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Perfluorinated Polycyclic Aromatic Hydrocarbons: Anthracene, Phenanthrene, Pyrene, Tetracene, Chrysene, and Triphenylene

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The properties of perfluoroanthracene (1-$C_{14}F_{10}$), perfluorophenanthrene (2-$C_{14}F_{10}$), perfluoropyrene ($C_{16}F_{10}$), perfluorotetracene (1-$C_{18}F_{12}$), perfluorochrysene (2-$C_{18}F_{12}$), and perfluorotriphenylene (3-$C_{18}F_{12}$) and their radical anions have been studied using density functional theory (DFT). Three measures of neutral-anion energy separations reported in this work are the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE). The vibrational frequencies of these perfluoro PAHs and their radical anions are also examined. The predicted adiabatic electron affinities (DZP++ B3LYP) are: 1.84 eV, 1-$C_{14}F_{10}$; 1.41 eV, 2-$C_{14}F_{10}$; 1.72 eV, $C_{16}F_{10}$; 2.39 eV, 1-$C_{18}F_{12}$; 1.83 eV (C_i symmetry) and 1.88 eV (C_2 symmetry), 2-$C_{18}F_{12}$; and 1.69 eV, 3-$C_{18}F_{12}$. The perfluorotetracene is clearly the most effective electron captor. Perfluorophenanthrene, perfluoropyrene, perfluorochrysene, and perfluorotriphenylene, as well as their radical anions deviate from planarity. For example, the nonplanar perfluorochrysene structures are predicted to lie 7−13 kcal/mol below the pertinent C_{2h} stationary points.

Introduction

Perfluoro polycyclic aromatic hydrocarcons (PAHs) have attracted recent attention,[1−8] since they have greater electron attracting properties than the corresponding PAHs.[9,10] The high stability of benzenoid aromatic compounds gives the perfluorinated structures potential interest as electron acceptors in novel magnetic materials. Previous theoretical studies of perfluorobenzene, perfluoronaphthalene and perfluoroanthracene have predicted that the adiabatic electron affinities are 0.69, 1.02 and 1.84 eV, respectively.[11] The analogous perfluoro PAH *radicals* have higher EAs, namely 3.28 eV for the C_6F_5 radical, 3.08 and 3.38 eV for the two isomers of the $C_{10}F_7$ radical, and 3.19, 3.50, and 2.88 eV for the three isomers of $C_{14}F_9$ radical.[12] The predicted adiabatic electron affinities for analogous cyanocarbons are even higher, namely 3.53, 4.35, and 5.02 eV for $C_6(CN)_6$, $C_{10}(CN)_8$, and $C_{14}(CN)_{10}$, respectively.[13]

Thus the perfluoro-aromatic compounds are effective electron acceptors, and are promising candidates for reactive substances related to interesting new chemistry and materials. In the present research we predict molecular structures, vibrational frequencies, and neutral-anion energy separations for perfluoroanthracene (1-$C_{14}F_{10}$), perfluorophenanthrene (2-$C_{14}F_{10}$), perfluoropyrene ($C_{16}F_{10}$), perfluorotetracene (1-$C_{18}F_{12}$), perfluorochrysene (2-$C_{18}F_{12}$) and perfluorotriphenylene (3-$C_{18}F_{12}$) in order to achieve a more comprehensive view of the electron attracting properties of the larger perfluoro PAHs, for which there is still a lack of experimental data.

The calibrated DFT methods used here are known to predict electron affinities reliably. A rather comprehensive review of DFT electron affinities by Rienstra-Kiracofe and co-workers[14] showed that functionals such as B3LYP can achieve average errors of only 0.15 eV compared to the most reliable experiments. For the polycyclic aromatic hydrocarbons (PAHs), the theoretical work of Rienstra-Kiracofe, Barden, Brown, and Schaefer[15] showed that the BLYP and B3LYP functionals have average errors of 0.18 and 0.19 eV. These results are encouraging, suggesting that theory can be a valuable tool when the experimental results are unavailable.

The adiabatic electron affinities (EA_{ad}), the vertical electron affinities (EA_{vert}), and the vertical detachment energies (VDE) have been evaluated here as the difference of total energies according to the following definitions:

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

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

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

Theoretical Methods

The four different density functional or hybrid Hartree−Fock/density functional forms used here are as follows:

(a) The half-and-half-exchange functional[16] with the LYP correlation functional (BHLYP);[17]

(b) Becke's three-parameter hybrid exchange functional[18] with the LYP correlation functional (B3LYP);

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TABLE 1: Zero-Point Vibrational Energies within the Harmonic Approximation for the Title Systems in eV (kcal/mol in Parentheses)

compound	BHLYP	B3LYP	BP86	BLYP
1-$C_{14}F_{10}$	3.19 (73.6)	3.04 (70.1)	2.93 (67.6)	2.91 (67.1)
1-$C_{14}F_{10}^-$	3.06 (70.6)	2.92 (67.3)	2.81 (64.8)	2.78 (64.1)
Δ(neutral-anion)	0.13 (3.0)	0.12 (2.8)	0.12 (2.8)	0.13 (3.0)
2-$C_{14}F_{10}$	3.18 (73.3)	3.03(69.8)	2.92 (67.3)	2.89 (66.6)
2-$C_{14}F_{10}^-$	3.03 (69.9)	2.89 (66.6)	2.78 (64.1)	2.75 (63.4)
Δ(neutral-anion)	0.15 (3.4)	0.14 (3.2)	0.14 (3.2)	0.14 (3.2)
$C_{16}F_{10}$	3.51 (80.9)	3.35 (77.2)	3.22 (74.3)	3.20 (73.8)
$C_{16}F_{10}^-$	3.37 (77.7)	3.22 (74.2)	3.10 (71.5)	3.07 (70.8)
Δ(neutral-anion)	0.14 (3.2)	0.13 (3.0)	0.12 (2.8)	0.13 (3.0)
1-$C_{18}F_{12}$	4.07 (93.7)	3.88 (89.3)	3.73 (86.0)	3.70 (85.3)
1-$C_{18}F_{12}^-$	3.94 (90.8)	3.75 (86.4)	3.61 (83.2)	3.58 (82.6)
Δ(neutral-anion)	0.13 (2.9)	0.13 (2.9)	0.12 (2.8)	0.12 (2.7)
2-$C_{18}F_{12}(C_2)$	4.04 (93.0)	3.84 (88.6)	3.71 (85.5)	3.67 (84.6)
2-$C_{18}F_{12}^-(C_2)$	3.91 (90.0)	3.72 (85.7)	3.58 (82.6)	3.54 (81.7)
Δ(neutral-anion)	0.13 (3.0)	0.12 (2.9)	0.13 (2.9)	0.13 (2.9)
2-$C_{18}F_{12}(C_i)$	4.03 (92.9)	3.84 (88.5)	3.71 (85.4)	3.67 (84.5)
2-$C_{18}F_{12}^-(C_i)$	3.90 (89.9)	3.71 (85.5)	3.58 (82.6)	3.54 (81.6)
Δ(neutral-anion)	0.13 (3.0)	0.13 (3.0)	0.13 (2.8)	0.13 (2.9)
3-$C_{18}F_{12}(C_2)$	4.04 (93.2)	3.84 (88.6)	3.71 (85.5)	3.67 (84.6)
3-$C_{18}F_{12}^-(C_2)$	3.91 (90.0)	3.72 (85.6)	3.58 (82.5)	3.54 (81.5)
Δ(neutral-anion)	0.13 (3.2)	0.12 (3.0)	0.13 (3.0)	0.13 (3.1)

