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The Perfluoroadamantyl Radicals C$_{10}$F$_{15}$ and Their Anions

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Abstract: The optimized geometries, electron affinities, and harmonic vibrational frequencies of perfluoroadamantyl radicals (C$_{10}$F$_{15}$) have been obtained using four carefully calibrated density functional theory methods in conjunction with diffuse function augmented double-ζ plus polarization (DZP++) basis sets. There are two C$_{10}$F$_{15}$ isomers with close energies. With the DZP++ B3LYP method, the C_{3v} isomer (1-C$_{10}$F$_{15}$) lies energetically *above* the C_s isomer (2-C$_{10}$F$_{15}$) by 0.086 eV (2.0 kcal/mol), while the anionic 1-C$_{10}$F$_{15}^{-}$ isomer is predicted to lie *below* 2-C$_{10}$F$_{15}^{-}$ anion by 1.00 eV (23.0 kcal/mol). The DZP++ B3LYP method predicts the ZPVE-corrected adiabatic electron affinity for the C_{3v} isomer (1-C$_{10}$F$_{15}$) to be 4.16 eV, and that for the C_s isomer (2-C$_{10}$F$_{15}$) is 3.10 eV. These EA$_{ad}$ values are significantly larger than that (1.31 eV) of the parent molecule perfluoroadamantane (C$_{10}$F$_{16}$). For the 1-C$_{10}$F$_{15}$ radical, the C*−C bond length is shortened by 0.043 Å upon removal of F from the C$_{10}$F$_{16}$ molecule. The C*−C bond distance for the 1-C$_{10}$F$_{15}^{-}$ anion is 0.068 Å shorter than that for C$_{10}$F$_{16}$. Similarly, for 2-C$_{10}$F$_{15}$ the C*−C distance is 0.053 Å shorter than for C$_{10}$F$_{16}$, while r$_e$(C*−C) for the anion is 0.061 Å shorter than for C$_{10}$F$_{16}$.

Introduction

Both adamantane (C$_{10}$H$_{16}$) and, surprisingly, the two adamantyl radicals (C$_{10}$H$_{15}$) have been predicted to have negative adiabatic electron affinities (EAs) with carefully calibrated density functional theory (DFT) methods.[1] That is, these systems do not readily attract an electron.[2] However, in the same theoretical study, it was suggested that suitably substituted adamantyl radicals would be expected to have positive electron affinities.[1] Perfluorohydrocarbons have generated recent attention because of their ability to bind an additional electron.[3−7] The perfluoroadamantane (C$_{10}$F$_{16}$) molecule is predicted to have a substantial EA$_{ad}$ value (1.31 eV).[7] One would expect the perfluoroadamantyl radicals to have even larger electron affinities.

For the larger perfluorohydrocarbons reliable experimental electron affinities (EAs) are lacking. Theoretical studies can often aid in the interpretation of experimental photoelectron spectra and usually provide accurate predictions of electron affinities.[8] DFT methods have been systematically applied to large molecules, and the average error for the B3LYP results is about 0.15 eV compared to experiment.[8,9] In the present study we examine the two isomers of the perfluoroadamantyl radical, namely 1-C$_{10}$F$_{15}$ and 2-C$_{10}$F$_{15}$, and their anions using four selected DFT methods in conjunction with DZP++ basis sets, with the goal of establishing reliable theoretical predictions for the unknown EAs. We also compare these radical EAs with that for the C$_{10}$H$_{15}$ radicals and those for their parent molecule C$_{10}$F$_{16}$.

Three neutral-anion energy separations, i.e., the adiabatic electron affinity (EA$_{ad}$), the vertical electron affinity (EA$_{vert}$), and the vertical detachment energy (VDE), have been

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predicted as differences in total energies according in the following manner:

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

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

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

Theoretical Methods

Similar to previous studies,[6,7] the four DFT methods employed in the present research have been denoted BHLYP, B3LYP, BP86 and BLYP. The functional named BHLYP by the developers of the GAUSSIAN programs combines a modification of Becke's half and half exchange functional[10] with the Lee, Yang, and Parr (LYP) correlation functional.[11] The B3LYP method is a hybrid Hartree−Fock/density functional (HF/DFT) method using Becke's three-parameter hybrid functional[12] with the LYP correlation functional. The BP86 approach is Becke's 1988 exchange functional[13] in conjunction with Perdew's 1986 correlation functional.[14] The BLYP functional combines Becke's 1988 exchange functional[13] with the LYP correlation functional.

Basis sets of double-ζ quality plus polarization functions augmented with diffuse functions (DZP++) were used in the present work. They are the Huzinage−Dunning[15,16] contracted Gaussian double-ζ functions appended with one set of five d-type polarization functions, plus a set of *sp* diffuse functions based on an "even-tempered" formula.[17] For fluorine, the orbital exponents of the polarization function are $\alpha_d(F) = 1.00$ and the exponents of the diffuse functions are $\alpha_s(F) = 0.10490$ and $\alpha_p(F) = 0.08260$. For carbon, the exponents are $\alpha_d(C) = 0.75$, $\alpha_s(C) = 0.04302$ and $\alpha_p(C) = 0.03629$. Thus the final basis sets may be described as C, F(10s6p1d/5s3p1d). All computations for open-shell systems were done in a spin-unrestricted formalism.

