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Electron Affinities of Perfluoro Polycyclic Aromatic Hydrocarbon Radicals: C_6F_5, $C_{10}F_7$, and $C_{14}F_9$

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The optimized geometries, electron affinities, and vibrational frequencies of perfluoro polycyclic aromatic hydrocarbon radicals, namely, C_6F_5, $C_{10}F_7$, and $C_{14}F_9$, have been studied using four density functional theory methods in conjunction with augmented double-ζ plus polarization (DZP+) basis sets. Three measures of neutral/anion energy differences reported in this work are the adiabatic electron affinity, the vertical electron affinity, and the vertical detachment energy. The vibrational frequencies of these radicals are also examined. The reliable predicted adiabatic electron affinities [DZP+ B3LYP (Becke's three-parameter hybrid exchange functional with the Lee, Yang, and Parr correlation functional)] are 3.24 eV (for C_6F_5), 3.04 eV (α) and 3.34 eV (β) for the two isomers of $C_{10}F_7$, and 3.14 eV (α), 3.46 eV (β), and 2.83 eV (γ) for the three isomers of $C_{14}F_9$.

Introduction

Although benzene and naphthalene have negative electron affinities (EAs), larger polycyclic aromatic hydrocarbons (PAHs) do have the ability to bind an additional electron (possess positive EAs), and they have been frequent subjects for both experimental and theoretical analyses.[1−8] Perfluoro PAHs have also drawn recent attention.[9,10] Theoretical studies have predicted the EAs of perfluorobenzene, perfluoronaphthalene, and perfluoroanthracene to be 0.69, 1.02, and 1.84 eV, respectively.[11] Thus, the perfluoroaromatics are predicted to be effective electron acceptors, and to be important for the study of reactive intermediates related to interesting new chemistry and materials. However, the radicals derived from the perfluoro PAHs have not been studied before.

Electron affinities obtained with calibrated density functional theory (DFT) methods are rather reliable. The previous studies of various DFT functionals for EA predictions of atoms, atomic anions, and small- and medium-sized molecules[12−16] have shown that DFT results are in good agreement with experiment. A rather exhaustive review of DFT electron affinities by Rienstra-Kiracofe, Tschumper, Schaefer, Nandi, and Ellison[17] showed that functionals such as B3LYP can achieve average errors of about 0.15 eV compared to experiment. For the larger polycyclic aromatic hydrocarbons, the early work of Rienstra-Kiracofe, Barden, Brown, and Schaefer showed that the BLYP and B3LYP functionals have average absolute errors of only 0.18 and 0.19 eV when compared to experimental values.[7] Given the great difficulty associated with the experimental measurement of EAs, this is an encouraging achievement, indicating that theory can be a valuable guide in situations where meaningful experiments are not currently feasible. Accurate EA predictions on very large molecules with the DFT methods have just begun. The EAs for perfluoro PAH radicals are of special interest. Using four selected DFT methods in conjunction with DZP+ basis sets, in the present paper we examine the electron affinities of the C_6F_5, $C_{10}F_7$, and $C_{14}F_9$ radicals to establish reliable theoretical predictions in the absence of experimental results. We also compare these radical EAs with those for the corresponding closed-shell molecules.

The adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE) have been calculated as the difference of total energies according to the following formulas:

$$EA_{ad} = E(\text{optimized neutral}) - E(\text{optimized anion})$$

$$EA_{vert} = E(\text{optimized neutral}) - E(\text{anion at the optimized neutral geometry})$$

$$VDE = E(\text{neutral at the optimized anion geometry}) - E(\text{optimized anion}).$$

Theoretical Methods

The application of DFT is almost always based upon self-consistent Kohn−Sham procedures. The four different density functional or hybrid Hartree−Fock/density functional forms used here are as follows: (a) the half and half exchange functional[18] with the Lee, Yang, and Parr (LYP) correlation functional (BHLYP);[19] (b) Becke's three-parameter hybrid exchange functional[20] with the LYP correlation functional (B3LYP); (c) Becke's 1988 exchange functional[21] with Perdew's 1986 correlation functional[22] (BP86); (d) Becke's 1988 exchange functional[21] with the LYP correlation functional (BLYP).

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TABLE 1: ZPVE (eV) within the Harmonic Approximation for the C_6F_5/$C_6F_5^-$, $C_{10}F_7$/$C_{10}F_7^-$, and $C_{14}F_9$/$C_{14}F_9^-$ Systems

compd	BHLYP	B3LYP	BP86	BLYP
C_6F_5	1.34	1.27	1.22	1.20
$C_6F_5^-$	1.31	1.23	1.18	1.17
α-$C_{10}F_7$	2.20	2.09	2.01	2.00
α-$C_{10}F_7^-$	2.16	2.05	1.97	1.95
β-$C_{10}F_7$	2.20	2.09	2.00	1.98
β-$C_{10}F_7^-$	2.16	2.05	1.97	1.94
α-$C_{14}F_9$	3.06	2.92	2.81	2.78
α-$C_{14}F_9^-$	3.02	2.87	2.76	2.73
β-$C_{14}F_9$	3.05	2.91	2.79	2.76
β-$C_{14}F_9^-$	3.02	2.87	2.76	2.73
γ-$C_{14}F_9$	3.06	2.92	2.81	2.79
γ-$C_{14}F_9^-$	3.02	2.87	2.76	2.73