(c) Becke's 1988 exchange functional[19] with Perdew's 1986 correlation functional[20] (BP86);

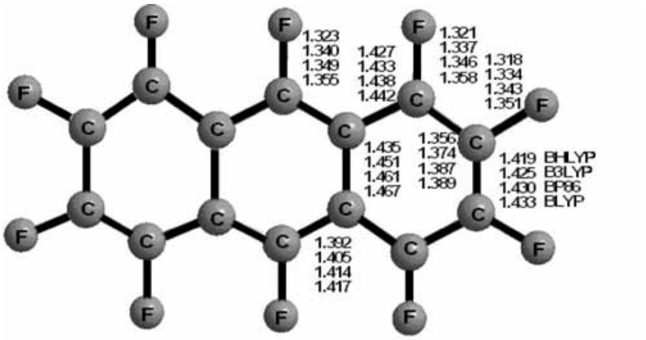
(d) Becke's 1988 exchange functional[19] with Lee, Yang and Parr's correlation functional (BLYP).

A standard double-ζ plus polarization (DZP) basis set is constructed from the Huzinaga−Dunning[21,22] 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.[23] 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.

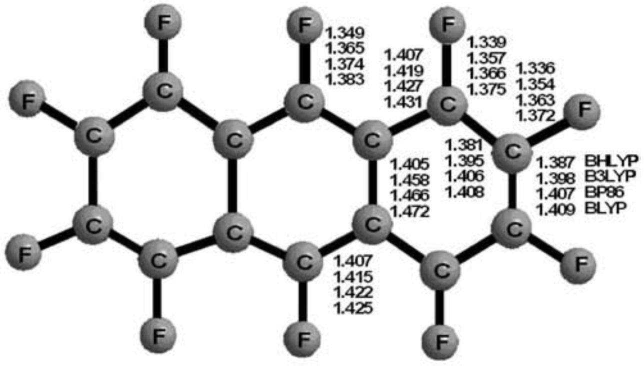
The total energeties, optimized geometries, and harmonic vibrational frequencies for each structure were determined using the above four DFT methods. Zero point vibrational energies (ZPVE) evaluated at each theoretical level are presented in Table 1. The ZPVE differences between the neutrals and the corresponding anions are not large, in the range 0.12−0.15 eV. These differences are then used for the correction of the electron affinities. Our computations were conducted with the Gaussian94 programs.[24] The default integration grid (75,302) of Gaussian94 was applied.

Results

A. 1-$C_{14}F_{10}$/1-$C_{14}F_{10}^-$ (Perfluoroanthracene). Perfluoroanthracene (1-$C_{14}F_{10}$) is the global minimum, and its electron affinity has been reported with the DZP++ B3LYP method in our previous study.[11] In the present research, we extend the latter study using the three additional DFT methods. Our optimized geometries for both neutral 1-$C_{14}F_{10}$ and the anionic 1-$C_{14}F_{10}^-$ are shown in Figure 1. All four methods predict that the D_{2h} structure for the neutral 1-$C_{14}F_{10}$ in its ^1A_g electronic state is a genuine minimum. The geometrical parameters predicted by the four DFT methods are in qualitative agreement with each other, and the trend of the C−C and C−F bond distances is in the order BLYP > BP86 > B3LYP > BHLYP. The B3LYP results are often thought to give the most reliable results,[25] and the C−C bond lengths for the neutral are in the range from 1.374 to 1.451 Å.



Neutral (D_{2h})



Anion (D_{2h})

Figure 1. Optimized geometries of the neutral perfluorinated anthracene (1-$C_{14}F_{10}$) and its radical anion. All bond lengths are in Å.

The anionic 1-$C_{14}F_{10}^-$ minimum also has D_{2h} symmetry in its $^2B_{3u}$ ground state. The C−C bond lengths for this anion range from 1.395 to 1.458 Å (B3LYP). The C−F distances for 1-$C_{14}F_{10}^-$ are found to be consistently longer than those predicted for the neutral molecule, by about 0.020 Å to 0.025 Å.

Table 2 reports our predictions for the adiabatic electron affinities (EA_{ad}), vertical electron affinities (EA_{vert}) for the neutral 1-$C_{14}F_{10}$, and vertical detachment energies (VDE) for the anionic 1-$C_{14}F_{10}^-$. The EA_{ad} value is predicted to be 1.87 eV (BP86), 1.84 eV (B3LYP), 1.74 eV (BLYP), and 1.62 eV (BHLYP), among which the BHLYP results are typically less reliable.[14] The EA_{ad} value for perfluoroanthracene (1-$C_{14}F_{10}$) is much higher than that for anthracene ($C_{14}H_{10}$), which is only 0.58 eV with the B3LYP method,[15] confirming that the perfluoro-PAHs have the significantly stronger tendency to bind an additional electron. However, as expected, the EA_{ad} for 1-$C_{14}F_{10}$ is much lower than the $C_{14}F_9$ *radical* EAs, which are 3.14 eV (α-$C_{14}F_9$ radical), 3.46 eV (*β*-$C_{14}F_9$ radical), and 2.83 eV (*γ*-$C_{14}F_9$ radical) with the same B3LYP method.[13] The theoretical EA_{vert} is in the range of 1.37 − 1.71 eV, while the theoretical VDE for the 1-$C_{14}F_{10}^-$ anion is in the range of 1.86 − 2.02 eV. The trends of EA_{vert} and VDE follow the order BP86 > B3LYP > BLYP > BHLYP.

