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Perfluoroadamantane and Its Negative Ion

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As a general rule, saturated hydrocarbons are unable to bind an electron, i.e., their electron affinities are negative, but the corresponding perfluorinated molecules can have significant electron affinities, especially in the case of branched and ring systems. Four different density functional theory (DFT) methods in conjunction with double-ζ plus polarization function augmented diffuse function basis sets (DZP++) have been employed to study the equilibrium geometries, electron affinities, and vibrational frequencies of the adamantane ($C_{10}H_{16}$) and perfluoroadamantane ($C_{10}F_{16}$) molecules. Three types of neutral-anion separations reported are the adiabatic electron affinity, the vertical electron affinity, and the vertical detachment energy. The adiabatic electron affinity predicted at the DZP++ B3LYP level of theory for adamantane is, as expected, negative (−0.58 eV), while that for perfluoroadamantane is distinctly positive, namely, 1.06 eV (or 1.31 eV after correction for zero-point vibrational energies).

Introduction

Adamantane and its derivatives are among the organic molecules frequently studied in modern chemistry.[1−5] Theoretical predictions on the properties of adamantane and its different radicals[6] determined by Yan, Brinkmann, and Schaefer have provided valuable information concerning their relative stabilities and reactivities. The electron affinities (EA) for the unsubstituted adamantane radicals are predicted to be negative, which means they do not attract an electron. On the other hand, unsaturated perfluorohydrocarbons have drawn recent attention[7−9] because of some much larger EAs than the analogous hydrocarbons, indicating that perfluorohydrocarbons are effective electron acceptors, and may play important roles in chemistry and in the design of new materials. Thus, the perfluoroadamantane molecule is an intriguing candidate as a potential electron acceptor.

As early as 1978, Lagow and co-workers suggested a direct fluorination method for the adamantane derivatives.[10] In 1982, a method of production of perfluoroadamantane appeared in a patent application.[11] In 1983, perfluoroadamantane was prepared by Adock and Robin using an aerosol direct fluorination method.[12] In 1987 and 1988, two similar papers reported that a lecithin-based perfluoroadamantane emulsion has been used in medical experiments.[13,14] In 1998, Hargittai et al. determined the molecular structure of perfluoroadamantane using gas-phase electron diffraction.[15] A complete vibrational analysis of perfluoroadamantane has been carried out with a joint application of experimental and theoretical methods.[16]

An exhaustive review of density functional theory (DFT)[17] shows that selected functionals, such as B3LYP, can yield average absolute errors of only 0.15 eV for EAs compared to experiment. Further research shows that the BLYP and B3LYP functionals have average absolute errors of only 0.18 and 0.19 eV for larger polycyclic aromatic hydrocarbons.[18] Since reliable experimental EAs are lacking for the large saturated perfluorocarbons including perfluoroadamantane, in the present study we examine the EAs for perfluoroadamantane ($C_{10}F_{16}$), and the analogous study of adamantane ($C_{10}H_{16}$) is carried out for comparison.

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

Four different density functional or hybrid Hartree−Fock/density functional methods were used and have been denoted BHLYP, B3LYP, BP86, and BLYP. The BHLYP functional is the half and half exchange functional[19] with the Lee, Yang, and Parr (LYP) correlation functional.[20] The B3LYP functional arises from Becke's three-parameter hybrid functional[21] and the LYP correlation functional. The BP86 functional is Becke's 1988 exchange functional[22] with Perdew's 1986 correlation functional.[23] The last method (BLYP) is Becke's 1988 exchange functional[22] with the LYP correlation functional.