TABLE 2: EA_{ad}, EA_{vert}, and VDE for the Title Systems (eV)[a]

compd	method	EA_{ad}	EA_{vert}	VDE
C_6F_5	BHLYP	2.96	2.61	3.34
	B3LYP	3.24	2.90	3.62
	BP86	3.31	2.96	3.68
	BLYP	3.21	2.86	3.58
α-$C_{10}F_7$	BHLYP	2.80	2.41	3.20
	B3LYP	3.04	2.46	3.43
	BP86	3.07	2.70	3.46
	BLYP	2.96	2.59	3.34
β-$C_{10}F_7$	BHLYP	3.08	2.71	4.26
	B3LYP	3.34	2.98	3.74
	BP86	3.38	3.02	3.78
	BLYP	3.28	2.91	4.00
α-$C_{14}F_9$	BHLYP	2.89	2.51	3.29
	B3LYP	3.14	2.77	3.53
	BP86	3.18	2.82	3.56
	BLYP	3.06	2.71	3.44
β-$C_{14}F_9$	BHLYP	3.19	2.82	3.58
	B3LYP	3.46	3.10	3.84
	BP86	3.51	3.15	3.89
	BLYP	3.40	3.04	3.77
γ-$C_{14}F_9$	BHLYP	2.64	2.20	3.07
	B3LYP	2.83	2.41	3.27
	BP86	2.84	2.41	3.28
	BLYP	2.71	2.29	3.14

[a] Values are not corrected for ZPVE and were obtained with the DZP+ basis sets.

All computations for open-shell systems were done in a spin-unrestricted formalism. A standard double-ζ plus polarization (DZP) basis set is constructed from the Huzinage−Dunning[23,24] set of contracted Gaussian functions augmented with one set of five d-type polarization functions on each atom, with $\alpha_d(C) = 0.75$ and $\alpha_d(F) = 1.00$. The DZP basis is further augmented with diffuse functions; each atom receives one additional s-type and one additional set of p-type functions. The diffuse function orbital exponents are determined in an "even-tempered" sense according to the formula of Lee and Schaefer.[25] For fluorine, the exponents of the diffuse functions are $\alpha_s(F) = 0.10490$ and $\alpha_p(F) = 0.08260$. For carbon, the exponents of the diffuse functions are $\alpha_s(C) = 0.04302$ and $\alpha_p(C) = 0.03629$. The augmented basis, which will be denoted DZP+, has the technical designation (10s6p1d/5s3p1d) for both C and F.

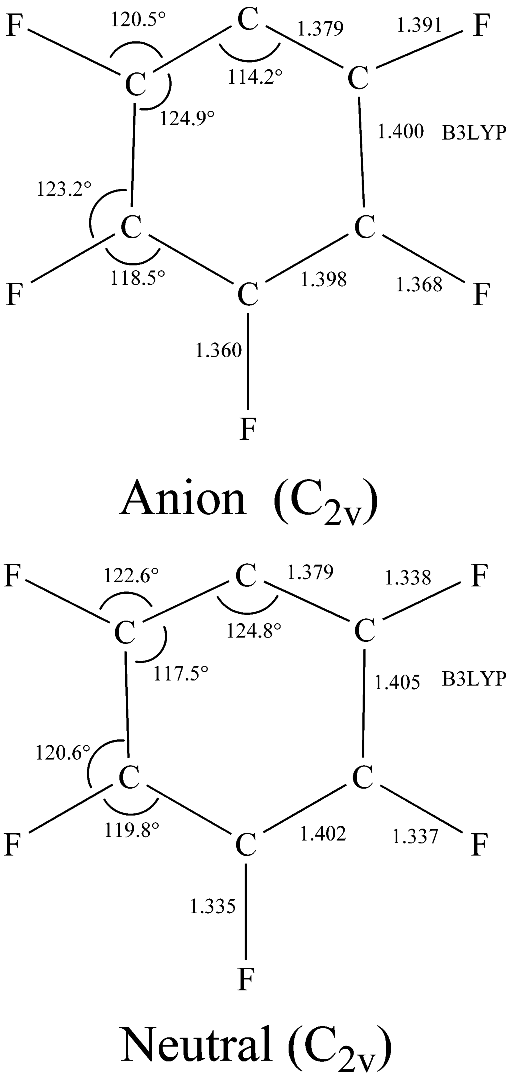


Figure 1. B3LYP-optimized geometries of the C_6F_5 radical and the $C_6F_5^-$ anion. All bond lengths are in angstroms.

Absolute energetics, optimized geometries, and harmonic vibrational frequencies for each structure were determined using the above four DFT methods. Zero-point vibrational energies (ZPVEs) evaluated at each level are presented in Table 1. The ZPVE differences between the neutrals and the corresponding anions are quite small, in the range 0.03−0.06 eV. These differences are then used for the correction of the electron affinities. Our computations were conducted with the Gaussian94 programs.[26] The default integration grid (75 302) of Gaussian94 was applied.