Absolute total energies, optimized geometries, and harmonic vibrational frequencies for each structure were predicted using the above four DFT methods. Zero-point vibrational energies (ZPVEs) were evaluated at each level. The ZPVE differences between the neutrals and the corresponding anions are then used for the correction of the electron affinities. Our computations were performed with the Gaussian94 programs.[18] The default integration grid (75,302) of Gaussian94 was applied, and the tight SCF convergence was required. Cartesian coordinates for all structures are reported in the Supporting Information, Table S1. Total energies are reported in Table 1.

Results and Discussion

A. 1-$C_{10}F_{15}$ and 1-$C_{10}F_{15}^-$. There are two structural types of carbon atoms forming the perfluoroadamantane ($C_{10}F_{16}$, T_d) skeleton: four vertex carbon atoms, each connected to other three carbon atoms, and six bridging carbons, each bonding to other two carbon atoms.

The first isomer of perfluoroadamantyl radical (1-$C_{10}F_{15}$) is the structure in which a fluorine atom is removed from a vertex carbon atom, and this radical has C_{3v} symmetry. The

Table 1. Total Energies (in Hartree) for the $C_{10}F_{16}$/$C_{10}F_{16}^-$, 1-$C_{10}F_{15}$/1-$C_{10}F_{15}^-$, and 2-$C_{10}F_{15}$/2-$C_{10}F_{15}^-$ Systems

compound	BHLYP	B3LYP	BP86	BLYP
$C_{10}F_{16}$	−1978.23483	−1978.98955	−1978.99646	−1978.75110
$C_{10}F_{16}^-$	−1978.24388	−1979.02862	−1979.05271	−1978.80430
1-$C_{10}F_{15}$	−1878.34193	−1879.06063	−1879.06834	−1878.82976
1-$C_{10}F_{15}^-$	−1878.48337	−1879.21185	−1879.22118	−1878.97875
2-$C_{10}F_{15}$	−1878.34358	−1879.06379	−1879.07106	−1878.83350
2-$C_{10}F_{15}^-$	−1878.44503	−1879.17528	−1879.18482	−1878.94441
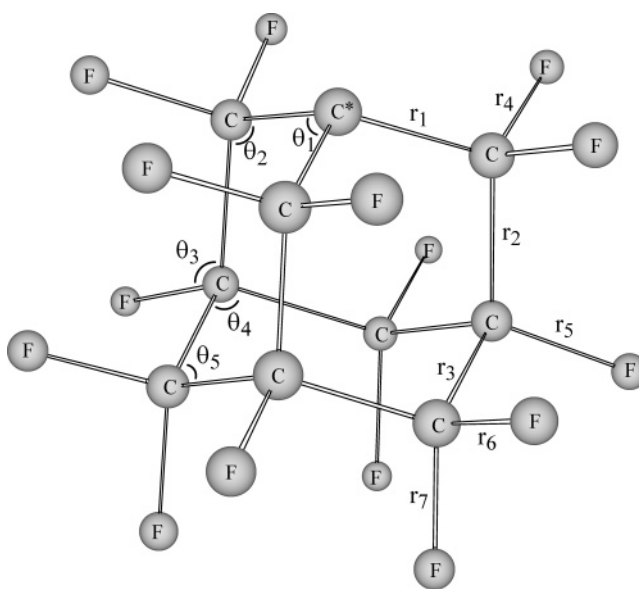
1-$C_{10}F_{15}$

Figure 1. Sketch of the C_{3v} structures for the 1-$C_{10}F_{15}$ radical and the 1-$C_{10}F_{15}^-$ anion. The optimized geometrical parameters for these structures are reported in Tables 2 and 3, respectively.

neutral 1-$C_{10}F_{15}$ radical has a $^2A_1$ ground electronic state, and the corresponding anionic 1-$C_{10}F_{15}^-$ has a closed-shell $^1A_1$ ground state. Vibrational frequency analyses show that both C_{3v} neutral and anion structures are genuine minima, with all real harmonic frequencies predicted by the four DFT methods. Our optimized structures for the neutral 1-$C_{10}F_{15}$ and the anionic 1-$C_{10}F_{15}^-$ are displayed in Figure 1, and their geometrical parameters are summarized in Tables2 and 3 and Figure 2. The geometry predictions by the four DFT methods are in reasonably good agreement with each other, and the trend for the bond distances predicted by the different functionals is BHLYP < B3LYP < BP86 < BLYP.

Compared with the closed-shell perfluoroadamantane molecule ($C_{10}F_{16}$),[7] the changes for the geometry of the 1-$C_{10}F_{15}$ radical are substantial, especially for those bond lengths and bond angles related to the radical carbon atom (Table 2). At the DZP++ B3LYP level, the C*−C (C* indicating the radical site C atom) bond distance (r_1) *decreases* by 0.043 Å, whereas the C−C bond (r_2) *increases* by 0.013 Å. The C−C*−C angle (θ_1) *increases* by 4.1° upon the removal of one F atom, while the C*−C−C angle (θ_2) *decreases* by 4.0°.