B. 2-$C_{14}F_{10}$ and 2-$C_{14}F_{10}^-$ (Perfluorophenanthrene). There are no similar studies for perfluorophenanthrene (2-$C_{14}F_{10}$), either experimental or theoretical. Our optimized geometries for both neutral 2-$C_{14}F_{10}$ and the anionic 2-$C_{14}F_{10}^-$ are reported in

TABLE 2: Adiabatic Electron Affinities (EA_{ad}), Vertical Electron Affinities (EA_{vert}), and Vertical Detachment Energies (VDE) for the Title Systems in eV (kcal/mol in Parentheses)[a]

compound	method	EA_{ad}	EA_{vert}	VDE
1- $C_{14}F_{10}$	BHLYP	1.62 (37.3)	1.37 (31.7)	1.86 (42.8)
	B3LYP	1.84 (42.4)	1.65 (38.0)	2.02 (46.7)
	BP86	1.87 (43.1)	1.71 (39.4)	2.02 (46.7)
	BLYP	1.74 (40.2)	1.58 (36.5)	1.90 (43.9)
2-$C_{14}F_{10}$	BHLYP	1.17 (27.0)	0.84 (19.5)	1.50 (34.6)
	B3LYP	1.41 (32.4)	1.14 (26.4)	1.71 (39.4)
	BP86	1.48 (34.3)	1.23 (28.4)	1.83 (42.3)
	BLYP	1.37 (31.7)	1.11 (25.7)	1.74 (40.0)
$C_{16}F_{10}$	BHLYP	1.51 (34.9)	1.28 (29.5)	1.75 (40.4)
	B3LYP	1.72 (39.6)	1.54 (35.5)	1.90 (43.8)
	BP86	1.74 (40.2)	1.60 (36.9)	1.89 (43.7)
	BLYP	1.62 (37.4)	1.47 (34.0)	1.77 (40.9)
1-$C_{18}F_{12}$	BHLYP	2.20 (50.8)	2.01 (46.3)	2.40 (55.3)
	B3LYP	2.39 (55.2)	2.25 (51.9)	2.54 (58.6)
	BP86	2.41 (55.7)	2.30 (53.0)	2.53 (58.4)
	BLYP	2.28 (52.6)	2.16 (49.8)	2.40 (55.4)
2-$C_{18}F_{12}$ (C_i)	BHLYP	1.60 (36.8)	1.36 (31.4)	1.84 (42.3)
	B3LYP	1.83 (42.3)	1.64 (37.8)	2.04 (47.1)
	BP86	1.92 (44.2)	1.74 (40.1)	2.12 (50.3)
	BLYP	1.79 (41.3)	1.61 (37.1)	2.00 (46.1)
2-$C_{18}F_{12}$ (C_2)	BHLYP	1.66 (38.3)	1.41 (32.6)	1.94 (44.8)
	B3LYP	1.88 (43.4)	1.68 (38.9)	2.03 (46.7)
	BP86	1.94 (44.7)	1.78 (41.0)	2.11 (48.6)
	BLYP	1.81 (41.7)	1.65 (38.2)	1.98 (45.8)
3-$C_{18}F_{12}$ (C_2)	BHLYP	1.44 (33.3)	1.10 (25.5)	1.81 (41.7)
	B3LYP	1.69 (39.0)	1.40 (32.4)	2.02 (46.5)
	BP86	1.78 (41.1)	1.52 (35.0)	2.09 (48.2)
	BLYP	1.67 (38.4)	1.40 (32.2)	1.98 (45.7)

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

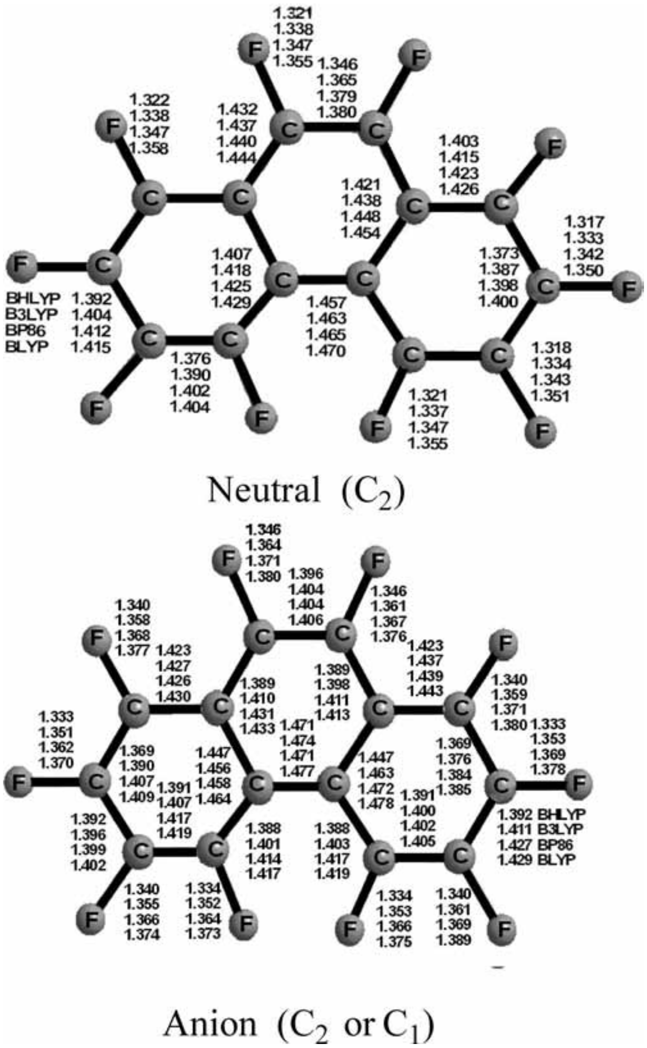


Figure 2. Optimized geometries of the neutral perfluorinated phenanthrene (2-$C_{14}F_{10}$) and its radical anion. All bond lengths are in Å.

Figure 2. For the neutral 2-$C_{14}F_{10}$, the planar C_{2v} geometry is predicted to have an imaginary vibrational frequency by all four DFT methods (55i cm^{-1} by BP86 and 54i cm^{-1} by the other three methods). Following the related normal mode, the minimum with C_2 symmetry for its ^1A electronic ground-state is obtained. This C_2 structure lies 2.3 kcal/mol with B3LYP, (2.1−2.4 kcal/mol with other methods) in energy below the C_{2v} strucuture. Compared with the anthracene 1-$C_{14}F_{10}$ structure, this nonplanar 2-$C_{14}F_{10}$ minimum is predicted to lie 2.9 kcal/mol (B3LYP) higher in energy.

Similarly, the C_{2v} geometry for the anionic 2-$C_{14}F_{10}^-$ at its $^2A_2$ ground-state is not a minimum, with an imaginary vibrational frequency for the BHLYP and B3LYP functionals, or three imaginary vibrational frequencies for the other two pure DFT methods (BP86 and BLYP). The minimum for the 2-$C_{14}F_{10}^-$ anion displays C_2 symmetry with the BHLYP functional and C_1 symmetry by the other three DFT functionals. The C_1 structure for 2-$C_{14}F_{10}^-$ is 4.2 kcal/mol (B3LYP) lower than that of the C_{2v} symmetry. Compared with the anionic anthracene 1-$C_{14}F_{10}^-$ minimum, the 2-$C_{14}F_{10}^-$ minimum is 10.6 kcal/mol (B3LYP) higher in energy.