Double-ζ basis sets with polarization and diffuse functions, denoted DZP++, are employed. The DZP starting basis was constructed from the Huzinage−Dunning[24,25] contracted double-ζ Gaussian results with one set of polarization functions [one set of the p-type functions for H atoms with $\alpha_p(H) = 0.75$ and one set of five d-type functions for C and F atoms with $\alpha_d(C) = 0.75$, and $\alpha_d(F) = 1.00$]. To complete the DZP++

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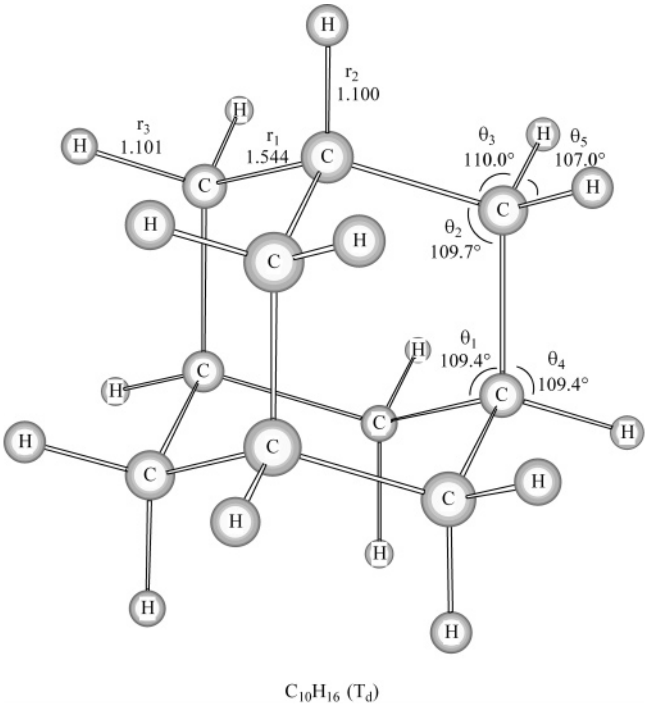

Figure 1. Structure of the neutral adamantane $C_{10}H_{16}$ molecule at the DZP++ B3LYP level of theory. The structure of its anion $C_{10}H_{16}^-$ is essentially identical to that of the neutral.

basis, one even-tempered s diffuse function was added to each H atom and even-tempered s and p diffuse functions to all other atoms [$\alpha_s(H) = 0.04415$, $\alpha_s(C) = 0.04302$, $\alpha_p(C) = 0.03629$, $\alpha_s(F) = 0.10490$, and $\alpha_p(F) = 0.08260$] with orbital exponents determined by the formula expressed by Lee and Schaefer.[26] Thus, the final basis sets may be described as H (5s1p/3s1p), C and F (10s6p1d/5s3p1d).

In the present study, the equilibrium geometries, total energies, and harmonic vibrational frequencies are determined for both neutral and anion species using the above four DFT methods. Zero-point vibrational energies (ZPVE) are evaluated for the purpose of correcting the electron affinities. Our computations were conducted with the Gaussian94 programs.[27] The default integration grid (75,302) was applied.

Results and Discussion

A. $C_{10}H_{16}$ and $C_{10}H_{16}^-$. In 1972, Hargittai et al. determined the molecular structure of adamantane using gas-phase electron diffraction.[4] The theoretical geometry of the T_d symmetry adamantane predicted by Yan, Brinkmann, and Schaefer[6] was in excellent agreement with the electron diffraction experiments. Their B3LYP geometry is the closest to experiment, with the C−C bond distances of 1.544 Å, the C−H distances of 1.100 Å, and the $C-C_{sec}-C$ and $C-C_{ter}-C$ bond angles of 109.7 and 109.4°, respectively.

The structure for neutral $C_{10}H_{16}$ is displayed in Figure 1. The geometry for the neutral $C_{10}H_{16}$ ($^1A_1$ ground state with T_d symmetry) is the same as that from Yan, Brinkmann, and Schaefer.[6] The anionic $C_{10}H_{16}^-$ with a $^2A_1$ ground state is also found to have T_d symmetry. The C−C bond lengths predicted by the different functionals range from 1.533 to 1.557 Å. The vibrational frequency analyses demonstrate only real harmonic frequencies for both $C_{10}H_{16}$ and $C_{10}H_{16}^-$ with all methods used. It is noteworthy that the geometries for the neutral and anion are essentially identical, showing only slight differences in bond lengths and angles. This, of course, is consistent with a picture in which the last electron is not bound to the molecule. With the B3LYP method, the C−C bond length for the neutral is 1.544 Å, and that for the anion is 1.542 Å.