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Table 2. Optimized Geometries for the 1-C$_{10}$F$_{15}$ Radical (C$_{3v}$)[a]

	BHLYP	B3LYP	BP86	BLYP
r_1(C*−C)	1.516	1.525	1.528	1.534
r_2	1.561	1.581	1.591	1.602
r_3	1.555	1.572	1.580	1.588
r_4	1.332	1.350	1.363	1.370
r_5	1.340	1.357	1.368	1.375
r_6	1.331	1.350	1.352	1.368
r_7	1.331	1.350	1.362	1.369
θ_1	113.2°	113.5°	113.8°	113.7°
θ_2	105.8°	105.6°	105.4°	105.6°
θ_3	109.0°	108.9°	108.8°	108.8°
θ_4	109.3°	109.3°	109.7°	109.3°
θ_5	110.2°	110.2°	110.2°	110.1°

[a] Bond lengths are in Å and bond angles are in degrees. Geometrical parameters correspond to those identified in Figure 1.

Table 3. Optimized Geometries for the 1-C$_{10}$F$_{15}$$^{-}$ Anion (C$_{3v}$)[a]

	BHLYP	B3LYP	BP86	BLYP
r_1(C*−C)	1.494	1.500	1.503	1.509
r_2	1.558	1.573	1.577	1.587
r_3	1.548	1.564	1.572	1.581
r_4	1.353	1.374	1.387	1.395
r_5	1.360	1.382	1.399	1.406
r_6	1.338	1.358	1.371	1.378
r_7	1.345	1.364	1.376	1.384
θ_1	110.3°	110.8°	111.4°	111.3°
θ_2	110.6°	110.1°	109.5°	109.8°
θ_3	108.4°	108.3°	108.2°	108.2°
θ_4	108.9°	108.9°	108.8°	108.8°
θ_5	110.3°	110.3°	110.6°	110.4°

[a] Bond lengths are in Å and bond angles are in degrees. Geometrical parameters correspond to those identified in Figure 1.

For the 1-C$_{10}$F$_{15}$$^{-}$ anion (Table 3), the geometry also differs considerably from that[6] of the radical anion C$_{10}$F$_{16}$$^{-}$. At the DZP++ B3LYP level, the C*−C bond (r_1) *decreases* by 0.051 Å, while the C−C bond distance (r_2) *increases* by 0.022 Å. The C−C*−C angle (θ_1) *increases* by 1.0°, while the C*−C−C angle (θ_2) *increases* by 1.3°.

The differences in the bond distances between the neutral 1-C$_{10}$F$_{15}$ radical and anionic 1-C$_{10}$F$_{15}$$^{-}$ are small. The C−C bonds for the neutral are longer than those for the anion. The largest difference is for the C*−C bonds (0.025 Å with the DZP++ B3LYP method), while the differences for other C−C bonds are only 0.008 Å (B3LYP, see Tables 2 and 3). In contrast, the C−F distances in the neutral are shorter (by 0.024, 0.025, 0.008, and 0.014 Å, respectively) than those for the anion. For the bond angles, only those close to the C* atom display significant differences between the neutral and anion. Angle θ_1 decreases by 2.7° from the neutral to the anion at the DZP++ B3LYP level, and angle θ_2 increases by 4.5°. This may be attributed to the "last" electron, which increases the electron density on the radical carbon atom, yielding a larger C−C*−C angle (θ_1) to provide more space for the anion lone pair.

Table 4 lists the DFT predicted EA$_{ad}$, EA$_{vert}$, and VDE values for the title radicals. For the 1-C$_{10}$F$_{15}$ radical, the adiabatic EA ranges from 3.85 eV (BHLYP) to 4.16 eV
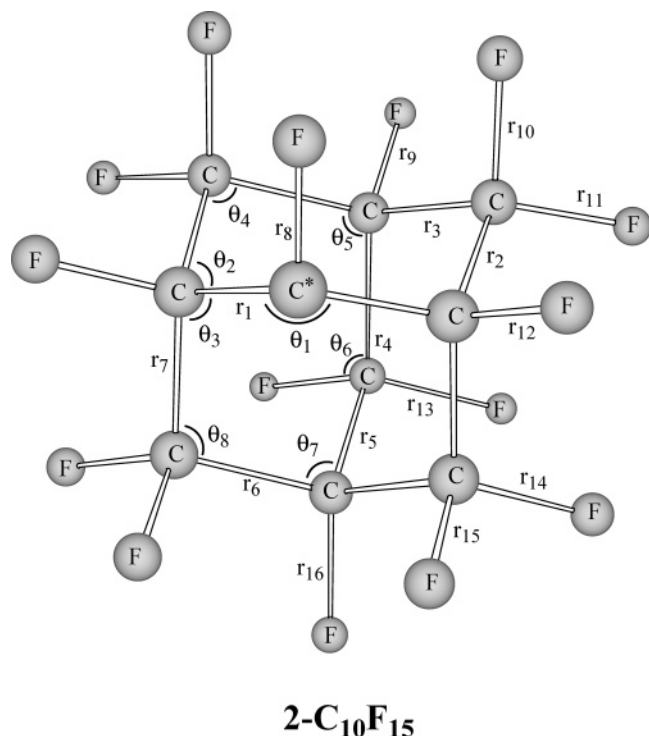

