.15	0.0 (planar minimum)
$c\text{-}C_6F_{12}^-$	17.06	16.35
$c\text{-}C_7F_{14}^-$	48.25	50.60

Table 2. Adiabatic Electron Affinities of Cyclic Perfluoroalkanes (in eV) with the DZP++ Basis Set. Zero-Point-Corrected AEAs Are Shown in Parentheses

molecule	KMLYP	B3LYP	BLYP	BP86	BHLYP
$c\text{-}C_3F_6$	0.07	0.47	0.69	0.73	−0.12
neutral D_{3h}	(0.24)	(0.64)	(0.85)	(0.89)	(0.06)
anion D_{3h}					
$c\text{-}C_4F_8$	0.52	0.85	1.05	1.13	0.28
neutral D_{2d}	(0.70)	(1.04)	(1.23)	(1.30)	(0.47)
anion D_{4h}					
$c\text{-}C_5F_{10}$	0.59	0.94	1.17	1.25	0.33
neutral C_s	(0.77)	(1.12)	(1.35)	(1.42)	(0.51)
anion C_s					
$c\text{-}C_6F_{12}$	0.27	0.68	0.89	0.94	0.19
neutral D_{3d}	(0.40)	(0.82)	(1.04)	(1.16)	(0.33)
anion C_s					
$c\text{-}C_7F_{14}$	0.27	0.64	0.83	0.80	0.18
neutral C_2	(0.40)	(0.77)	(0.98)	(0.96)	(0.32)
anion C_1					

highly symmetrical geometries, but not in highly puckered rings or in acyclic *n*-PFAs. (b) The strain energy, which must be overcome in planarizing the *c*-PFA radical anion rings in order to benefit from the optimum electron delocalization. This strain energy is too great for the larger rings due to high angle strain in the planar conformations (see Table 1 and the discussion in the Electron Affinities section, below).

The bond length differences between the neutral and PFAs and their radical anions correspond nicely to the spin density

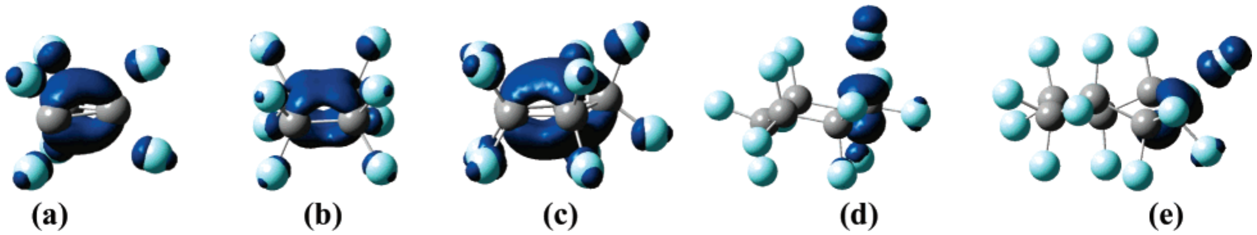

Figure 6. Spin density plots for molecular anions at B3LYP/DZP++, (a) *c*-$C_3F_6^-$, (b) *c*-$C_4F_8^-$, (c) *c*-$C_5F_{10}^-$, (d) *c*-$C_6F_{12}^-$, and (e) *c*-$C_7F_{14}^-$.

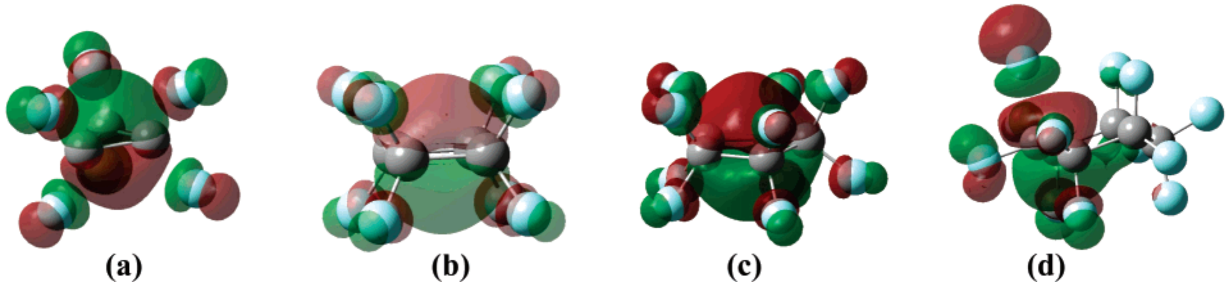

Figure 7. SOMO plots for molecular anions at B3LYP/DZP++, (a) *c*-$C_3F_6^-$, (b) *c*-$C_4F_8^-$, (c) *c*-$C_5F_{10}^-$, and (d) *c*-$C_6F_{12}^-$.