Results and Discussion

A. C_6F_5 and $C_6F_5^-$. Although there are no investigations, either experimental or theoretical, of the C_6F_5 radical, there are studies of benzene, naphthalene, and anthracene, as well as their perfluorinated species. Rienstra-Kiracofe, Barden, Brown, and Schaefer predicted the EAs for C_6H_6, $C_{10}H_8$, and $C_{14}H_{10}$ to be −0.88, −0.20, and 0.58 eV, respectively,[7] with the B3LYP functional. They also reported the EA of the C_6H_5 radical to be 1.01 eV,[27] a result below experiment[28] by only 0.08 eV. The theoretical predictions of the EAs for several closed-shell perfluoro PAHs (C_6F_6, $C_{10}F_8$, and $C_{14}F_{10}$) are 0.69, 1.02, and 1.84 eV, respectively.[11]

Our optimized geometries for both neutral C_6F_5 and the anion $C_6F_5^-$ are displayed in Figure 1. The equilibrium geometry of the neutral C_6F_5 in its $^2A_1$ ground state has C_{2v} symmetry. The anionic $C_6F_5^-$ has a $^1A_1$ ground state with qualitatively the same C_{2v} symmetry. Both C_6F_5 and $C_6F_5^-$ have all real harmonic vibrational frequencies with the four DFT functionals.

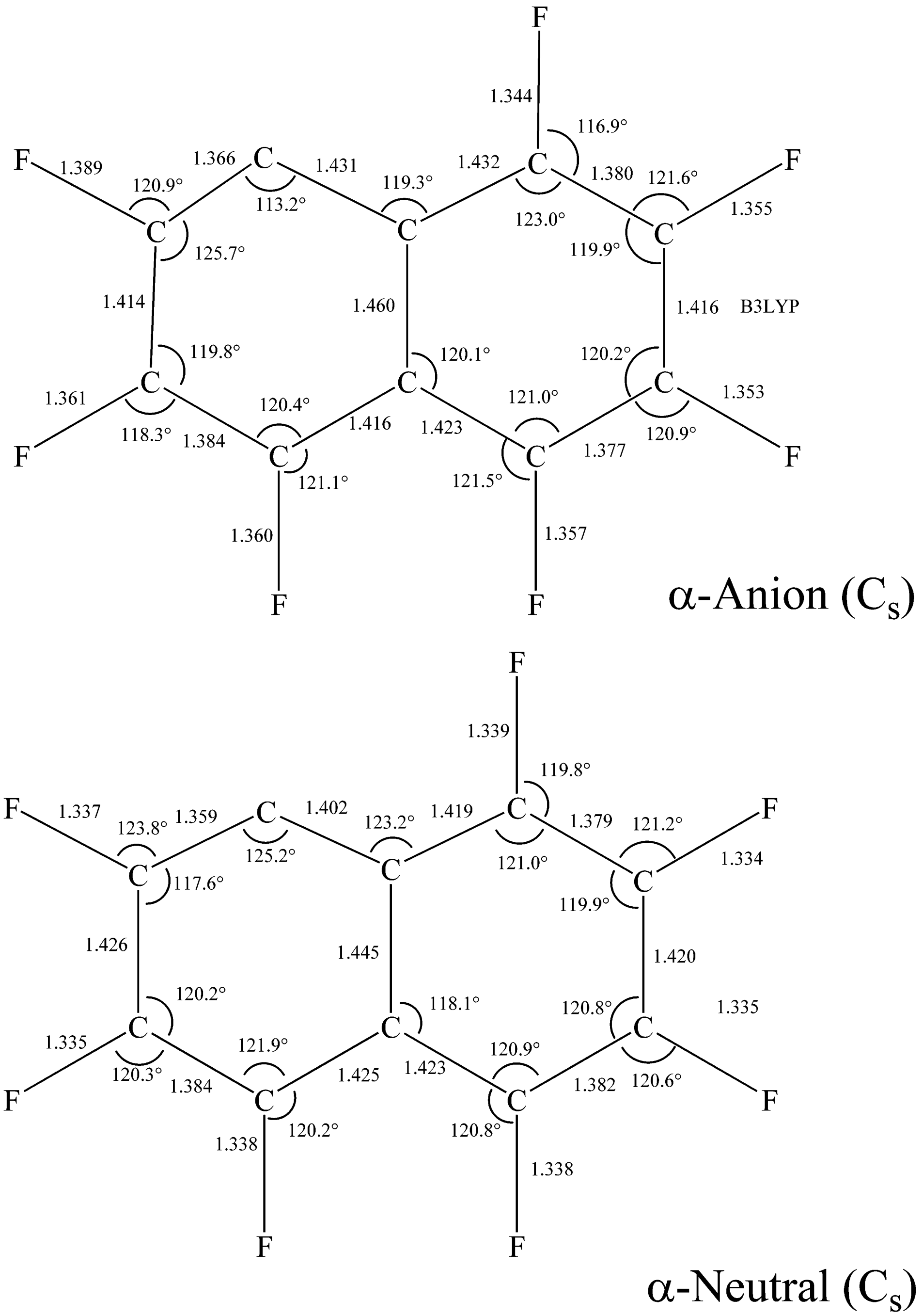


Figure 2. B3LYP-optimized geometries of the α-$C_{10}F_7$ radical and the α-$C_{10}F_7^-$ anion. All bond lengths are in angstroms.

The geometries of C_6F_5 and $C_6F_5^-$ are similar, with the most noticeable difference being a decrease in the C−C*−C angle by ~10° from the neutral to the anion (C* indicating the radical C atom). The additional electron added to form the anion increases the electron density on the radical carbon atom, and the increasing electron density causes the decrease in bond angle to provide more space for the anion lone pair. The C−C bond distances do not reveal significant differences in comparing the geometries of C_6F_5 and $C_6F_5^-$. With the B3LYP method (often thought to give the best results), the C−C bond lengths for the neutrals are in the range from 1.379 to 1.405 Å, and those for the anion are from 1.379 to 1.400 Å. We do find the C−F distances in $C_6F_5^-$ to be consistently longer than those predicted for the neutral molecule. With the DZP+ B3LYP method, these anion−neutral C−F bond distance differences range from 0.025 to 0.053 Å.