$$C_{10}F_{16}/1\text{-}C_{10}F_{15}/1\text{-}C_{10}F_{15}^{-}$$
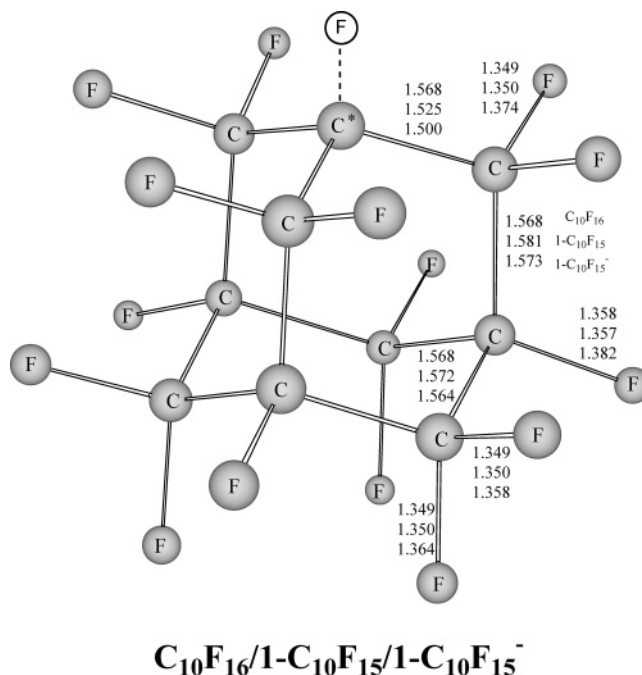
Figure 2. Bond distances for the 1-C$_{10}$F$_{15}$ radical and the 1-C$_{10}$F$_{15}$$^{-}$ anion. The bond distances for perfluoroadamantane C$_{10}$F$_{16}$ are also shown for comparison.

Table 4. Adiabatic Electron Affinities (EA$_{ad}$) and Vertical Electron Affinities (EA$_{vert}$) for the C$_{10}$F$_{15}$ Radicals and Vertical Detachment Energies (VDE) for the C$_{10}$F$_{15}$$^{-}$ Anions in eV (kcal/mol in parentheses)[a]

compound	method	EA$_{ad}$	EA$_{vert}$	VDE
1-C$_{10}$F$_{15}$	BHLYP	3.85 (88.8)	3.49 (80.4)	4.22 (97.3)
	B3LYP	4.11 (94.9)	3.76 (86.8)	4.48 (103.2)
	BP86	4.16 (95.9)	3.82 (88.0)	4.51 (104.0)
	BLYP	4.05 (93.5)	3.71 (85.5)	4.40 (101.6)
2-C$_{10}$F$_{15}$	BHLYP	2.76 (63.7)	2.03 (46.8)	3.46 (79.9)
	B3LYP	3.03 (70.0)	2.34 (54.0)	3.68 (85.0)
	BP86	3.10 (71.4)	2.44 (56.3)	3.69 (85.1)
	BLYP	3.02 (69.6)	2.37 (54.6)	3.62 (83.4)

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

(BP86). The trend of the theoretical EAs is in the order of BP86 > B3LYP > BLYP > BHLYP. The B3LYP EA$_{ad}$ prediction of 4.11 eV is expected to be the most reliable. The value of EA$_{vert}$ is predicted to be 3.76 eV (B3LYP), while the VDE is 4.48 eV (B3LYP). Yan, Brinkmann, and Schaefer[1] predicted the EA$_{ad}$ for the two C$_{10}$H$_{15}$ radicals to be negative (−0.13 eV with the B3LYP functional). Our results show that the perfluorination of adamantyl radical dramatically improves the ability to bind an electron.

It should also be noted that the predicted electron affinity of the 1-C$_{10}$F$_{15}$ radical is also much larger than that for the closed-shell C$_{10}$F$_{16}$ molecule (1.06 eV, B3LYP),[7] demonstrating that the radical has a much stronger tendency than the corresponding closed-shell molecule to bind an additional electron. This is, of course, because the addition of an electron to the radical makes it a stable closed-shell system, while an extra electron added to the stable closed-shell C$_{10}$F$_{16}$ molecule created a radical anion. Nevertheless, the magnitude

2-C₁₀F₁₅

Figure 3. Sketch of the C_s structures for the 2-$C_{10}F_{15}$ radical and the 2-$C_{10}F_{15}^-$ anion. The optimized geometrical parameters for these structures are reported in Tables 5 and 6, respectively.

of the increase (3.05 eV) in EA between $C_{10}F_{16}$ and 1-$C_{10}F_{15}$ is large.