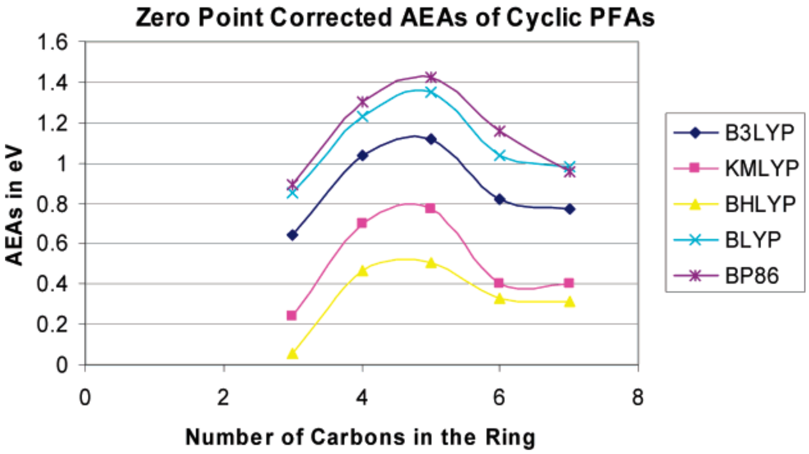

Figure 8. Plot of computed zero-point-corrected AEAs with respect to the ring size of cyclic perfluoroalkanes.

Table 3. Comparison of AEAs for Cyclic with Straight Chain PFAs at B3LYP/DZP++. Zero-Point Energy Corrected Results Are in Parentheses

No. of carbons in the ring or chain	AEA of *c*-C_nF_{2n}	AEA of *n*-C_nF_{2n+2}[a]
$n = 3$	0.47	0.26
	(0.64)	(0.39)
$n = 4$	0.85	0.40
	(1.04)	(0.53)
$n = 5$	0.94	0.50
	(1.12)	(0.65)
$n = 6$	0.68	0.56
	(0.82)	(0.69)
$n = 7$	0.64	0.58
	(0.77)	(0.71)

[a] Ref 52.

Table 4. Adiabatic Electron Affinities of Geometry Constrained Cyclic Perfluoroalkanes (in eV). Zero-Point Corrections are not Included

Neutral and anion constrained to D_{nh} symmetry	B3LYP/DZP++	KMLYP/DZP++
c-C_3F_6	0.47	0.07
c-C_4F_8	0.86	0.53
c-C_5F_{10}	1.13	0.82
c-C_6F_{12}	1.18	0.91
c-C_7F_{14}	1.08	0.86

plots and SOMOs of *c*-$C_3F_6^-$, *c*-$C_4F_8^-$, *c*-$C_5F_{10}^-$, and *c*-$C_6F_{12}^-$ (Figures 6 and 7, at B3LYP/DZP++). The SOMOs of the smaller ring radical anions all have higher symmetry: a_2'' in *c*-$C_3F_6^-$, a_{2u} in *c*-$C_4F_8^-$, and a' in *c*-$C_5F_{10}^-$. Notably, the C−C bonding and C−F antibonding character of all these SOMOs correspond to the computed C−C bond shortening and C−F bond lengthening predicted for the three-, four-, and five-membered radical anions. The D_{3d} (but not the C_s) *c*-$C_6F_{12}^-$ minimum is similar. It's a' SOMO of C_S *c*-$C_6F_{12}^-$ corresponds mainly to a C−F σ^* antibonding orbital for the long C−F bond; the delocalization throughout the C−C framework is very modest. Likewise, the C_s *c*-$C_6F_{12}^-$ spin density plot shows the unpaired electron to be localized mainly in the C−F σ^* orbital.

C. Electron Affinities of *c*-PFAs. The magnitude of the computed adiabatic electron affinities (AEAs) for the *c*-PFAs in Table 2 vary inversely with the percentage of exact exchange in the functionals employed. The pure functionals, BP86 and BLYP (which do not include exact exchange), give the largest AEAs. The values from the B3LYP hybrid functional are

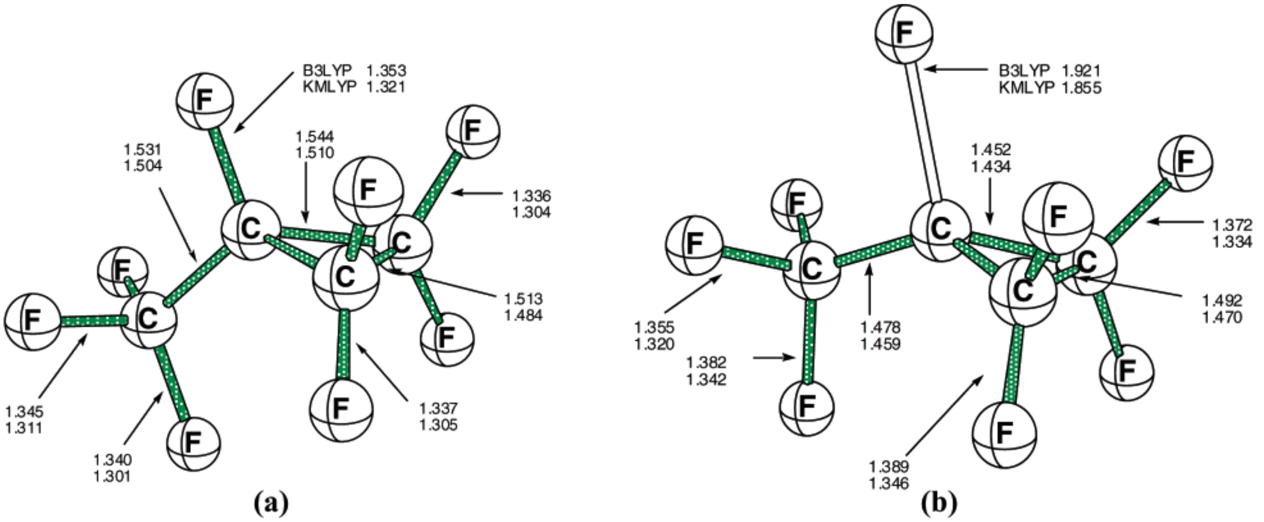

Figure 9. Optimized molecular geometries at the B3LYP/DZP++ and KMLYP/DZP++ level of theory of (a) neutral CF_3-c-C_3F_5 (C_s symmetry) and (b) anionic branched CF_3-c-$C_3F_5^-$ (C_s symmetry). All bond lengths reported are in angstroms.