Table 2 lists our predictions for the EA_{ad}, EA_{vert}, and VDE for the title radicals. For the C_6F_5 radical, our B3LYP EA_{ad} is 3.24 eV, and the EA_{vert} is 2.90 eV. The comparable VDE for the $C_6F_5^-$ anion is 3.62 eV. The trend of the theoretical EAs with the various methods is BP86 > B3LYP > BLYP > BHLYP, with the other three methods qualitatively confirming the B3LYP predictions.

As expected, the electron affinity of the C_6F_5 radical is much larger than that for the C_6F_6 molecule. For example, our B3LYP EA_{ad} for the C_6F_5 radical is 3.24 eV, compared with 0.69 eV for the C_6F_6 molecule,[11] demonstrating qualitatively that the

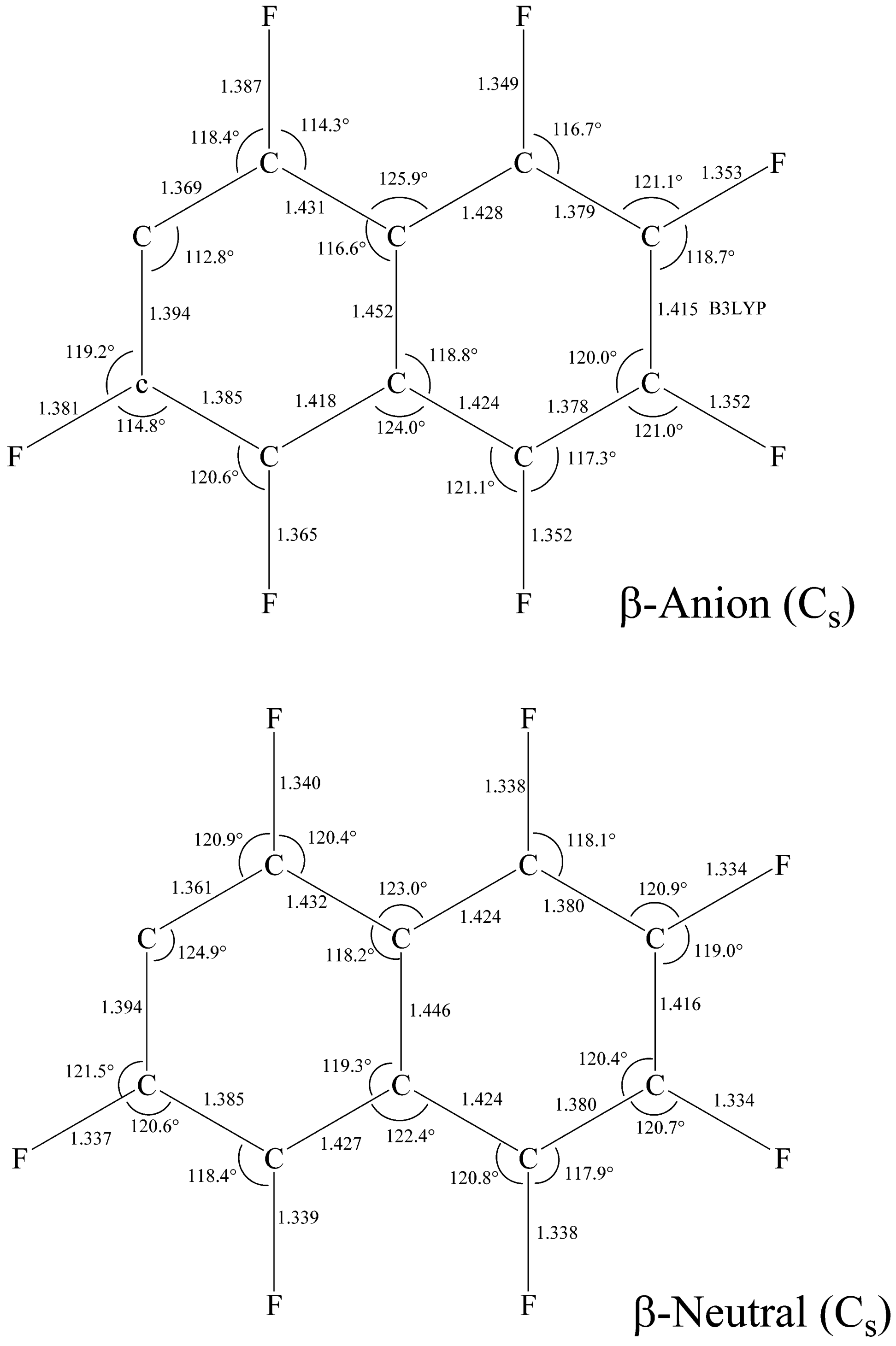


Figure 3. B3LYP-optimized geometries of the β-$C_{10}F_7$ radical and the β-$C_{10}F_7^-$ anion. All bond lengths are in angstroms.

radical has the much stronger tendency to bind an additional electron. This is expected because adding an electron to the radical makes it a more stable closed-shell system, while an extra electron added to the more stable C_6F_6 molecule makes it an open-shell system.