Figure 2 shows the geometrical parameters of the neutral 2-$C_{14}F_{10}$ and the anionic 2-$C_{14}F_{10}^-$. The C−C bond distances do not reveal major differences (within 0.04 Å) in comparing the geometries of 2-$C_{14}F_{10}$ and 2-$C_{14}F_{10}^-$. The C−C bond lengths for the neutral fall in the range from 1.365 to 1.463 Å, while those for the anion are from 1.376 to 1.474 Å. As with the case of 1-$C_{14}F_{10}$, we have found the C−F distances in 2-$C_{14}F_{10}^-$ to be consistently longer than those for the neutral molecule.

The EA_{ad} value (shown in Table 2) for 2-$C_{14}F_{10}$ is predicted to be 1.48 eV (BP86), 1.41 eV (B3LYP), 1.37 eV (BLYP), and 1.17 eV (BHLYP). Again, the less reliable BHLYP result is much lower than those predicted by the other functionals. The EA_{ad} for 2-$C_{14}F_{10}$ is lower than that of the anthracene 1-$C_{14}F_{10}$ (1.84 eV, B3LYP) by 0.43 eV. With the B3LYP method the EA_{vert} for the neutral is 1.14 eV, and the VDE for the 2-$C_{14}F_{10}^-$ anion is 1.71 eV (Table 2). The trend of EA_{vert} and VDE again follows the order BP86 > B3LYP > BLYP > BHLYP.

C. $C_{16}F_{10}$ and $C_{16}F_{10}^-$ (Perfluoropyrene). Theoretical optimized geometries for perfluoropyrene ($C_{16}F_{10}$) and its anion $C_{16}F_{10}^-$ are shown in Figure 3. Both the neutral $C_{16}F_{10}$ and the radical anion $C_{16}F_{10}^-$ have $C_{2\ h}$ symmetry (nonplanar), which is slightly (0.02−0.04 kcal/mol, dependent on the various methods) lower than the planar D_{2h} structure. The bond distances predicted by the four DFT methods are in reasonable agreement with each other. With the B3LYP method, the C−C bond lengths for neutral $C_{16}F_{10}$ range from 1.365 Å to 1.436 Å, with those for the anionic $C_{16}F_{10}^-$ from 1.384 Å to 1.446 Å. The C−F distances increases from the neutral $C_{16}F_{10}$ to the anionic $C_{16}F_{10}^-$, with the greatest change being 0.23 Å.

To our knowledge, no experimental EA value has been deduced for perfuoropyrene. Table 2 reports the EA_{ad} value for $C_{16}F_{10}$ to be 1.74 eV (BP86), 1.72 eV (B3LYP), 1.62 eV (BLYP), and 1.51 eV (BHLYP), with the trend of BP86 > B3LYP > BLYP > BHLYP. The most reliable prediction is thought to be provided by the B3LYP method. The B3LYP EA_{vert} for the neutral is 1.54 eV, and the VDE for the $C_{16}F_{10}^-$

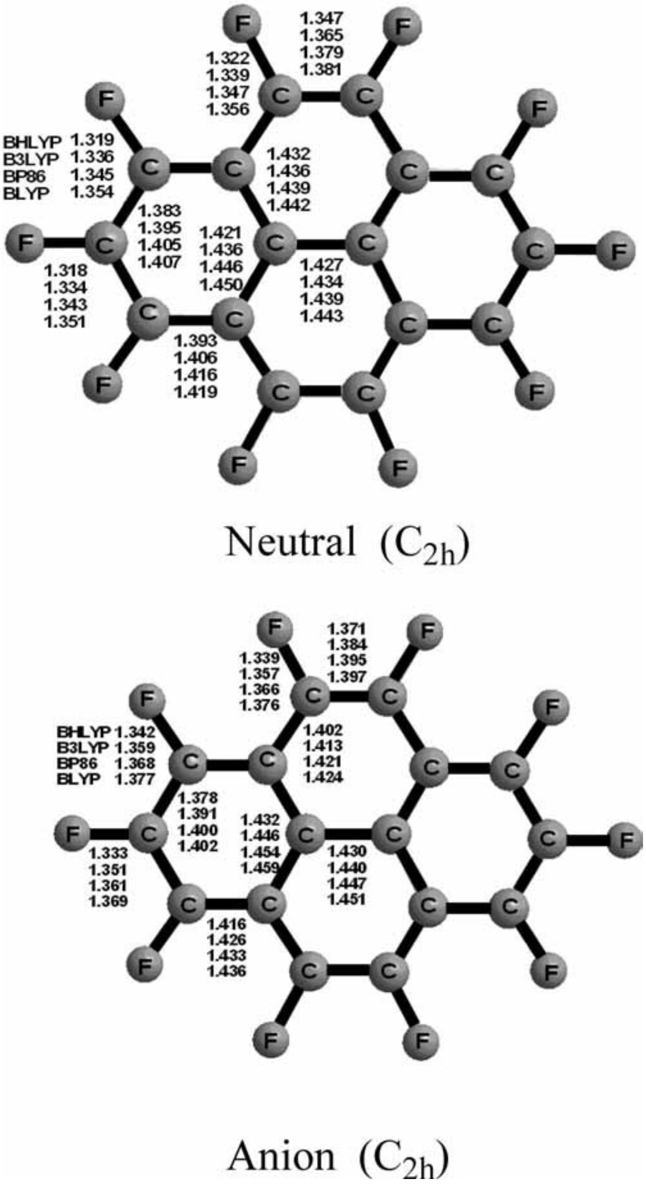


Figure 3. Optimized geometries of the neutral perfluorinated pyrene ($C_{16}F_{10}$) and its radical anion. All bond lengths are in Å.

anion is 1.90 eV. The trend of EA_{vert} and VDE values is again in the order of BP86 > B3LYP > BLYP > BHLYP.

D. 1-$C_{18}F_{12}$ and 1-$C_{18}F_{12}^-$ (Perfluorotetracene). We have examined three isomers for the $C_{18}F_{12}$ molecule: perfluorotetracene (1-$C_{18}F_{12}$), perfluorochrysene (2-$C_{18}F_{12}$), and perfluorotriphenylene (3-$C_{18}F_{12}$). Perfluorotetracene (1-$C_{18}F_{12}$) has the four aromatic rings fused in a linear fashion. Our optimized geometries for perfluorotetracene are displayed in Figure 4. The molecule has D_{2h} symmetry in its ^1A_g ground state. Similar to the case of $C_{16}F_{10}$, the C−C and C−F bond distances are in the order of BLYP > BP86 > B3LYP > BHLYP. The B3LYP results of the C−C bond lengths for the neutral are in the range from 1.371 to 1.457 Å.

Our optimized geometries for the radical anion 1-$C_{18}F_{12}^-$ are also displayed in Figure 4. This structure has D_{2h} symmetry in its ^2B_g ground state. Note that the geometric parameters for 1-$C_{18}F_{12}$ and 1-$C_{18}F_{12}^-$ predicted by the four DFT methods (Figure 4) are qualitatively similar. With the B3LYP method, the C−C and C−F bond distances for the anion range from 1.385 to 1.463 Å and from 1.350 to 1.359 Å, respectively. The most noticeable difference is a decrease in the C−F distances of about 0.016−0.020 Å from 1-$C_{18}F_{12}$ to 1-$C_{18}F_{12}^-$.