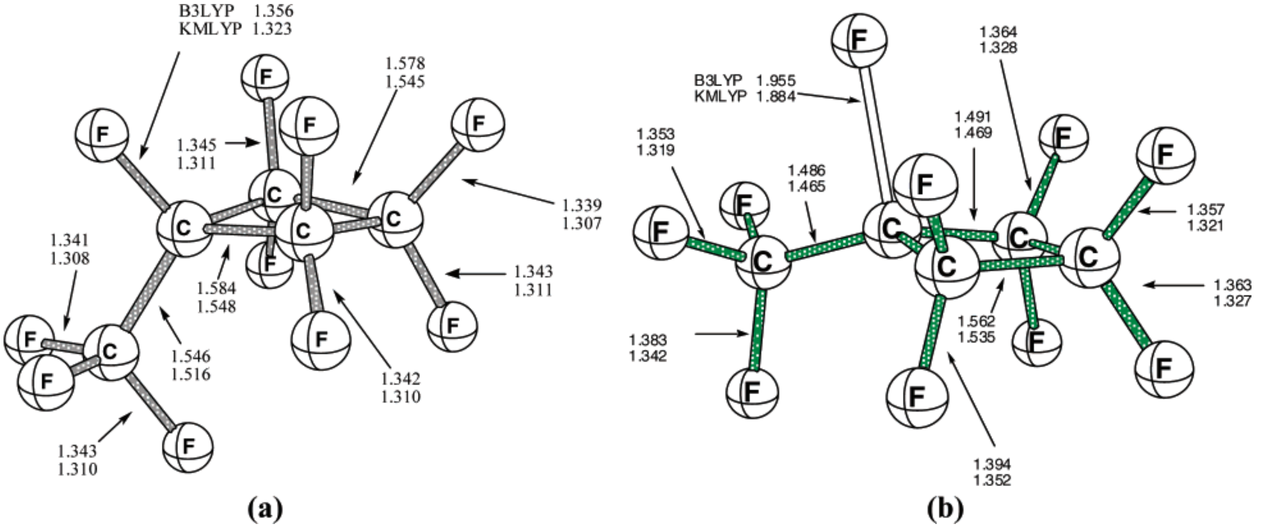

Figure 10. Optimized molecular geometries at the B3LYP/DZP++ and KMLYP/DZP++ level of theory of (a) neutral CF_3-c-C_4F_7 (C_s symmetry) and (b) anionic branched CF_3-c-$C_4F_7^-$ (C_s symmetry). All bond lengths reported are in angstroms.

smaller, and those predicted by KMLYP and BHLYP, which have the highest percentage of exact exchange, are the smallest. Brinkmann et al.'s computational AEAs of the related closed shell molecule, SF_6, were similar. [80] The zero-point corrections increase the AEAs since the frequencies of the radical anions are consistently smaller than those of the corresponding neutral PFAs. The zero-point corrections with different functionals exhibit minor variations for a particular PFA molecule studied. Note that the computed AEAs of the c-PFAs are higher than those of their linear chain counterparts (the n-PFAs) with the same number of fluorinated carbons (Table 3). Our findings thus verify Liebman's prediction that cyclic PFAs should have higher electron affinities than their linear chain analogues.[48]

The latest evaluations of the adiabatic electron affinity of c-C_4F_8 are 0.63 ± 05 eV experimentally and 0.59 and 0.64 eV at the G3(MP2) and MP2/6311G(dps) levels, respectively.[47,51] Our computations range from 0.47 to 1.30 eV, depending on the functional used (see the discussion above and Table 2). The zero-point-corrected KMLYP/DZP++ AEA, 0.70 eV, agrees best. BHLYP/DZP++ also performs fairly well in this respect. The AEAs predicted by B3LYP, BLYP, and BP86 grossly overestimate the AEA of c-C_4F_8. Thus, functionals with higher percentage of "exact exchange", such as KMLYP, may be the most suitable for predicting AEAs of related closed shell neutral molecules. As noted earlier, KMLYP also reproduces the AEA of SF_6 best.[80] The fact that KMLYP outperforms other functionals, such as B3LYP, BLYP, and BP86, in predicting AEAs of these molecules was further confirmed by quantum mechanical computations of AEAs using MP2 and CCSD(T) method. The nonzero-point-corrected AEA computed at MP2/aug-cc-pVTZ level of c-C_4F_8 is 0.56 eV, which shows good agreement with the corresponding KMLYP computed values of 0.52 eV (see Supporting Information for Table T3 of total energies and optimized geometries). The nonzero-point-corrected AEA of c-C_4F_8 at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory is 0.41 eV. The KMLYP-predicted AEA (nonzero-point-corrected) shows agreement within 0.10 eV, with highly reliable coupled cluster predicted values. By adding a zero-point correction of 0.19 eV (0.00687 au) from MP2/6-311G(d) computations[51] to our coupled cluster estimate of nonzero-point-corrected AEA, a reliable estimate of the zero-point AEA of