B. 2-$C_{10}F_{15}$ and 2-$C_{10}F_{15}^-$. The second isomer 2-$C_{10}F_{15}$ has a fluorine atom removed from one bridging carbon atom of $C_{10}F_{16}$, and this radical possesses C_s symmetry. The structures predicted for the neutral 2-$C_{10}F_{15}$ and the analogous anionic 2-$C_{10}F_{15}^-$ are displayed in Figure 3, and the corresponding geometrical parameters are summarized in Tables 5 and 6 and Figure 4. The neutral radical 2-$C_{10}F_{15}$ has a $^2A'$ ground electronic state, while the closed-shell anionic 2-$C_{10}F_{15}^-$ has a $^1A'$ ground state. Vibrational analyses show that both the neutral 2-$C_{10}F_{15}$ and the anion 2-$C_{10}F_{15}^-$ are genuine minima.

Compared with the closed-shell $C_{10}F_{16}$ molecule, the C^*-C bond distances of the 2-$C_{10}F_{15}$ (r_1) radical decrease by 0.053 Å, and the other C−C bonds (r_2 to r_7) have very small changes (with differences less than 0.004 Å, Table 5). The C−C*−C angle (θ_1) increases by 5.7° at the DZP++ B3LYP level, while the changes for other angles (θ_2-θ_8) are relatively small (Table 5).

For the closed-shell anionic 2-$C_{10}F_{15}^-$, the geometry changes with respect to $C_{10}F_{16}$ are similar to that predicted for 1-$C_{10}F_{15}^-$. At the DZP++ B3LYP level, the C*−C bonds (r_1) *decrease* by 0.044 Å, while the other C−C bonds *increase* by smaller amounts, i.e., by 0.017 Å (r_2), 0.005 Å (r_3), −0.005 Å (r_4), −0.006 Å (r_5), −0.014 Å (r_6) and −0.011 Å (r_7). The C−C*−C angle (θ_1) and the C*−C−C angle (θ_2) increase by 1.0° and 3.5°, respectively, while the changes for other angles are insignificant (Table 6).

The C−C bond distances do not reveal significant differences between the neutral radical 2-$C_{10}F_{15}$ and its anion

Table 5. Optimized Geometries for the 2-$C_{10}F_{15}$ Radical $(C_s)^a$

	BHLYP	B3LYP	BP86	BLYP
r_1(C*−C)	1.507	1.515	1.517	1.524
r_2	1.551	1.570	1.579	1.589
r_3	1.555	1.571	1.580	1.588
r_4	1.553	1.570	1.579	1.588
r_5	1.553	1.570	1.578	1.587
r_6	1.551	1.567	1.574	1.583
r_7	1.546	1.564	1.573	1.582
r_8(C*−F)	1.308	1.324	1.334	1.341
r_9	1.341	1.359	1.369	1.376
r_{10}	1.334	1.353	1.365	1.371
r_{11}	1.330	1.348	1.360	1.367
r_{12}	1.342	1.360	1.371	1.379
r_{13}	1.331	1.349	1.361	1.368
r_{14}	1.330	1.348	1.360	1.366
r_{15}	1.333	1.352	1.364	1.371
r_{16}	1.341	1.359	1.370	1.377
θ_1(C−C*−C)	114.8°	115.3°	115.6°	115.6°
θ_2	108.4°	108.4°	108.3°	108.4°
θ_3	107.5°	107.5°	107.5°	107.6°
θ_4	109.0°	108.9°	108.8°	108.8°
θ_5	109.3°	109.3°	109.2°	109.2°
θ_6	110.0°	110.0°	110.0°	110.1°
θ_7	109.2°	109.2°	109.2°	109.2°
θ_8	109.5°	109.5°	109.5°	109.5°

^{a} Bond lengths are in Å and bond angles are in degrees. Geometrical parameters correpond to those identified in Figure 3.
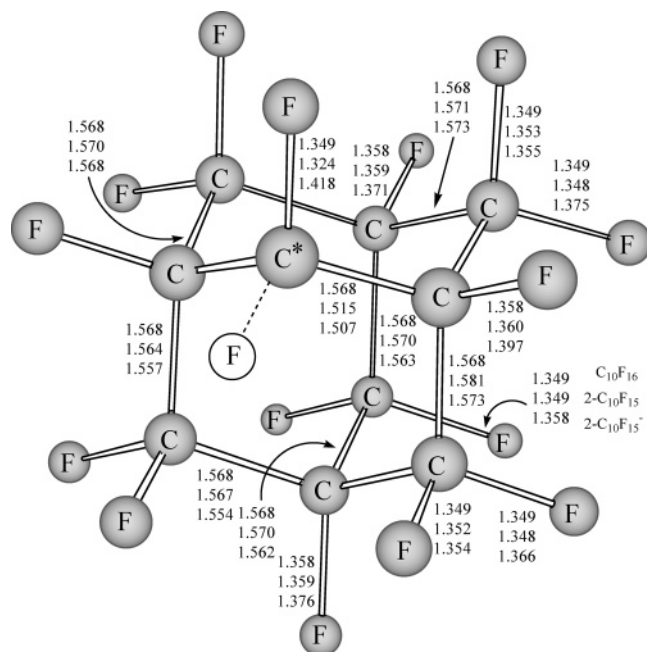
Table 6. Optimized Geometries for the 2-$C_{10}F_{15}^-$ Anion $(C_s)^a$