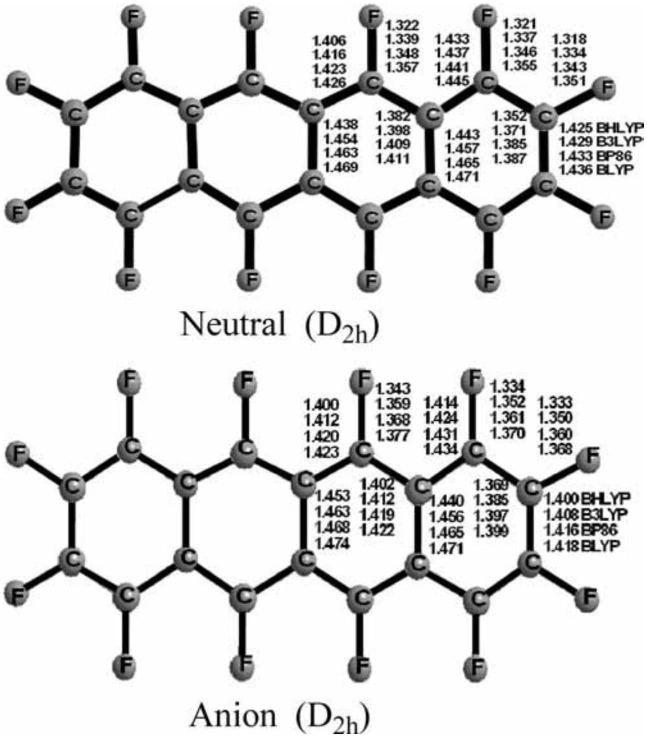


Figure 4. Optimized geometries of the neutral perfluorinated tetracene (1-$C_{18}F_{12}$) and its radical anion. All bond lengths are in Å.

The BP86 predicted EA_{ad} (2.41 eV, Table 2) is somewhat larger than that predicted by the other methods. The B3LYP EA_{ad} is next at 2.39 eV, followed by BLYP (2.28 eV) and BHLYP (2.20 eV). As expected, EA_{ad} for 1-$C_{18}F_{12}$ is much larger than that for the parent tetracene molecule $C_{18}H_{12}$ (EA_{ad} = 1.13 eV).[15] The EA_{vert} value (shown in Table 2) for the 1-$C_{18}F_{12}$ molecule is 2.25 eV. The comparable VDE for the 1-$C_{18}F_{12}^-$ radical anion is 2.54 eV.

E. 2-$C_{18}F_{12}$ and 2-$C_{18}F_{12}^-$ (Perfluorochrysene). The second $C_{18}F_{12}$ isomer considered here is perfluorochrysene (2-$C_{18}F_{12}$), which has the four aromatic rings fused in a zigzag arrangment. Unlike the parent chrysene ($C_{18}H_{12}$), the planar $C_{2\ h}$ structure for the neutral 2-$C_{18}F_{12}$ is predicted to have two small imaginary vibrational frequencies by all four DFT methods (76*i* and 69*i* cm^{-1} by BHLYP, 74*i* and 67*i* cm^{-1} by B3LYP, 74*i* and 66*i* cm^{-1} by BP86, and 72*i* and 65*i* cm^{-1} by BLYP).

Following the related two normal modes, two distinct nonplanar minima with C_2 symmetry (^1A ground state) and C_i symmetry (^1A_g ground state) emerge. These are the *cis* and *trans* isomers of perfluorochrysene. Our optimized geometries for these two conformers are displayed in Figures 5 and 6, respectively. These two structures lie below the perfectly C_{2h} structure by 10.5 and 6.6 kcal/mol (B3LYP), respectively, with the *cis* C_2 structure being lowest. Except for their respective *cis* and *trans* orientations the neutral C_2 and C_i structures have nearly identical geometrical parameters. Like the other structures, the C−C and C−F bond distances fall in the order BLYP > BP86 > B3LYP > BHLYP. The C−C bond lengths for the neutral lie in the range 1.370 to 1.456 Å for the *trans* C_i structure, while they are 1.372 to 1.452 Å for the *cis* C_2 structure. It is not unreasonable to ask whether the nonplanar *cis* and *trans* minima predicted here might be spurious. Certain basis sets combined with particular theoretical methods are known to erroneously predict benzene and other arenes to be nonplanar.[26,27]

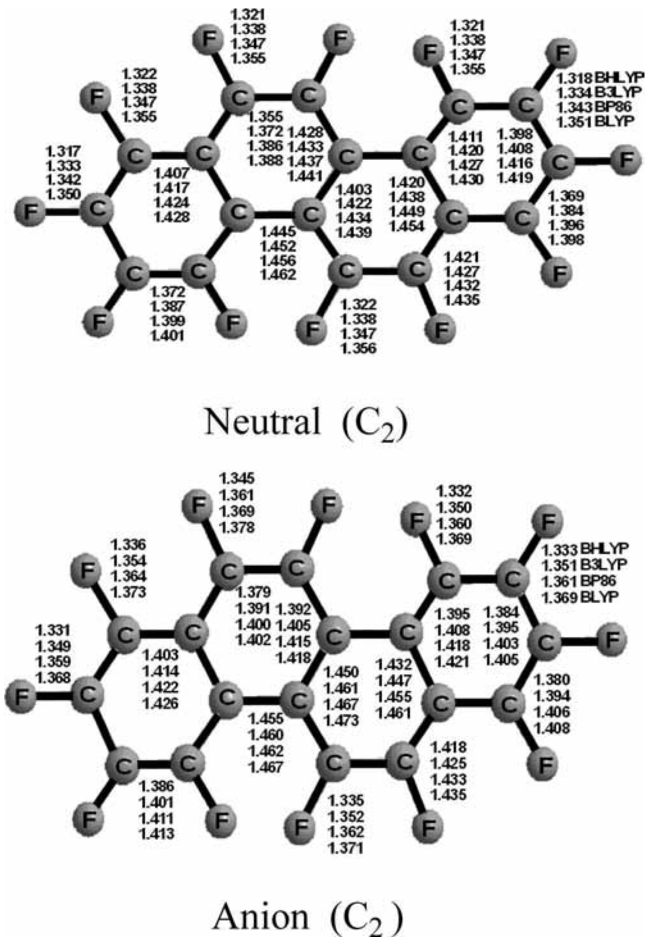


Figure 5. Optimized geometries of the neutral perfluorinated chrysene (2-$C_{18}F_{12}$) and its radical anion with C_2 symmetry. All bond lengths are in Å.