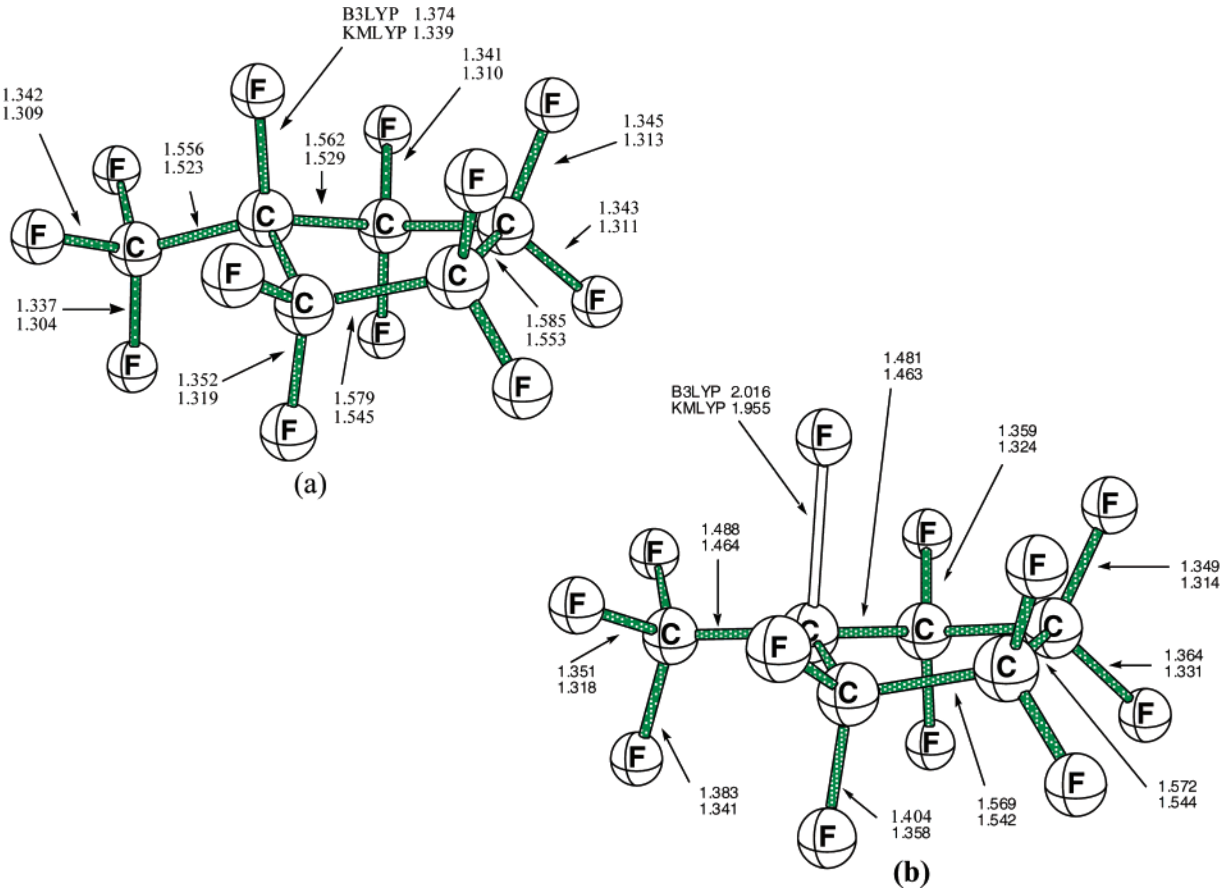

Figure 11. Optimized molecular geometries at the B3LYP/DZP++ and KMLYP/DZP++ level of theory of (a) neutral CF_3-*c*-C_5F_9 (C_s symmetry) and (b) anionic branched CF_3-*c*-$C_5F_9^-$ (C_s symmetry). All bond lengths reported are in angstroms.

c-C_4F_8 is 0.60 eV. (Note that the zero-point corrections from the DFT methods range from 0.17−0.19 eV.)

All the functionals predict an intriguing variation: the AEAs of the *c*-PFAs increase with ring size from 3 to 5 and then decrease abruptly for the six- and seven-membered rings (see Figure 8). *c*-C_5F_{10} has the highest AEA (0.77 eV at KMLYP/DZP++ + ZPE). The AEAs of the six-membered *c*-PFA are lower than those for the four-membered ring, but on average are slightly greater than the *c*-C_7F_{14} AEAs.

This variation of AEAs in the *c*-PFAs is quite unlike that of the straight chain *n*-PFA (*n*-C_nF_{2n+2}) series, where the AEAs increase with chain length.[52] This increase, which is due to anion stabilization by the larger number of electronegative CF_2 groups, falls off and ceases beyond $n = 7$.[52] Since the number of CF_2 groups increases with ring size, one would expect the AEAs to increase, as well, and to level off beyond a certain ring size. The incongruity between this expected monotonic AEA trend and that actually observed for the *c*-PFAs (Figure 8) is due to changes in the binding mode of the "extra electron" with increasing *c*-PFA ring size.