Compared with that of the C_6H_5 radical ($EA_{ad} = 1.01$ eV), the EA_{ad} for the C_6F_5 radical at the B3LYP level is greater by 2.23 eV. This may be correlated with their SOMO (a_1) orbital energies. Both C_6H_5 and C_6F_5 are σ radicals in $^2A_1$ ground states. The singly occupied orbital (a_1) of both molecules is in the plane on the radical carbon atom. The a_1 orbital energy for C_6F_5 (-0.33 au) is lower than that for C_6H_5 (-0.24 au).

B. $C_{10}F_7$ and $C_{10}F_7^-$. There are two isomers for the $C_{10}F_7$ radical: α-$C_{10}F_7$ (the radical electron is on the α-C position) and β-$C_{10}F_7$ (on the β-C position). Both isomers have $^2A'$ electronic ground states. Our optimized geometries for the two isomers of the $C_{10}F_7$ radical are shown in Figures 2 and 3. The α-$C_{10}F_7$ structure is predicted to lie 0.063 eV lower in energy than β-$C_{10}F_7$ (DZP+ B3LYP). The two corresponding anionic isomers, α-$C_{10}F_7^-$ and β-$C_{10}F_7^-$, have $^1A'$ closed-shell ground states, and the B3LYP energy for α-$C_{10}F_7^-$ is 0.24 eV higher than that for β-$C_{10}F_7^-$. A vibrational analysis was carried out for each radical and anion, and all are found to be genuine minima.

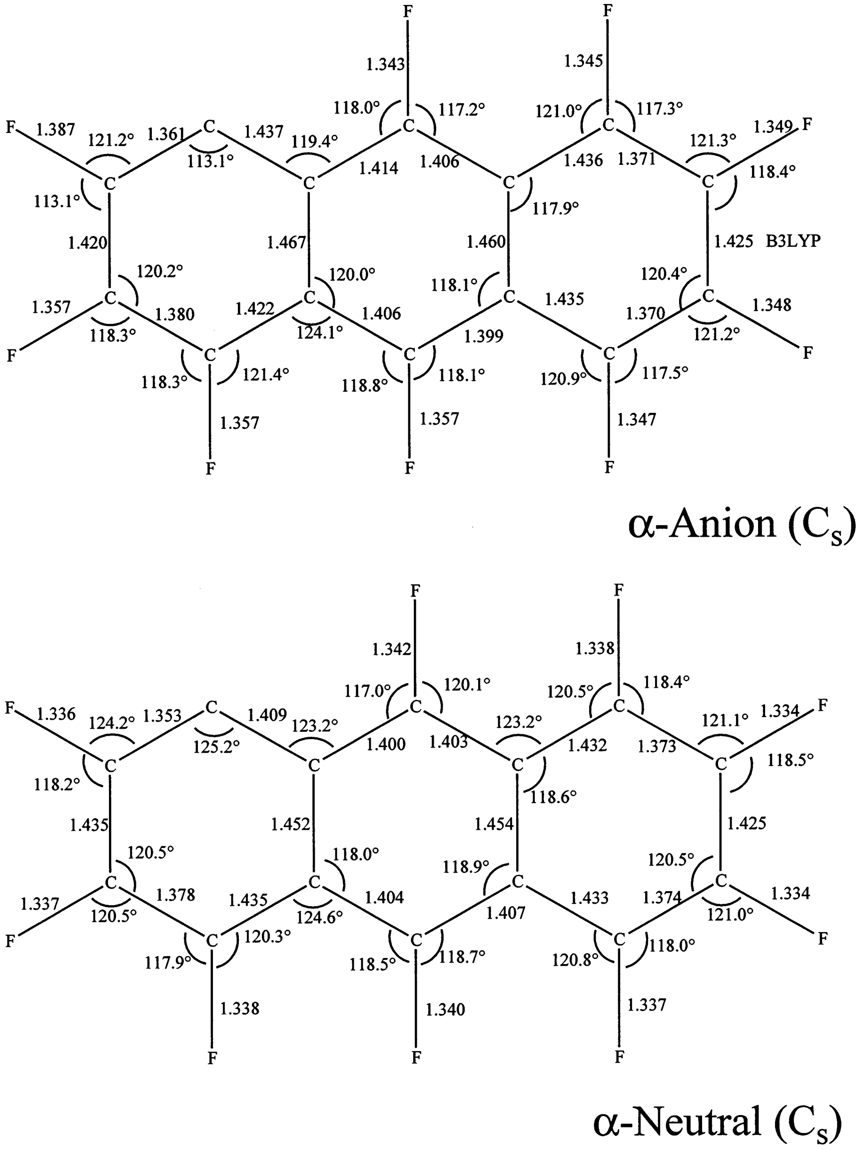


Figure 4. B3LYP-optimized geometries of the α-$C_{14}F_9$ radical and the α-$C_{14}F_9^-$ anion. All bond lengths are in angstroms.