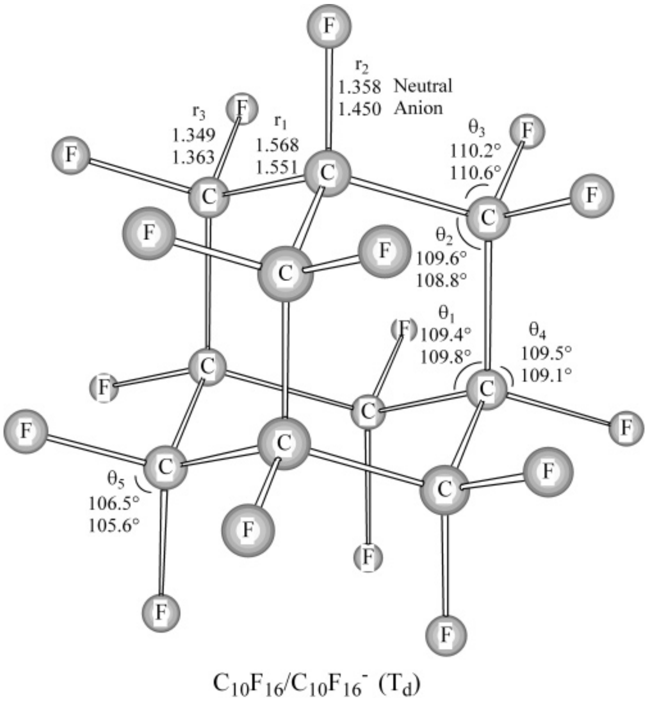

Figure 2. Structures of the neutral perfluoroadamantane ($C_{10}F_{16}$) molecule and its anion $C_{10}F_{16}^-$. Optimized geometrical parameters for both neutral and anion shown in the figure are predicted by the B3LYP method. Structures from other DFT methods are seen in Table 2.

TABLE 1: Adiabatic Electron Affinities (EA_{Ad}), Vertical Electron Affinities (EA_{Vert}), and Vertical Detachment Energies (VDE), with Values (in eV), for Adamantane ($C_{10}H_{16}$) and Perfluoroadamantane ($C_{10}F_{16}$)

	adamantane			perfluoroadamantane		
method	EA_{ad}	EA_{vert}	VDE	EA_{ad}	EA_{vert}	VDE
BHLYP	−0.84	−0.84	−0.84	0.25	−0.11	0.45
B3LYP	−0.58	−0.59	−0.58	1.06	0.61	1.70
BP86	−0.48	−0.49	−0.48	1.53	1.01	2.20
BLYP	−0.58	−0.58	−0.57	1.45	0.94	2.14

Yan, Brinkmann, and Schaefer did not present the electron affinity for the $C_{10}H_{16}$ molecule.[6] In the present study, we list our theoretical EA_{ad}, EA_{vert}, and VDE predictions for $C_{10}H_{16}$ and its anion in Table 1. The B3LYP result of EA_{ad} is −0.58 eV, and that of EA_{vert} is −0.59 eV. The B3LYP results of VDE for the $C_{10}H_{16}^-$ anion is −0.58 eV. These three neutral-anion energy separations are very close, corresponding to the geometrical similarity of the neutral and its anion. The other three DFT methods all reported negative EA values for the $C_{10}H_{16}$ molecule (Table 1). The trend of the theoretical EAs among functionals is BP86 > BLYP > B3LYP > BHLYP. It is obvious that $C_{10}H_{16}$ cannot bind an electron.