The *c*-$C_3F_6^-$, *c*-$C_4F_8^-$, and *c*-$C_5F_{10}^-$ radical anions favor planar or essentially planar geometries since all the fluorines are equivalent and help delocalize the unpaired electron in the symmetrical SOMO (Figure 7). This also is evident in the spin density plots for *c*-$C_3F_6^-$, *c*-$C_4F_8^-$, and *c*-$C_5F_{10}^-$ (Figure 6), which show that the extra electron is delocalized effectively to all the fluorines of each molecule. In contrast, for C_s $n = 6$ and $n = 7$, the extra electron is rather localized in a single C−F σ^* orbital (Figure 6). Consequently, there is an abrupt decrease in the AEA from the five- to the six-membered ring. As discussed above for the geometries, the computed AEA trends with increasing ring size (Figure 8) also arise from two competing factors: the stabilization due to the better delocalization of the extra electron in planar structures versus the strain energy associated with planarization of the rings.

The behavior of the planar forms of even the larger PFA rings in D_{nh} symmetries can readily be investigated computationally. The planarization energies are quite substantial for the six- and seven-membered neutral *c*-PFAs (31.1 and 64.1 kcal/mol, respectively, at the KMLYP level, Table 1). The angle strain in the planar D_{6h} six-membered ring, which is essentially eliminated in its nonplanar minimum, becomes greater and greater in the D_{nh} planar forms of the larger rings. In contrast, the angle strain of four- and five-membered neutral PFA rings is increased in nonplanar geometries; torsional strain is responsible for their relatively small nonplanar preferences.

Electron attachment reduces the planarization energies considerably, by about 14 kcal/mol, of the radical anions of the six- and seven-membered rings (to 16.4 kcal/mol for *c*-$C_6F_{12}^-$ and 50.6 kcal/mol for *c*-$C_7F_{14}^-$ at KMLYP/DZP++, Table 1). Unlike their neutral four- and five-membered ring counterparts, *c*-$C_4F_8^-$ and *c*-$C_5F_{10}^-$ are planar at KMLYP/DZP++. The planar radical anions are stabilized by the effective delocalization of the extra electron to all the fluorines, in contrast to the much greater localization of the extra electron in the nonplanar forms. However, the ca. 14 kcal/mol stabilization of *c*-$C_6F_{12}^-$ and

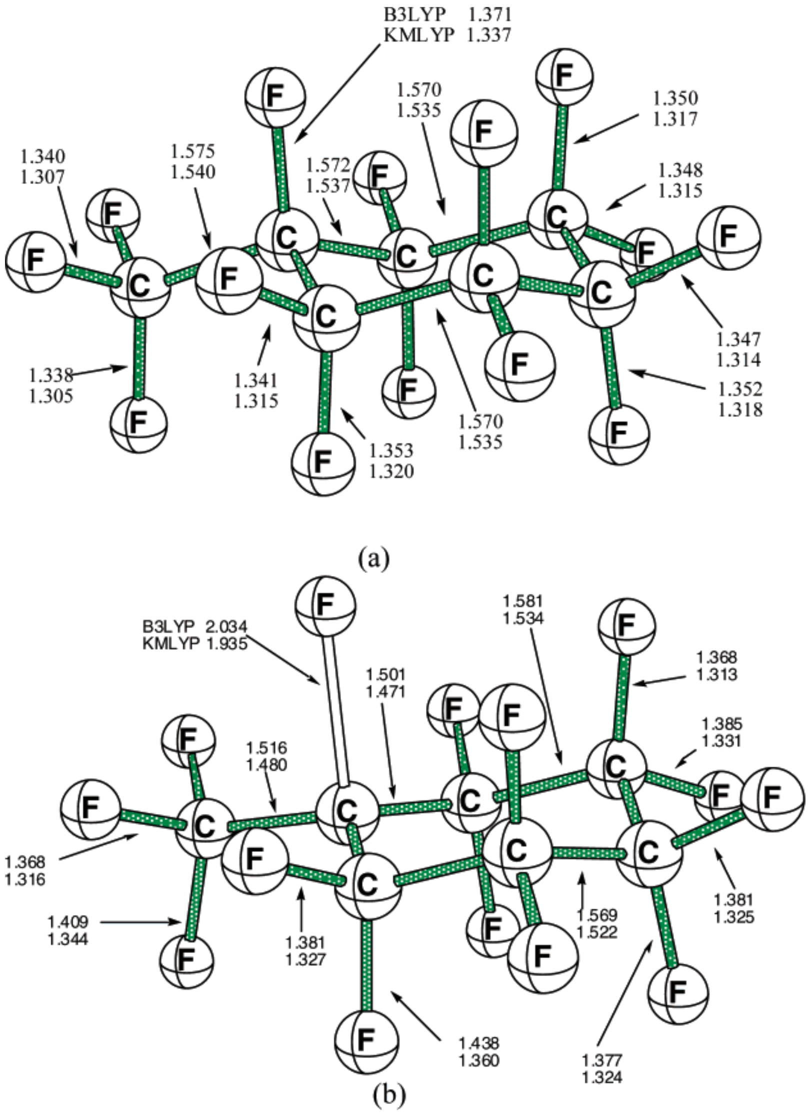

Figure 12. Optimized molecular geometries at the B3LYP/DZP++ and KMLYP/DZP++ level of theory of (a) neutral CF_3-*c*-C_6F_{11} (C_s symmetry) and (b) anionic branched CF_3-*c*-$C_6F_{11}^-$ (C_s symmetry). All bond lengths reported are in angstroms.