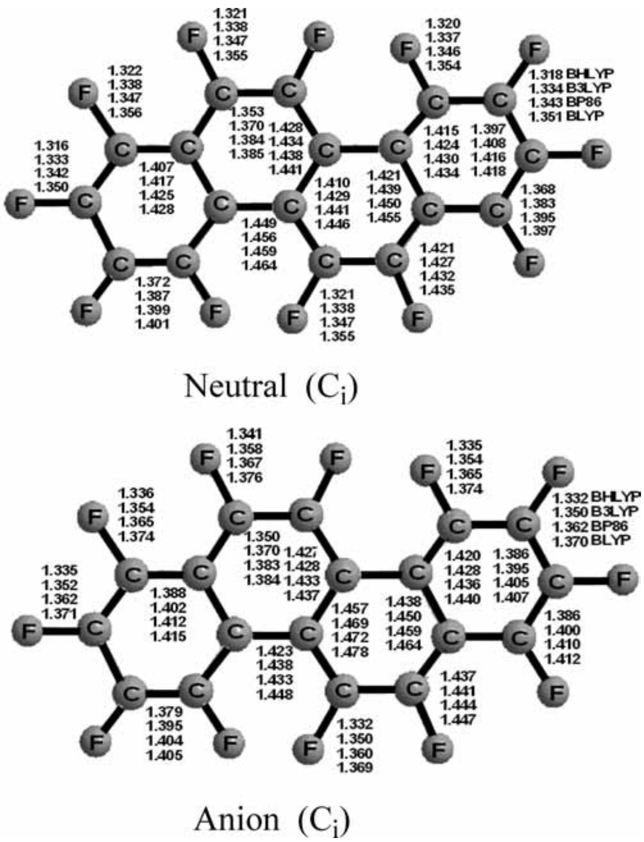


Figure 6. Optimized geometries of the neutral perfluorinated chrysene (2-$C_{18}F_{12}$) and its radical anion with C_i symmetry. All bond lengths are in Å.

However, the DZP++ basis set used here properly predicts the structures of such arenes to be planar. Hence, we expect that our nonplanar *cis* and *trans* minima for perfluorochrysene are genuine.

For the anionic 2-$C_{18}F_{12}^-$, the symmetry-constrained planar C_{2h} structure (in its ^2B_g ground state) has two small imaginary vibrational frequencies (76*i* and 69*i* cm^{-1} by BHLYP, 75*i* and 68*i* cm^{-1} by B3LYP, 77*i* cm^{-1} and 69*i* cm^{-1} for BP86, and 76*i* cm^{-1} and 69*i* cm^{-1} for BLYP). Similar to the neutral structure, these imaginary frequencies lead to two distinct minima: with C_2 symmetry (the *cis* ^2B ground state) and with C_i symmetry (the *trans* ^2A_g ground state). They are lower in energy than the C_{2h} structure by 12.5 or 7.5 kcal/mol (B3LYP), respectively, with the *cis* C_2 structure being lowest (as found for the neutral perfluorochrysecene). The C−C bond distances for the anion range from 1.370 to 1.469 Å for the C_i structure; and 1.391 to 1.461 Å for the C_2 structure. The C−F distances for the 2-$C_{18}F_{12}^-$ radical anion are consistently longer than those predicted for the neutral molecule. With the B3LYP method, these anion-neutral C−F bond distance differences range from 0.012 Å to 0.023 Å for the C_2 *cis* structure, and 0.012 Å to 0.020 Å for the C_i *trans* structure.

The predictions for the adiabatic electron affinities (EA$_{ad}$), vertical electron affinities (EA$_{vert}$) for the neutral 2-$C_{18}F_{12}$, and the vertical detachment energies (VDE) for the anionic 2-$C_{18}F_{12}^-$ are reported in Table 2. The local EA$_{ad}$ value for the C_i *trans* structure is predicted to be 1.92 eV (BP86), 1.83 eV (B3LYP), 1.79 eV (BLYP), and 1.60 eV (BHLYP), while that for the C_2 *cis* structure is predicted to be 1.94 eV (BP86), 1.88 eV (B3LYP), 1.81 eV (BLYP), and 1.66 eV (BHLYP). The EA$_{ad}$ value for the *trans* structure is slightly lower than that for the *cis* structure by ~0.05 eV (B3LYP). The theoretical EA$_{vert}$ is in the range of 1.36− 1.74 eV for the C_i structure; and 1.41 − 1.78 eV for the C_2 structure. The B3LYP theoretical VDE for the 2-$C_{18}F_{12}^-$ anion is 2.04 eV for the *trans* structure, 2.03 eV for the *cis* structure. The electron affinities fall in the order BP86 > B3LYP > BLYP > BHLYP.

F. 3-$C_{18}F_{12}$ and 3-$C_{18}F_{12}^-$ (Perfluorotriphenylene). The third isomer for the neutral $C_{18}F_{12}$ molecule is perfluorotriphenylene (3-$C_{18}F_{12}$), for which the structure is displayed in Figure 7. Perfluorotriphenylene (3-$C_{18}F_{12}$) has a propeller-like conformation with D_3 symmetry, which is a local minimum (Figure 7). The geometrical parameters of this propeller conformation predicted by four DFT methods are in general agreement with each other. The C−C bond lengths for this D_3 structure are in the range from 1.392 to 1.466 Å (B3LYP). The trend of the C−C and C−F bond distances is in the order of BLYP > BP86 > B3LYP > BHLYP.

The global minimum for perfluorotriphenylene has C_2 symmetry, with one of the outer phenyl groups twisting in the opposite way to the other two. The C_2 structure lies lower in energy than the D_3 conformation by 3.9−4.8 kcal/mol with four different DFT methods. The B3LYP optimized geometry of the C_2 conformation is in reasonable agreement with the experimental crystal geometry,[28] which is also shown in Figure 7 (in italics).

Since the D_3 conformation for the neutral has a doubly degenerate (*e*) LUMO, the corresponding radical anion should have lower symmetry because of Jahn−Teller effect, and the structure with C_2 symmetry is the only minimum predicted by