method	BHLYP	B3LYP	BP86	BLYP
r_1(C*−C)	1.505	1.507	1.507	1.512
r_2	1.552	1.568	1.571	1.581
r_3	1.554	1.573	1.584	1.593
r_4	1.547	1.563	1.571	1.580
r_5	1.546	1.562	1.567	1.576
r_6	1.541	1.554	1.559	1.567
r_7	1.543	1.557	1.564	1.572
r_8(C*−F)	1.405	1.418	1.420	1.431
r_9	1.353	1.371	1.384	1.391
r_{10}	1.336	1.355	1.368	1.374
r_{11}	1.352	1.375	1.393	1.401
r_{12}	1.371	1.397	1.418	1.427
r_{13}	1.339	1.358	1.371	1.378
r_{14}	1.347	1.366	1.378	1.385
r_{15}	1.334	1.354	1.367	1.374
r_{16}	1.354	1.376	1.393	1.401
θ_1(C−C*−C)	109.1°	109.8°	110.6°	110.6°
θ_2	113.6°	113.3°	112.6°	112.8°
θ_3	108.1°	108.4°	108.6°	108.6°
θ_4	107.9°	107.5°	107.1°	107.1°
θ_5	109.2°	109.2°	109.2°	109.2°
θ_6	110.5°	110.5°	110.4°	110.5°
θ_7	109.2°	109.1°	109.0°	109.1°
θ_8	109.3°	109.3°	109.5°	109.4°

^{a} Bond lengths are in Å and bond angles are in degrees. Geometrical parameters correspond to those identified in Figure 3.

2-$C_{10}F_{15}^-$. With the DZP++ B3LYP method, the C−C bond lengths for the neutral 2-$C_{10}F_{15}$ are predicted to be 1.515− 1.571 Å, and those for the anionic species are 1.507−1.573

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$$C_{10}F_{16}/2\text{-}C_{10}F_{15}/2\text{-}C_{10}F_{15}^{-}$$

Figure 4. Bond distances for the 2-$C_{10}F_{15}$ radical and the 2-$C_{10}F_{15}^{-}$ anion. The bond distances for perfluoroadamantane $C_{10}F_{16}$ are also shown for comparison.

Å, with the C−C bonds for the neutral being slightly longer than those for the anion. For most C−F bonds (r_9 to r_{16}), the differences between the neutral and the anion are quite small, with those in the neutral being slightly shorter than those in anion. However, the C*−F bond (r_8) predicted for the neutral is 0.094 Å shorter than that in the anion. This is the largest structural difference predicted for these adamantine systems.

The trend for the predicted C−C and C−F bond lengths is in the order of BHLYP < B3LYP < BP86 < BLYP. The C−C*−C angle (θ_1) in the neutral is larger than that in the anion by 5.5°, while the C*−C−C angles (θ_2) in the neutral are smaller by 4.9° (B3LYP). The differences in other angles between the neutral and the anion are quite small. It is also found that the four methods predict very similar values for the bond angles (Tables 5 and 6).

Energetically, the four DFT methods predict that the neutral 2-$C_{10}F_{15}$ radical lies close to the neutral 1-$C_{10}F_{15}$ isomer. (Total energies are shown in Table 1.) For instance, the B3LYP method predicts the radical structure 2-$C_{10}F_{15}$ lies below 1-$C_{10}F_{15}$ by only 2.0 kcal/mol. However, the anionic 2-$C_{10}F_{15}^{-}$ isomer lies much higher than the anionic 1-$C_{10}F_{15}^{-}$ isomer (e.g., by 23.0 kcal/mol at B3LYP). This is because the orbital energy for the singly occupied molecular orbital (a_1) for 1-$C_{10}F_{15}$ (−0.206 hartree at B3LYP) is much lower than that (a') for 2-$C_{10}F_{15}$ (−0.157 hartree at B3LYP). Consequently, the neutral-anion energy separations (including EA_{ad}) of the isomer 2-$C_{10}F_{15}$ will be much smaller than those of the isomer 1-$C_{10}F_{15}$. The EA_{ad} and EA_{vert} values for the 2-$C_{10}F_{15}$ radical and the VDE for its 2-$C_{10}F_{15}^{-}$ anion are reported in Table 4 with four DFT methods. The BHLYP method predicts the lowest EA_{ad} value of 2.76 eV, followed by BLYP (3.02 eV) and B3LYP (3.03 eV), while the BP86