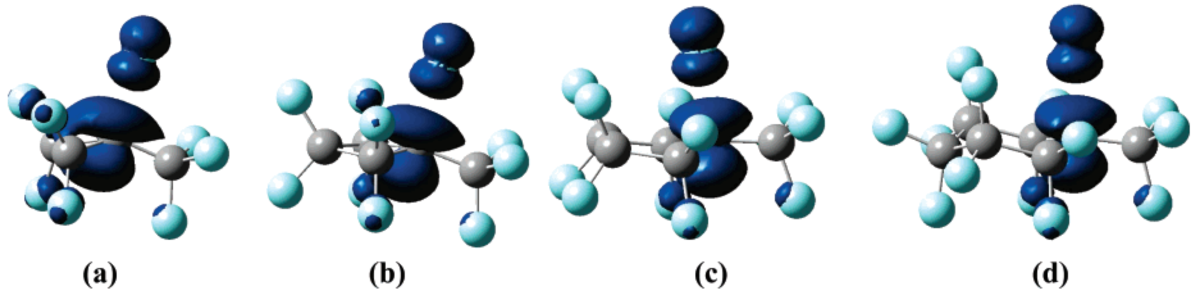

Figure 13. Spin density plots for molecular anions at B3LYP/DZP++, (a) CF_3-*c*-$C_3F_5^-$, (b) CF_3-*c*-$C_4F_7^-$, (c) CF_3-*c*-$C_5F_9^-$, and (d) CF_3-*c*-$C_6F_{11}^-$.

c-$C_7F_{14}^-$ radical anions in the D_{nh} molecular geometries is reduced, but is not large enough to overcome the high planarization energies. Hence, these radical anions prefer "localized" structures resembling the *n*-PFA molecular anions. Not surprisingly, the AEAs of *c*-C_6F_{12} and *c*-C_7F_{14} also are like those of their linear counterparts.[52] For example, the AEA difference between *c*-C_7F_{14} and *n*-C_7F_{16} is only 0.06 eV at B3LYP/DZP++ (Table 3). In contrast, the smaller *c*-PFAs have much higher AEAs than their straight chain counterparts.[52] For instance, the AEA of *n*-C_4F_{10} is 0.32 eV, whereas the AEA of *c*-C_4F_8 is 0.85 eV at B3LYP/DZP++.

Thus, the abrupt downturn in the AEA trend for the *c*-PFAs (Figure 8) is due to the change in the binding mode of the extra electron. When both the neutral and the radical anion geometries of the *c*-PFAs were constrained to D_{nh} symmetry (planar rings), the AEAs increase with increasing ring size and then fall off slightly (Table 4; note that the data are not ZPE-corrected). The planar constraint forces the *c*-PFAs to bind the extra electron

Table 5. Vertical Electron Affinities of Cyclic Perfluoroalkanes (in eV) Zero-Point Corrections are not Included

molecule	KMLYP	B3LYP	BLYP	BP86	BHLYP
c-C_3F_6	−1.11	−0.71	−1.17	−0.72	−1.33
c-C_4F_8	−0.80	−0.40	−0.18	−0.25	−0.99
c-C_5F_{10}	−0.77	−0.22	0.04	0.08	−1.0
c-C_6F_{12}	−0.66	−0.33	−0.01	−0.01	−0.87
c-C_7F_{14}	−0.61	−0.30	0.05	0.06	−0.81

Table 6. Vertical Detachment Energies of Cyclic Perfluoroalkanes Anions (in eV) Zero-Point Corrections are not Included

molecule	KMLYP	B3LYP	BLYP	BP86	BHLYP
c-C_3F_6	1.89	2.18	2.31	2.35	1.69
c-C_4F_8	1.88	2.17	2.33	2.39	1.64
c-C_5F_{10}	1.82	2.11	2.31	2.38	1.55
c-C_6F_{12}	3.64	3.45	3.11	1.94	3.52
c-C_7F_{14}	3.58	3.39	3.01	2.07	3.44

Table 7. Adiabatic Electron Affinities of CF_3-Monosubstituted PFAs (in eV) Zero-Point-Corrected AEAs are Shown in Parentheses

molecule	B3LYP/DZP++	KMLYP/DZP++
CF_3-c-C_3F_5	0.96 (1.09)	0.57 (0.70)
CF_3-c-C_4F_7	1.27 (1.39)	0.90 (1.03)
CF_3-c-C_5F_9	1.51 (1.62)	1.20 (1.32)
CF_3-c-C_6F_{11}[a]	1.45 (1.56)	1.13 (1.25)

[a] Experimental value 1.06 ± 0.15 eV.[58]

in a similar fashion and hence leads to an AEA trend similar to that observed for the *n*-PFAs. AEAs increase when more fluorines are present, but a limit is reached.