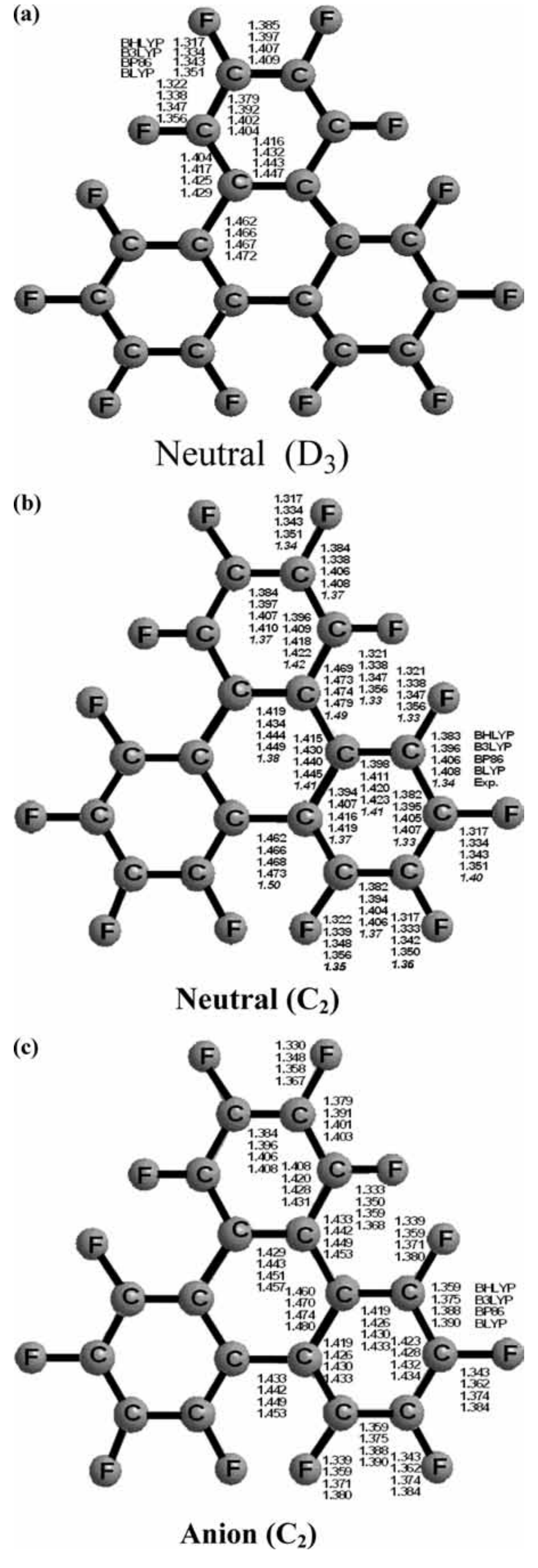


Figure 7. Optimized geometries of the neutral perfluorinated triphenylene (3-$C_{18}F_{12}$) and its radical anion with C_2 symmetry. As a comparison, the experimental crystal geometrical parameters for the neutral system are also listed. All bond lengths are in Å.

TABLE 3: ZPVE-Corrected Adiabatic Electron Affinities for the Title Systems in eV (kcal/mol in Parentheses)[a]

compound	BHLYP	B3LYP	BP86	BLYP
1-$C_{14}F_{10}$	1.75 (40.0)	1.96 (46.0)	1.99 (46.0)	1.87 (43.2)
2-$C_{14}F_{10}$	1.32 (30.4)	1.55 (35.7)	1.62 (37.4)	1.51 (34.8)
$C_{16}F_{10}$	1.65 (38.0)	1.85 (42.7)	1.86 (42.9)	1.75 (40.4)
1-$C_{18}F_{12}$	2.33 (53.7)	2.52 (58.1)	2.53 (58.8)	2.40 (55.3)
2-$C_{18}F_{12}$ (C_2)	1.79 (41.3)	2.00 (46.3)	2.07 (47.6)	1.94 (44.6)
2-$C_{18}F_{12}$ (C_i)	1.73 (39.8)	1.96 (45.3)	2.05 (47.0)	1.92 (44.2)
3-$C_{18}F_{12}$ (C_2)	1.57 (36.5)	1.81 (42.0)	1.91 (44.1)	1.80 (41.5)

[a] All results were obtained with the DZP++ basis.

the DFT methods, except for BHLYP, which predicts a small imaginary vibrational frequency ($69i$ cm^{-1}). The BHLYP minimum has C_1 symmetry (slightly distorted from C_2 structure), and it has an energy lower than the C_2 structure by a minuscule 0.12 kcal/mol. The C−C bond lengths for the anion range 1.375 to 1.470 Å (B3LYP). The C−F distances for the 3-$C_{18}F_{12}^-$ anion are consistently longer than those for the neutral, with the difference 0.012 to 0.029 Å.

Table 2 reports our predictions for the adiabatic electron affinities (EA_{ad}), vertical electron affinities (EA_{vert}), and vertical detachment energies (VDE). The EA_{ad} for perfluorotriphenylene is predicted to be 1.78 eV (BP86), 1.69 eV (B3LYP), 1.67 eV (BLYP), and 1.44 eV (BHLYP). The theoretical EA_{vert} falls in the range 1.10 − 1.52 eV, and the VDE value for the 3-$C_{18}F_{12}^-$ anion is in the range 1.81 − 2.09 eV. The trend of EA_{vert} and VDE are also in the order BP86 > B3LYP > BLYP > BHLYP. With the B3LYP method (presumably the most reliable method of the four methods) the EA_{vert} is 1.40 eV, while VDE is 2.02 eV.

G. ZPVE Corrections. The ZPVE differences between the neutrals and the corresponding anions are reported in Table 1, and are in the range 0.12 − 0.15 eV. The ZPVE corrected adiabatic electron affinities for the title molecules are shown in Table 3. It may be seen that the ZPVE corrected EA_{ad} is 1.96 eV (B3LYP) for 1-$C_{14}F_{10}$ (raised by 0.12 − 0.13 eV) and 1.55 eV for 2-$C_{14}F_{10}$ (raised by 0.14−0.15 eV). Relatively speaking, the ZPVE corrections raise the EA_{ad} values by 6.5% for perfluoroanthracene, and 9.9% for perfluorophenanthrene, but both are less significant than the ZPVE correction for the corresponding (lower mass) anthracene $C_{14}H_{10}$ (24%).[15]

The ZPVE corrections raise the EA_{ad} for perfluoropyrene by 0.12 − 0.14 eV with the four DFT methods. Our reliable B3LYP ZPVE correction of $C_{16}F_{10}$ (0.13 eV) raises the EA_{ad} (to 1.85 eV) by 7.6%. Our B3LYP ZPVE corrected EA_{ad} values are 2.39 eV for perfluorotetracene, 1.83 eV (C_i) and 1.88 eV (C_2) for perfluorochrysene, 1.81 eV for perfluorotriphenylene. The ZPVE correction raises the EA_{ad} values by 5.4% for the 1-$C_{18}F_{12}$ molecule; by 7.1% (C_i) and 6.4% (C_2) for the 2-$C_{18}F_{12}$ molecule; and 7.1% for 3-$C_{18}F_{12}$ molecule. The ZPVE corrected results raise the EA_{ad} by 0.12−0.13 eV for the 1-$C_{18}F_{12}$ and 2-$C_{18}F_{12}$ molecules and by 0.12−0.13 eV for the 3-$C_{18}F_{12}$ molecule.