Table 7. Harmonic Vibrational Frequencies (in cm^{-1}) for the 1-$C_{10}F_{15}$ Radical and the 1-$C_{10}F_{15}^{-}$ Anion with the B3LYP Method[a]

sym	neutral	anion
a_1	192 (0)	194 (0)
	255 (1)	250 (5)
	294 (4)	308 (0)
	364 (0)	308 (5)
	457 (17)	416 (3)
	614 (15)	438 (5)
	654 (6)	593 (4)
	717 (3)	638 (10)
	981 (273)	684 (2)
	1069 (3)	954 (498)
	1236 (2)	1178 (26)
	1270 (1)	1210 (1)
	1282 (435)	1249 (421)
	1311 (24)	1282 (30)
a_2	129 (0)	129 (0)
	223 (0)	234 (0)
	244 (0)	257 (0)
	269 (0)	277 (0)
	385 (0)	385 (0)
	427 (1)	840 (0)
	847 (0)	1037 (0)
	1082 (0)	1054 (35)
	1154 (0)	1141 (0)
e	136 (0)	138 (0)
	194 (0)	195 (0)
	204 (0)	213 (0)
	242 (0)	247 (0)
	252 (0)	256 (0)
	262 (0)	264 (0)
	294 (8)	298 (2)
	296 (0)	300 (2)
	379 (2)	383 (0)
	399 (10)	409 (8)
	431 (6)	431 (0)
	599 (0)	589 (0)
	642 (36)	636 (30)
	779 (0)	779 (16)
	947 (400)	925 (620)
	995 (60)	980 (44)
	1061 (0)	1021 (2)
	1070 (78)	1055 (12)
	1154 (28)	1146 (124)
	1224 (12)	1170 (0)
	1245 (0)	1216 (410)
	1277 (532)	1241 (128)
	1304 (648)	1286 (934)

[a] The infrared intensities in km/mol are listed in parentheses.

gives the highest (3.10 eV). Among these we conclude that the B3LYP result 3.03 eV is the most reliable, being 1.08 eV smaller than that for 1-$C_{10}F_{15}$. The B3LYP method also predicts the EA_{vert} value to be 2.34 eV and the VDE value for the anion to be 3.68 eV (Table 4). Although the neutral-anion energy separations for 2-$C_{10}F_{15}$/$C_{10}F_{15}^{-}$ are smaller than those for 1-$C_{10}F_{15}$/$C_{10}F_{15}^{-}$, they are indeed much larger than those for the $C_{10}F_{16}$ molecule.[7]

C. Vibrational Frequencies and ZPVE Corrections. The B3LYP predicted harmonic vibrational frequencies for the 1-$C_{10}F_{15}$/$C_{10}F_{15}^{-}$ systems are reported in Table 7, and those

Table 8. Harmonic Vibrational Frequencies (in cm^{-1}) for the 2-$C_{10}F_{15}$ Radical and the 2-$C_{10}F_{15}^-$ Anion with the B3LYP Method[a]

sym	neutral	anion
a′	113 (0)	137 (0)
	160 (0)	184 (0)
	177 (0)	193 (1)
	209 (0)	206 (1)
	246 (0)	239 (1)
	250 (0)	250 (1)
	252 (1)	252 (1)
	258 (1)	266 (1)
	270 (0)	272 (0)
	294 (4)	295 (1)
	298 (1)	300 (2)
	320 (2)	318 (0)
	369 (2)	371 (3)
	391 (1)	391 (1)
	406 (3)	401 (11)
	411 (9)	409 (2)
	464 (8)	448 (8)
	540 (5)	546 (12)
	567 (1)	549 (0)
	628 (8)	623 (6)
	658 (9)	656 (10)
	691 (0)	678 (1)
	848 (0)	832 (12)
	961 (276)	918 (245)
	978 (298)	942 (344)
	1009 (21)	966 (164)
	1055 (8)	1018 (5)
	1064 (1)	1034 (7)
	1090 (4)	1078 (2)
	1206 (29)	1126 (63)
	1239 (19)	1130 (5)
	1254 (169)	1178 (41)
	1265 (174)	1205 (48)
	1277 (196)	1243 (82)
	1290 (74)	1265 (87)
	1294 (8)	1267 (265)
	1313 (96)	1277 (229)
	1390 (134)	1288 (40)
a″	107 (0)	124 (0)
	115 (0)	130 (0)
	182 (0)	192 (0)
	200 (0)	206 (0)
	232 (0)	226 (0)
	246 (0)	242 (0)
	249 (0)	248 (0)
	257 (1)	262 (0)
	264 (1)	263 (1)
	268 (0)	270 (0)
	279 (3)	280 (0)
	298 (4)	302 (2)
	384 (0)	378 (1)
	385 (0)	382 (0)
	406 (4)	407 (1)
	434 (9)	433 (3)
	591 (1)	593 (2)
	645 (15)	638 (15)
	795 (1)	757 (6)
	845 (0)	838 (0)
	948 (215)	913 (311)
	991 (36)	971 (13)
	1063 (4)	1010 (26)
	1083 (6)	1046 (49)
	1119 (0)	1085 (10)
	1148 (4)	1126 (38)
	1170 (0)	1157 (58)
	1228 (4)	1197 (343)
	1244 (22)	1215 (19)
	1287 (533)	1234 (1)
	1313 (1)	1271 (212)

[a] The infrared intensities in km/mol are listed in parentheses.