The VEAs (Table 5) are generally negative and vary rather erratically from one theoretical level to another. There are no consistent trends, in contrast to the AEAs, but KMLYP predicts that the VEAs decrease with increasing ring size, plausible in view of the increasing number of inductively stabilizing $-CF_2$ units.

With the exception of the BP86 data (Table 6), the VDEs of the three-, four-, and five-membered ring radical anions are nearly the same at each DFT level and are consistently much smaller than the six- and seven-membered ring radical anion VDEs. The small ring neutral and radical anion geometries are nearly the same, but the larger ring radical anions have elongated C⋯F bonds, a very unfavorable structural feature for the neutrals.

D. Molecular Geometries and Electron Affinities of Perfluoromethylcycloalkanes: Our earlier finding that the presence of a tertiary C−F bond in branched PFAs enhanced electron binding[52] confirmed electron attachment results on PFAs with a tertiary C−F bond, for example, i-C_4F_{10} and perfluoromonomethylcyclohexane.[43] These species form stable radical anions when bombarded with low-energy electrons. Moreover, defluorination in perfluoromonomethylcyclohexane can be achieved by employing solvated electrons,[84] which involves the loss of the "vulnerable" fluorine on the tertiary C−F bond of the molecule, initiated through radical anion formation and subsequent fluoride ion loss. Do the intriguing variations in behavior of the *c*-PFA rings toward electron attachment extend to the perfluoromonomethylcycloalkanes (CF_3-*c*-PFAs), CF_3-c-C_nF_{2n-1} (for $n = 3-6$)?

Not so, as the optimized geometries of the neutral CF_3-*c*-PFAs and their radical anions show (Figures 9−12). In sharp contrast to the *c*-PFA radical anions, all the CF_3-*c*-PFA radical anions have similar geometric features, characterized by an exceptionally long tertiary C−F bond, and resemble C_s c-$C_6F_{12}^-$ and c-$C_7F_{14}^-$ (Figures 4b and 5b). The tertiary C−F bond length is 1.337 Å in neutral CF_3-c-C_6F_{12}, but 1.935 Å in CF_3-c-$C_6F_{12}^-$ (at KMLYP/DZP++). This structure, like c-$C_6F_{12}^-$ (compare Figures 4b and 12b), also is that of an F^- anion bound to an open shell perfluorocarbon radical. All the C−C bonds to the substituted carbon in CF_3-c-$C_6F_{12}^-$ are ca. 0.06 Å shorter than those in the neutral analogue.

Moreover, the C−F bonds *anti-periplanar* to the elongated tertiary C−F bond are lengthened. The extra electron in CF_3-c-$C_6F_{12}^-$ is accommodated in a σ^* orbital dominated by the

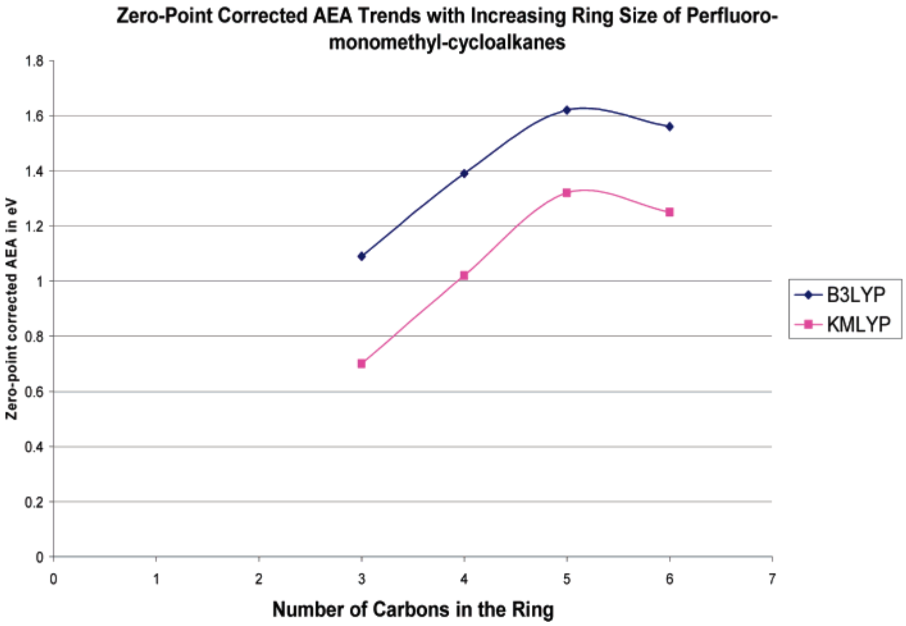

Figure 14. Plot of computed zero-point-corrected AEAs with respect to increasing ring size of CF_3-*c*-PFAs.

tertiary C−F bond but with the properly aligned three *anti-periplanar* C−F bonds helping to delocalize the negative charge through negative hyperconjugation.[52]

These geometric features of CF_3-*c*-$C_6F_{12}^-$ are very similar to those of *i*-$C_4F_{10}^-$.[52] Although there are many experimental reports concerning the perfluoromonomethylcyclohexane radical anion in the literature,[53−63] theoretical geometries and electron affinities have not been predicted before. Our zero-point-corrected AEA of perfluoromonomethylcyclohexane, 1.25 eV at KMLYP/DZP++, confirms the experimental value, 1.06 ± 0.15 eV.[57] The unusually long tertiary C−F bond in CF_3-*c*-$C_6F_{12}^-$ suggests that defluorination could take place readily by electron attachment followed by F^- cleavage. PFAs with tertiary C−F bonds should generally be vulnerable to reducing agents.