B. $C_{10}F_{16}$ and $C_{10}F_{16}^-$. The neutral $C_{10}F_{16}$ molecule in its $^1A_1$ ground state displays T_d symmetry. The geometry of neutral perfluoroadamantance $C_{10}F_{16}$ was determined by Hargittai et al. with the gas-phase electronic diffraction method.[15] Our optimized geometry for the neutral $C_{10}F_{16}$ is shown in Figure 2, and the B3LYP results are in good agreement (within 0.01 Å for the bond distances) with the experimental geometrical parameters (also listed in Table 2). The four different functionals predict geometric parameters in reasonable agreement with each other, e.g., the predictions of the C−C bonds with the four functionals are within 0.033 Å. The trend for the C−C bond

TABLE 2: Optimized Geometries of Perfluoroadamantane ($C_{10}F_{16}$, T_d) and Its Anion ($C_{10}F_{16}^-$, T_d)[a]

	perfluoroadamantane					perfluoroadamantane anion			
parameter	BHLYP	B3LYP	BP86	BLYP	exp[b]	BHLYP	B3LYP	BP86	BLYP
r_1	1.552	1.568	1.576	1.585	1.560	1.537	1.551	1.557	1.565
r_2	1.340	1.358	1.368	1.375	1.363	1.420	1.450	1.467	1.478
r_3	1.330	1.349	1.361	1.368	1.340	1.343	1.363	1.377	1.384
θ_1	109.4°	109.4°	109.4°	109.4°	110.3°	109.8°	109.8°	109.8°	109.8°
θ_2	109.6°	109.6°	109.7°	109.6°	107.7°	108.8°	108.8°	108.8°	108.8°
θ_3	110.1°	110.2°	110.2°	110.2°	110.5°	110.5°	110.6°	110.6°	110.6°
θ_4	109.5°	109.5°	109.6°	109.6°	108.6°	109.1°	109.1°	109.2°	109.1°
θ_5	106.8°	106.5°	106.4°	106.3°	106.9°	105.9°	105.6°	105.5°	105.4°

[a] Bond lengths are in Å, and bond angle are degrees. Geometrical parameters correspond to those labeled in Figure 2. [b] Ref 15.

TABLE 3: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Their Infrared Intensities (km/mol, in parentheses) for Adamantane ($C_{10}H_{16}$), Perfluoroadamantane ($C_{10}F_{16}$), and the Anionic $C_{10}F_{16}^{-}$[a]

		adamantane		perfluoroadamantane			
		neutral		neutral			anion
		B3LYP	exp[b]	B3LYP	IR[c]	Raman[c]	B3LYP
a_1	ν_1	3050 (0)	2950	1323 (0)		1315	1254 (0)
	ν_2	3014 (0)	2913	1274 (0)		1298	983 (0)
	ν_3	1519 (0)	1472	695 (0)		700	644 (0)
	ν_4	1049 (0)	990	559 (0)		568	472 (0)
	ν_5	755 (0)	756	360 (0)		370	364 (0)
a_2	ν_6	1124 (0)	1189	226 (0)			235 (0)
e	ν_7	3016 (0)	2900	1254 (0)			1198 (0)
	ν_8	1483 (0)	1439	1005 (0)			986 (0)
	ν_9	1401 (0)	1370	603 (0)			588 (0)
	ν_{10}	1228 (0)	1217	305 (0)		310	288 (0)
	ν_{11}	923 (0)	953	250 (0)			234 (0)
	ν_{12}	412 (0)	402	204 (0)			205 (0)
t_1	ν_{13}	3056 (0)		1163 (0)			1205 (0)
	ν_{14}	1342 (0)	1321	1091 (0)			1061 (0)
	ν_{15}	1318 (0)	1288	854 (0)			810 (0)
	ν_{16}	1125 (0)		385 (0)			383 (0)
	ν_{17}	1060 (0)	1043	271 (0)			266 (0)
	ν_{18}	901 (0)		246 (0)			251 (0)
	ν_{19}	340 (0)		130 (0)			130 (0)
t_2	ν_{20}	3061 (327)	2940	1303 (45)	1306 s		1268 (1242)
	ν_{21}	3038 (531)	2910	1293 (1440)	1289 s		1164 (210)
	ν_{22}	3016 (120)	2850	1236 (0)	1273 w		1091 (1143)
	ν_{23}	1497 (33)	1455	1067 (0)	1060 vw		935 (174)
	ν_{24}	1380 (0)	1359	974 (957)	973 s		617 (132)
	ν_{25}	1340 (0)	1310	648 (45)	654 w		548 (3066)
	ν_{26}	1116 (9)	1105	438 (30)	441 w		421 (0)
	ν_{27}	981 (3)	970	402 (15)	400 vw		316 (372)
	ν_{28}	817 (3)	800	298 (12)	301 w		286 (330)
	ν_{29}	657 (0)	640	259 (3)	260 vw		192 (213)
	ν_{30}	458 (0)	444	191 (0)	202 vw		172 (684)