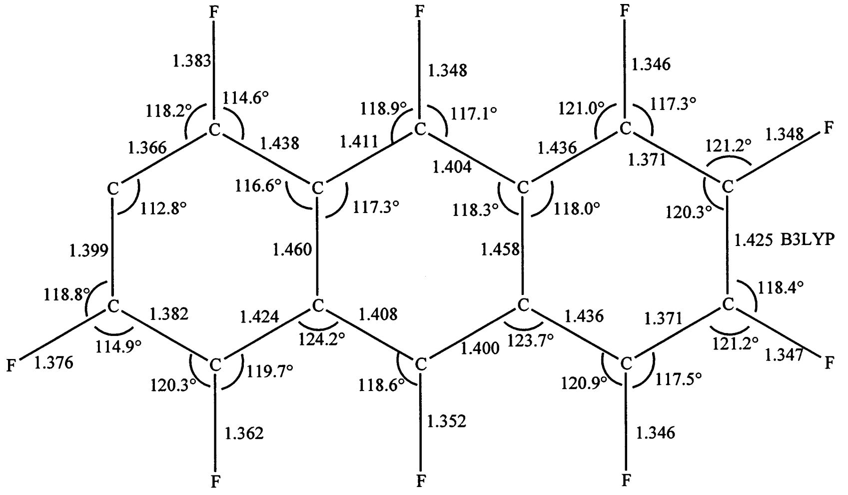
Figures 2 and 3 show that the neutral and anion geometries are quite similar. With the B3LYP method, the C−C bond lengths for neutral $C_{10}F_7$ are predicted to be 1.359−1.446 Å, and those for the anionic species are 1.366−1.460 Å. While the bond distances change only slightly, the C−C*−C angle decreases from the neutral to the anion by about 12° for both α-$C_{10}F_7$ and β-$C_{10}F_7$, in a manner analogous to the case for C_6F_5.

To our knowledge, no experimental EA values have been reported for $C_{10}F_7$. The trend of the EAs for $C_{10}F_7$ radicals predicted by the four DFT methods is similar to that for the C_6F_5 radical, in the order BP86 > B3LYP > BLYP > BHLYP. Our predicted EA_{ad} for α-$C_{10}F_7$ is from 2.80 to 3.07 eV, while for β-$C_{10}F_7$ it is from 3.08 to 3.38 eV. Our most reliable predicted EA_{ad} values, obtained with the B3LYP method, are 3.04 eV (for α-$C_{10}F_7$) and 3.34 eV (for β-$C_{10}F_7$), which are significantly larger than that for the closed-shell $C_{10}F_8$ (1.02 eV).[11]

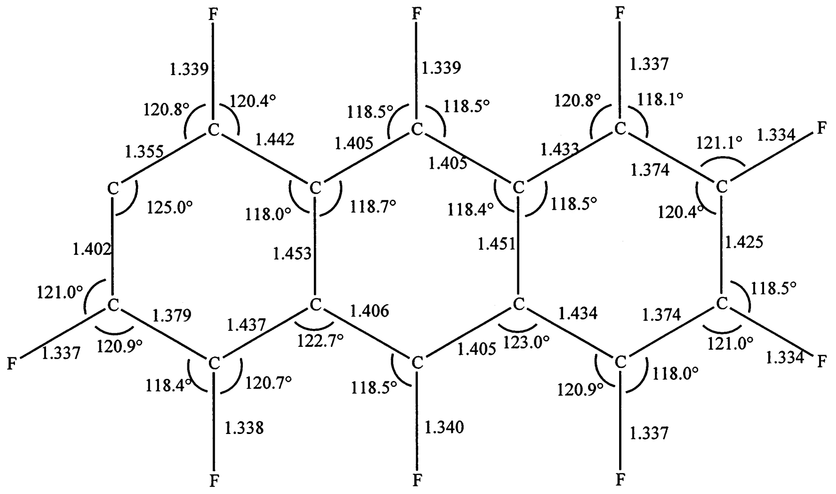
C. $C_{14}F_9$ and $C_{14}F_9^-$. We have examined three isomers for the $C_{14}F_9$ radical: α-$C_{14}F_9$, β-$C_{14}F_9$, and γ-$C_{14}F_9$ (Figures 4−6). Two of them, α-$C_{14}F_9$ and β-$C_{14}F_9$, display C_s symmetry in their $^2A'$ ground states. Their anionic counterparts, α-$C_{14}F_9^-$ and β-$C_{14}F_9^-$, have $^1A'$ ground states. The third isomer, γ-$C_{14}F_9$, has C_{2v} symmetry geometry in its $^2A_1$ ground state, and its corresponding anion, γ-$C_{14}F_9^-$, displays a $^1A_1$ ground state. The more symmetrical neutral γ-$C_{14}F_9$ structure is the global minimum, while α-$C_{14}F_9$ lies 0.02 eV above it (B3LYP), and β-$C_{14}F_9$ lies higher, 0.11 eV above the global minimum. For the anionic counterparts, the order is just the opposite. Structure β-$C_{14}F_9^-$ is the global minimum, α-$C_{14}F_9^-$ lies 0.24 eV above it with B3LYP, and the relative energy of γ-$C_{14}F_9^-$ is 0.52 eV.

Vibrational analyses show that all these structures are genuine minima, except the neutral radical β-$C_{14}F_9$, which is predicted to have an imaginary vibrational frequency by two pure DFT methods (264i cm^{-1} for BP86 and 722i cm^{-1} for BLYP), and the corresponding normal mode leads to out-of-plane C−F bonds. The minimum with C_1 symmetry has a slightly lower energy (0.6 kcal/mol by BP86 and 1.2 kcal/mol by BLYP) than the C_s structure. The geometrical change from the C_s structure to the C_1 structure is accordingly small. (The C_1 geometry predicted by BP86 and BLYP is available in the Supporting Information.)