The spin density plots of the CF_3-*c*-PFA radical anions confirm that the extra electron occupies the tertiary C−F σ^* orbital-dominated SOMO (Figure 13). The AEAs of the mono-CF_3-substituted perfluorocycloalkanes (Table 7) are substantially higher than those of the analogous *c*-PFAs at the same theoretical level. The CF_3-*c*-C_nF_{2n-1} AEAs increase from $n = 3$ to $n = 5$, but then decrease slightly at $n = 6$ (see Figure 14). However, this small falloff in AEA contrasts with the sharp decrease from $n = 5$ to $n = 6$ exhibited by the *c*-PFAs (Figure 8). The trend of CF_3-*c*-C_nF_{2n-1} AEAs versus ring size (Figure 14) is strikingly similar to the AEA trends for *n*-PFAs.[52] The binding mode of the extra electron is similar in all the CF_3-*c*-$C_nF_{2n-1}^-$ radical anions; the AEAs are dominated by the presence of the tertiary C−F bond and the stabilizing $-CF_3$ substituent, which provides additional negative hyperconjugative and inductive stabilization.[85] The ring CF_2 groups provide additional inductive stabilization.

Conclusions

The ability of most perfluoroalkanes to attract electrons is remarkable. The electron count of the resulting radical anions violates the octet rule, at least formally. However, the extra electron in most PFA radical anions is accommodated in the σ^* orbital of an elongated C−F bond. As in the acyclic PFA radical anions, this feature was found here in the larger cyclic *c*-PFAs as well as in all the mono-CF_3-substituted *c*-PFA rings.[84] The AEAs of these CF_3-*c*-C_nF_{2n-1} radical anions are the largest computed here (e.g., 1.32 eV for CF_3-*c*-C_5F_9 at KMLYP+ ZPE). The extra electron in the tertiary C−F bond is stabilized inductively by the greater number of electronegative fluorines in the vicinity as well as by negative hyperconjugation.

The adiabatic electron affinities of smaller cyclic perfluoroalkanes with three- to five-membered rings are exceptional. Their AEAs are greater than not only those of comparable acyclic PFAs but also those of the larger rings. The trend with increasing ring size is unusual. The AEAs of *c*-PFAs increase, but only from *c*-C_3F_6 to *c*-C_5F_{10}, which has the largest AEA among all the *c*-PFAs. Of the various density functionals investigated, the KMLYP/DZP++ AEA estimate (0.70 eV) of *c*-C_4F_8 reproduces experiment (0.63 ± 0.05 eV)[47] best. The predicted AEA of *c*-C_4F_8 at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory is 0.60 eV, with zero-point corrections from MP2/6-311G(d) computations.[51] Comparison of AEAs predicted by several DFT methods with the results from ab initio correlated methods and experimental results convincingly demonstrates that functionals with higher percentage of "exact exchange", like KMLYP in conjunction with DZP++ basis set, can provide reliable estimate for AEAs of saturated closed shell molecules. The radical anions of these smaller rings are planar or nearly so, and the negative charge is delocalized to all the fluorines: the SOMOs have high symmetry and exhibit cyclic electron delocalization.

The significant decrease in the AEA of *c*-C_6F_{12} (which has a C_s and a less stable D_{3d} isomer) stems from the inability of the *c*-$C_6F_{12}^-$ radical anion to adopt a planar ring conformation—the strain energy is too great. *c*-PFAs radical anions with more than five carbons have nonplanar rings. Both the C_s *c*-$C_6F_{12}^-$ and the C_1 *c*-$C_7F_{14}^-$ radical anion minima have an exceptionally long C−F bond akin to the same structural feature in acyclic *n*-PFA radical anions.[52] The same is true of all radical anions of the perfluoromonomethylcycloalkanes CF_3-*c*-C_nF_{2n-1}. Although $-CF_3$ substitution increases the adiabatic electron affinities substantially, these rings do not show the anomalous AEA delocalization behavior of the smaller perfluorocycloalkanes.

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Supporting Information Available: Additional information on total energies, GAUSSIAN 94 archive entries, and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(84) Chen, X.; Lemal, D. M. *J. Org. Chem.* **2004**, *69*, 8205.

(85) This conclusion was tested and confirmed by computations on the 1,3,5-tris-equatorial-perfluorocyclohexane radical anion. The C_{3v} symmetry of its neutral precursor was not retained, even though this might have permitted delocalization of the extra electron simultaneously to three axial C−F bonds. Instead, a lower symmetry minimum with only a single, elongated C−F bond was favored. Moreover, the AEA of perfluoro-1,1-dimethylcyclobutane, which does not have a tertiary C−F bond (0.92 eV B3LYP/DZP++ +ZPE), was substantially lower than the AEA of CF_3-*c*-C_5F_{11}.