[a] The available experimental results are listed for comparison. [b] Ref 28. [c] Ref 16.

length is in the order of BHLYP < B3LYP < BP86 < BLYP. It is also noteworthy that the bond angle differences predicted by the four functionals are quite small, excepting the F−C−F angle θ_5, which changes by as much as 0.5°.

The $C_{10}F_{16}^-$ anion has a $^2A_1$ ground state, and its geometric parameters are also shown in Figure 2 and Table 2. To our knowledge, there is no experimental report for the $C_{10}F_{16}^-$ anion. The four DFT methods predict the anionic geometry also in agreement with each other, with the C−C bond difference < 0.028 Å. The neutral and anion $C_{10}F_{16}$ geometries are rather different, given that they share T_d symmetry (Figure 2 and Table 2). The change of the C−C bond distances is not excessive from the neutral $C_{10}F_{16}$ to anionic $C_{10}F_{16}^-$. With the B3LYP method, the C−C bond length for the neutral is 1.568 Å, and that for the anion is 1.551 Å. It is found that the C−C distances in $C_{10}F_{16}^-$ are consistently shorter (by 0.015−0.020 Å) than those in the neutral molecule, while the C−F distances in $C_{10}F_{16}^-$ are longer than those in the neutral molecule. These anion−neutral differences for the two kinds of C−F bonds are 0.092 Å (r_2) and 0.014 Å (r_3), respectively. This large shift in r_3(C−F) may be correlated with the singly occupied orbital (a_1) for the anionic $C_{10}F_{16}^-$, which displays bonding character for the C−C bonds and antibonding character for the C−F bonds.

The theoretical EA_{ad}, EA_{vert}, and VDE predictions for $C_{10}F_{16}$ and its anion are shown in Table 1. It is known that the BHLYP method does not predict the energy well, and the B3LYP method is the best for the EAs.[17] The B3LYP predicted EA_{ad} is 1.06 eV, and the EA_{vert} is 0.61 eV. The related VDE for the $C_{10}F_{16}^-$ anion is 1.70 eV. Compared with the neutral-anion energy separations of adamantane, the perfluorination dramatically increases EA_{ad}, EA_{vert}, and VDE. At the B3LYP level, the EA_{ad} value increases from adamantane to perfluoroadamantane by $1.06 - (-0.58) = 1.64$ eV. This is close to the EA_{ad} change from benzene (−0.88 eV)[18] to perfluorinated benzene (0.69 eV)[9] at the same theoretical level. Other unsaturated perfluorohydrocarbons follow the same trend.[7−9] Therefore, it is expected that the perfluoroadamantane molecule should have a strong tendency to bind an electron.