The geometrical parameters predicted by these four different DFT methods are in general agreement with each other, with BHLYP predicting the shortest bond lengths and BLYP predicting the longest. The geometries of the anions are fairly similar



β-Anion (C_s)



β-Neutral (C_s)

Figure 5. B3LYP-optimized geometries of the β-$C_{14}F_9$ radical and the β-$C_{14}F_9^-$ anion. All bond lengths are in angstroms.

to those of their corresponding neutrals. Most bond lengths and bond angles have small changes, except those close to the radical carbon atom. With the B3LYP functional, the largest change for a C−C bond is 0.028 Å, for the longer bond to the radical carbon atom in α-$C_{14}F_9$/$C_{14}F_9^-$. Again, for the same reason as noted earlier for C_6F_5 and $C_{10}F_7$, the C−C*−C angle decreases from the neutral to the anion. The magnitudes of this decreaseare 12.1°, 12.2°, and 13.0° for the three $C_{14}F_9$ structures, respectively, with the B3LYP method.

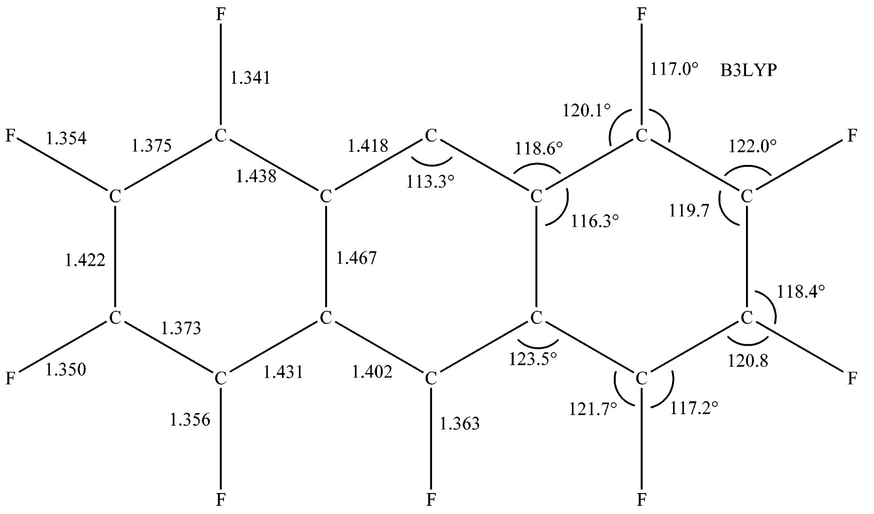
The four functionals yield the EA_{ad}, EA_{vert}, and VDE of the $C_{14}F_9$ radicals, in the order BP86 > B3LYP > BLYP > BHLYP. There are no experimental or previous theoretical data for comparison, but we expect all EAs except the BHLYP values to be reliable. From Table 2, one readily sees that the values of the electron affinities are rather different for the different isomers. For the α-$C_{14}F_9$ radical, our predicted B3LYP EA_{ad} is 3.14 eV. For the β-$C_{14}F_9$ radical, B3LYP yields an EA_{ad} somewhat higher, 3.46 eV. For the γ-$C_{14}F_9$ radical, the EA_{ad} is the lowest, 2.83 eV. Thus, the range of electron affinities is substantial, namely, 0.63 eV. The predictions for EA_{vert} and VDE follow the same trend.

D. ZPVE Corrections. When the systems of study become larger and larger, the ZPVE correction could be more and more significant. In studies of PAH EAs,[7] ZPVE corrections were found to be several tenths of an electronvolt in magnitude and to account for a significant portion (as much as 40% for coronene) of the overall EAs. It appeared that EAs for larger PAHs could be affected by the accuracy of the harmonic vibrational frequencies, regardless of the method employed.

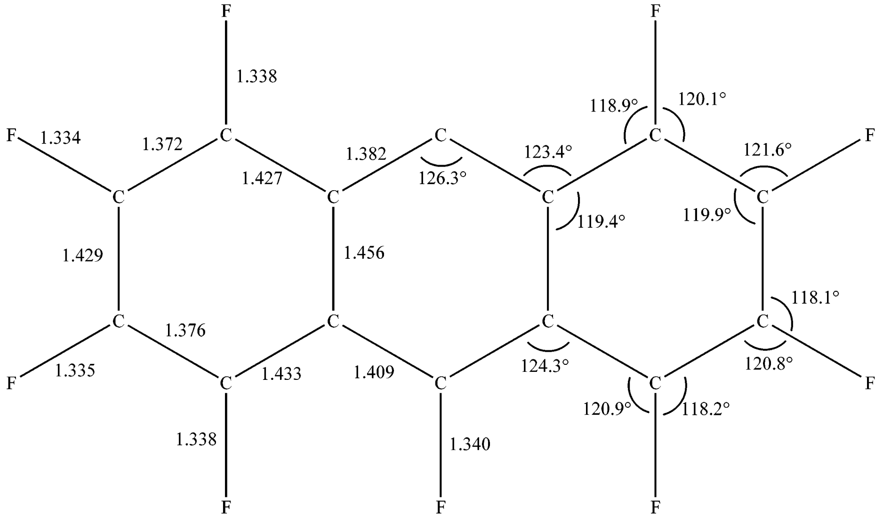
The ZPVE-corrected adiabatic electron affinities for the perfluoro PAH radicals are shown in Table 3. The ZPVE-corrected results raise the EA_{ad} by only 0.03−0.06 eV. For the C_6F_5 radical, our ZPVE-corrected EA_{ad} is 3.28 eV (B3LYP). This value raises the EA_{ad} for the C_6F_5 radical by 1%, which is much smaller than that for the parent C_6H_5 radical (6%), given by Rienstra-Kiracofe, Graham, and Schaefer.[27] The ZPVE corrections raise the EA_{ad} by an average of about 0.04 eV (1.3%) for the two $C_{10}F_7$ structures, and about 0.04 eV (1.3%) for the three $C_{14}F_9$ structures. Unlike the cases of $C_{10}H_8$ and $C_{14}H_{10}$,[7] the ZPVE corrections for perfluoro PAH radical EAs are fortunately small.