Table 9. Zero-Point Vibrational Energies (ZPVE) and ZPVE-Corrected Adiabatic Electron Affinities EA$_{ad(ZPVE)}$ in eV (kcal/mol in parentheses) for the $C_{10}F_{15}$ Radicals

compound	BHLYP	B3LYP	BP86	BLYP
1-$C_{10}F_{15}$	3.06 (70.6)	2.87 (66.1)	2.74 (63.1)	2.69 (62.0)
1-$C_{10}F_{15}^-$	3.02 (69.6)	2.82 (65.0)	2.69 (62.0)	2.64 (60.8)
Δ(ZPVE)	0.04 (1.0)	0.05 (1.1)	0.05 (1.1)	0.05 (1.2)
EA$_{ad(ZPVE)}$	3.89 (89.8)	4.16 (96.0)	4.21 (97.0)	4.10 (94.7)
2-$C_{10}F_{15}$	3.06 (70.6)	2.87 (66.2)	2.74 (63.2)	2.70 (62.2)
2-$C_{10}F_{15}^-$	3.00 (69.2)	2.80 (64.6)	2.66 (61.4)	2.62 (60.3)
Δ(ZPVE)	0.06 (1.4)	0.07 (1.6)	0.08 (1.8)	0.08 (1.9)
EA$_{ad(ZPVE)}$	2.82 (65.1)	3.10 (71.6)	3.18 (73.2)	3.10 (71.5)

for the 2-$C_{10}F_{15}$/$C_{10}F_{15}^-$ species are listed in Table 8. All of the vibrational frequencies are real, suggesting that all these systems (neutral and anion) are genuine minima on their potential hypersurfaces. Although no experimental results are available for these systems, the B3LYP predictions should be qualitatively reliable.

When molecular systems under study become larger, the ZPVE corrections to electron affinities are sometimes substantial. In a study of polycyclic aromatic hydrocarbon (PAH) EAs,[9] the ZPVE corrections were found to be several tenths of an electronvolt and to account for a significant portion (as much as 40% for coronene) of the overall EAs. In research on the unsubstituted hydrocarbon $C_{10}H_{15}$ radicals,[1] the ZPVE corrections were found to be 0.13 and 0.10 eV, respectively, corresponding to the same magnitude as the EA$_{ad}$ values.

Zero-point vibrational energies (ZPVEs) for the perfluoro-adamantyl radicals and the related anions are presented in Table 9. The ZPVE differences between the neutrals and the anions are in the range 0.04−0.08 eV, which are then used for the correction of the electron affinities. After the ZPVE corrections the EA$_{ad}$ values (B3LYP) increase to 4.16 eV for 1-$C_{10}F_{15}$ and 3.10 eV for 2-$C_{10}F_{15}$ (Table 9). Compared with the aromatic radicals[5] C_6F_5, $C_{10}F_7$ and $C_{14}F_9$, the ZPVE corrections for the perfluoroadamantyl radicals are relatively small, i.e., 0.05 eV (1.2%) for 1-$C_{10}F_{15}$ and 0.07 eV (2.3%) for 2-$C_{10}F_{15}$ at the B3LYP level.

Concluding Remarks

There are two forms of perfluoroadamantyl radicals ($C_{10}F_{15}$): 1-$C_{10}F_{15}$ with C_{3v} symmetry and 2-$C_{10}F_{15}$ with C_s symmetry. The neutral 1-$C_{10}F_{15}$ isomer has a slightly higher energy (by 0.086 eV or 1.98 kcal/mol, at the B3LYP level) than the 2-$C_{10}F_{15}$ radical, while the anionic 1-$C_{10}F_{15}^-$ isomer lies *below* the 2-$C_{10}F_{15}^-$ anion by 1.00 eV (23.0 kcal/mol). Both isomers are predicted to have large positive adiabatic electron affinities. The reliable predicted adiabatic electron affinities with the DZP++ B3LYP method are 4.11 and 3.03 eV for the two perfluoroadamantyl radicals, respectively. It is shown that the perfluoroadamantyl radicals have consider-able ability to bind an additional electron and may thus be useful in the study of new materials and new chemical reactions. The ZPVE corrections for the EA$_{ad}$ values are not substantial, i.e., 0.05 eV (1.2%) for 1-$C_{10}F_{15}$ and 0.07 eV (2.3%) for 2-$C_{10}F_{15}$ at the DZP++ B3LYP level, and the ZPVE-corrected EA$_{ad}$ are 4.16 and 3.10 eV, respectively. It

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is hoped that the present theoretical predictions will stimulate further experimental studies on these and related systems. In light of the very large electron affinity of the $1\text{-}C_{10}F_{15}$ radical, it would be of special interest to examine the perfluorinated superadamantyl systems[19] $C_{35}F_{36}$, $C_{35}F_{35}$, and $C_{35}F_{35}^{-}$.

Supporting Information Available: Cartesian coordinates for all molecular structures predicted by the B3LYP method (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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