Discussion

We adopt four different DFT methods (BHLYP, BP86, BLYP, and B3LYP) in the present study to predict the neutral-anion energy separations. A comprehensive review[14] and previous work on PAHs[15] have shown that the B3LYP and BLYP functionals are the more reliable. It is nevertheless interesting to compare their performance for the perfluorinated PAHs. Figure 8 (based on the results in Table 2) shows the relationship of the adiabatic EAs predicted by BHLYP, BP86, and BLYP with respect to the B3LYP results. From Figure 8,

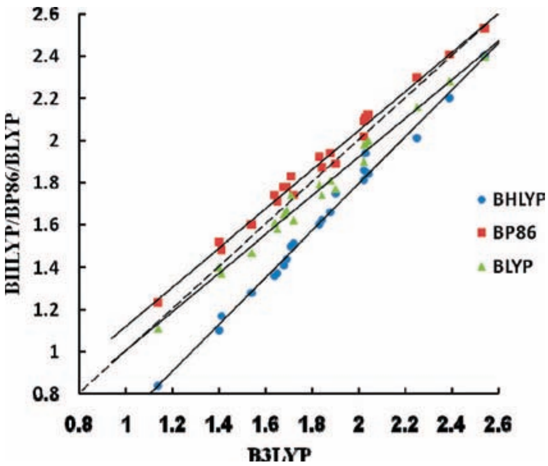


Figure 8. Regression analyses among the electron affinities predicted from the four DFT methods (BHLYP, BP86, and BLYP vs B3LYP).

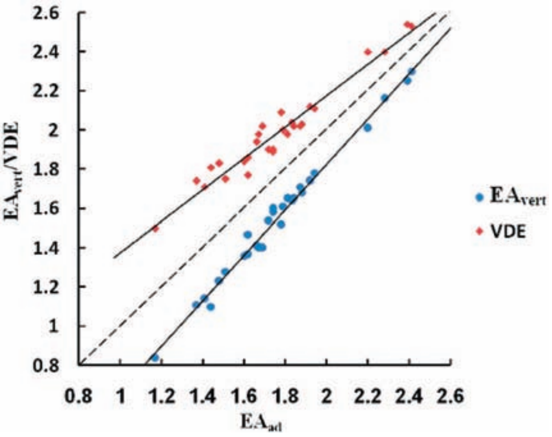


Figure 9. Relationship of EA_{vert} and VDE values with respect to EA_{ad}.

we observe the clear correlation (with the high confidence level, $R^2 > 0.98$) among the EAs predicted by the different functionals. The EAs from these four functionals are essentially in agreement with each other. The BP86 method predicts EA values slightly larger, and the BLYP method predicts slightly smaller. The performance of the BHLYP functional seems somewhat poor for the smaller molecule (with smaller EAs), but it improves for the larger molecules (with larger EAs).

Figure 9 shows the relationship for EA_{vert} and VDE with respect to EA_{ad}, based on the results in Table 2. Of course, the VDE values are always larger than the EA_{ad} predictions, and the EA_{vert} values are always smaller. Figure 9 also shows that the difference among these three neutral-anion energy separations is substantial for the smaller molecules (as EA ~ 1.2 eV), while this difference becomes less for the larger molecules (as EA ~ 2.4 eV). This might be anticipated, because the geometry changes from neutral to anion for the large systems should be less, compared with the small molecules.

Figure 10 is a summary for the predicted EA_{ad} from the present work and comparison with previous work. It is known that benzene and naphthalene do not bind an electron. Their electron affinities are reported to be negative (−0.88 eV for benzene and −0.20 eV for naphthalene at the DZP B3LYP level of theory).[15] For the other polycyclic aromatic hydrocarbon (PAHs), the EAs increase as the number of benzene rings increases. It was reported that anthracene and tetracene have positive EAs, (0.58 and 1.13 eV, respectively at the same level of theory).[15] Compared with the corresponding PAH molecules, the perfluorinated PAHs have much higher EAs. At the same level of theory, for the first four simple perfluorinated PAHs, the EAs are 0.69, 1.02, 1.84, and 2.39 eV, respectively.[11] Figure 10 shows the theoretical EAs for the first four simple PAHs and their perfluorinated counterparts. Two features may be seen in Figure 10. First, both series (PAHs and their perfluorinated PAHs) display notable increases in EA with respect to the number of benzene rings. When the size of molecules increases by an additional ring, the EA increases by ~0.6 eV. Second, the perfluorinated effect is significant. The difference of EA_{ad} values is about 1.2 eV (1.6 eV for the single ring compounds) between the perfluorinated PAHs and their corresponding PAHs. Thus the perfluorinated PAHs, especially the larger ones, will be very effective electron acceptors, and could be used for the development of new materials and new reactions.

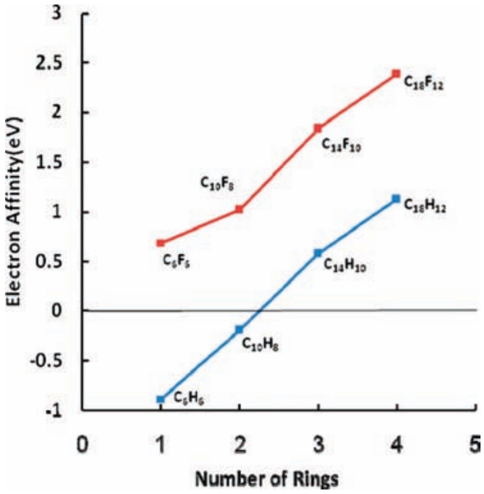


Figure 10. Theoretical EAs for the first four simple PAHs and their perfluorinated counterparts.

Concluding Remarks

The present research encourages the use of perfluorinated benzenoid compounds (as effective electron acceptors) to introduce the analogous radical anions into novel stable magnetic materials. The reliable predicted ZPVE-corrected adiabatic electron affinities from the DZP++ B3LYP method are as follows: 1.96 eV for 1-$C_{14}F_{10}$ (perfluoroanthracene), 1.55 eV for 2-$C_{14}F_{10}$ (perfluorophenanthrene), 1.85 eV for $C_{16}F_{10}$ (perfluoropyrene), 2.52 eV for 1-$C_{18}F_{12}$ (perfluorotetracene), 1.96 eV (C_i), 2.00 eV (C_2) for 2-$C_{18}F_{12}$ (perfluorochrysene), and 1.81 eV for 3-$C_{18}F_{12}$ (perfluorotriphenylene). The ZPVE corrections raise the predicted EA_{ad} values by 5−10%. The perfluorotetracene is clearly the most effective electron acceptor.

It is important to note that there are only two radical anions (those of anthracene and tetracene) which adopt strictly planar structures as the local minima on their potential energy surfaces. Both of these structures display linear arrangements of their benzene rings. The large electron affinities of these two compounds suggest that the unpaired electron density is distribute more evenly on the molecular frame for the linear structures as compared with the other structures. The qualitative characteristics of conjugation remain while introducing an extra electron into these two linearly arranged perfluorinated PAH molecules.

In going from perfluoroanthracene to perfluorotetracene, the increase of the EA_{ad} is ~0.5 eV. The influence of molecular size on the electron affinity is positive only for the linear structures. The smaller or similar EA_{ad} values for perfluoropyrene, perfluorochrysene, and perfluorotriphenylene (as compared to that for perfluoroanthracene) suggest that the size effect is less pronounced than the influence of the structural arrangement. Therefore, it should be possible to combine these two effects to achieve the design of the perfluorinated PAH molecules with the electron affinities in the desired ranges.

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