Concluding Remarks

The reliable predicted ZPVE-corrected adiabatic electron affinities from the DZP+ B3LYP method are 3.28 eV for C_6F_5,



γ-Anion (C_{2v})



γ-Neutral (C_{2v})

Figure 6. B3LYP-optimized geometries of the γ-$C_{14}F_9$ radical and the γ-$C_{14}F_9^-$ anion. All bond lengths are in angstroms.

TABLE 3: ZPVE-Corrected Adiabatic Electron Affinities (eV) for C_6F_5, $C_{10}F_7$, and $C_{14}F_9$

compd	BHLYP	B3LYP	BP86	BLYP
C_6F_5	2.99	3.28	3.35	3.24
α-$C_{10}F_7$	2.84	3.08	3.11	3.01
β-$C_{10}F_7$	3.12	3.38	3.41	3.32
α-$C_{14}F_9$	2.93	3.19	3.23	3.11
β-$C_{14}F_9$	3.22	3.50	3.54	3.43
γ-$C_{14}F_9$	2.68	2.88	2.89	2.77

3.08 and 3.38 eV for the two isomers of $C_{10}F_7$, and 3.19, 3.50,and 2.88 eV for the three isomers of $C_{14}F_9$. It is clear that perfluorinated PAH radicals will be very effective electron acceptors and may thus be useful in the study of new materials and new reactions. The ZPVE corrections raise the predictedEA$_{ad}$ values by 0.04 eV (1%) for C_6F_5, 0.04 eV (1.3%) for $C_{10}F_7$, and 0.04 eV (1.3%) for $C_{14}F_9$, respectively, indicating that ZPVE corrections in perfluoro PAH radicals are not important. Finally, in Figure 7 we compare the electron affinities of the radicals studied here with those of the analogous closed-shell perfluoro PAHs. It is seen that the radical EAs are fairly constant with respect to the number of aromatic rings, while the closed-shell systems considered previously[11] show a very notable increase in EA with respect to the number of C_6 rings. It is hoped that the present theoretical predictions will stimulate further experimental and theoretical studies of the important perfluoro PAH radicals.

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Supporting Information Available: Tables containing harmonic vibrational frequencies and IR intensities for various radicals and anions and figure depicting optimized geome-tries and bond lengths of the radicals and anions. This material is available free of charge via the Internet at http://pubs.acs.org.

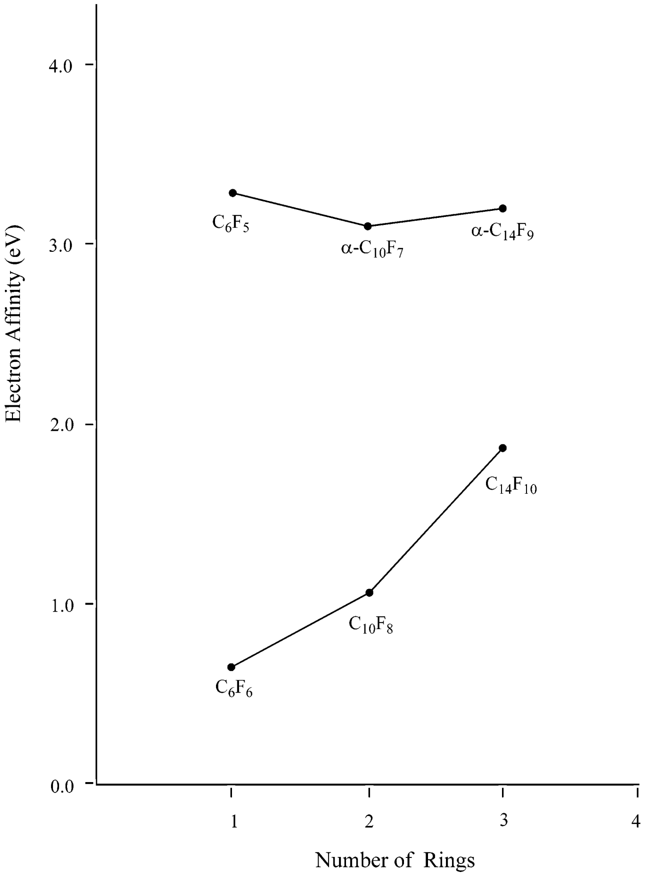

Figure 7. Comparison of the electron affinities of the closed-shell perfluorinated PAH molecules with those for the radicals formed by removal of one F atom. Note that those for $C_{10}F_7$ and $C_{14}F_9$ refer to the energy differences between the α-neutral and α-anion.

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