C. Vibrational Frequencies and the ZPVE Correction. The harmonic vibrational frequencies for the $C_{10}H_{16}$ and $C_{10}F_{16}$/$C_{10}F_{16}^-$ systems are listed in Table 3. All of the vibrational frequencies are real, suggesting that all these systems (neutrals and anions) are genuine minima on their potential hypersurfaces. The experimental observations for $C_{10}H_{16}$ and $C_{10}F_{16}$ are also listed in Table 3 for comparison.[16,28] Our B3LYP prediction for the vibrational frequencies of $C_{10}F_{16}$ are in good agreement with the experiments. Compared with the infrared active modes (t_1),[16] the deviations for most frequencies (ν_{20-21}, ν_{24-29}, gas-phase, in Table 3) are less than 6 cm^{-1}. The deviations are slightly larger for the very weak fundementals ν_{23} and ν_{30}, which can only observed in solid-phase. The only exception is ν_{22}, but the relative error there is still 3%. The agreement with the solid-phase Raman spectrum (a_1 and e modes)[16] is also quite good (Table 3).

The ZPVE correction could be used for the correction of the electron affinities. For the $C_{10}H_{16}$ molecule with the DZP++ B3LYP method, the ZPVE correction is 0.06 eV. However, applying a ZPVE correction is insignificant because the negative EA (−0.58 eV) reveals a nonbound anion for $C_{10}H_{16}$ molecule. ZPVE for $C_{10}F_{16}$/$C_{10}F_{16}^-$ systems evaluated at each level of theory and the ZPVE-corrected adiabatic electron affinity are presented in Table 4. Similar to the cases of the unsaturated systems anthracene ($C_{14}H_{10}$) and tetracene ($C_{18}H_{12}$),[18] the ZPVE correction for the $C_{10}F_{16}$ molecule is significant (e.g., 0.25 eV at the B3LYP level). Our ZPVE corrected EA_{ad} for $C_{10}F_{16}$ is predicted to be 1.31 eV at the DZP++ B3LYP level of theory.

It has been pointed out[18] that when the systems under consideration become larger, the ZPVE correction becomes more significant. In studies of polycyclic aromatic hydrocarbon (PAH) EAs,[18] the ZPVE corrections were found to be several

TABLE 4: Zero-Point Vibrational Energies (eV) within the Harmonic Approximation for the $C_{10}F_{16}/C_{10}F_{16}^-$ System and the ZPVE-Corrected Adiabatic Electron Affinities (eV) for $C_{10}F_{16}$

	BHLYP	B3LYP	BP86	BLYP
$C_{10}F_{16}$	3.20	3.00	2.88	2.82
$C_{10}F_{16}^-$	2.92	2.75	2.65	2.59
$\Delta(C_{10}F_{16}-C_{10}F_{16}^-)$	0.28	0.25	0.23	0.23
$EA_{ad\ (ZPVE-corrected)}$	0.53	1.31	1.76	1.68

tenths of an electronvolt in magnitude and to account for a significant portion (as much as 40% for coronene) of the overall EAs. Therefore, one should be cautious about the accuracy of the harmonic vibrational frequencies when the ZPVE correction is significant for the EAs.

Concluding Remarks

The classical adiabatic electron affinities predicted with the DZP++ B3LYP method are −0.58 eV for $C_{10}H_{16}$ and 1.06 eV for $C_{10}F_{16}$. It is shown that adamantane does not readily attract an electron, while the perfluorination of adamantane does strongly bind an electron. Thus, the perfluoroadamantane molecule is expected to be an effective electron acceptor, and may thus be useful in the study of new materials and new reactions. The ZPVE corrections raise the predicted EA_{ad} value by 0.25 eV (24%) for perfluoroadamantane, and the ZPVE corrected EA_{ad} for $C_{10}F_{16}$ is 1.31 eV. It is hoped that the present theoretical predictions will stimulate further experimental and theoretical studies of large perfluorohydrocarbons.

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