Article

The Perfluoro Cage Effect: A Search for Electron-Encapsulating Molecules

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ABSTRACT: Quantum chemical calculations have for some time predicted that perfluorinated polyhedral organic molecules should exhibit a low-energy LUMO consisting of the overlapping inward-pointing lobes of the C−F σ^* orbitals. Accordingly, these molecules should be able to encapsulate an electron within the interior of their cavities. Inspired by the recent confirmation of this prediction for perfluorocubane, we have sought to identify additional perfluorinated cage molecules capable of this remarkable behavior, which we refer to as the perfluoro cage effect (PCE). Using DFT calculations with multiple well-tested exchange-correlation functionals and large STO-QZ4P basis sets, we have identified several systems including [n]prismanes ($n = 3−6$), [n]asteranes ($n = 3−5$), twistane, and two norbornadiene dimer cages that clearly exhibit the PCE. In other words, they exhibit a low-energy LUMO belonging to the total symmetric irreducible representation of the point group in question and adiabatic electron affinities ranging from somewhat under 1 eV to over 2 eV. A pronounced size effect appears to hold, with larger cages exhibiting higher electron affinities (EAs). The largest adiabatic EAs, well over 3 eV, are predicted for perfluorinated dodecahedrane and C_{60}. In contrast, the PCE is barely discernible for perfluorinated tetrahedrane and bicyclo[1.1.1]pentane.
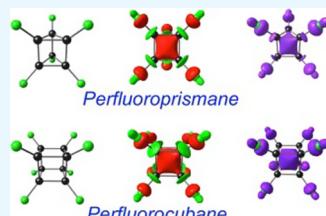
INTRODUCTION

Polyfluorination and perfluorination typically affect organic molecules in a profound manner.[1−3] One such influence is the so-called perfluoro effect, observed for planar conjugated molecules, in which the fluorines exert a much stronger stabilizing influence on the σ molecular orbitals than on the π molecular orbitals.[4−7] Perfluorinated polyhedral organic molecules have been theoretically examined and a key prediction is a low-energy, totally symmetric LUMO derived from the overlapping inward-pointing lobes of the C−F σ^* orbitals.[8,9] The molecules thus exhibit a significant electron affinity (EA), accommodating the electron largely within central cavity of the polyhedra. This prediction has now been experimentally realized in the form of the perfluorocubane anion radical with O_h symmetry.[10] Herein, we have used density functional theory (DFT) to explore both the generality and limitations of the electron-encapsulating effect across a wide range of organo-fluorine cages. The effect, hereafter referred to as the perfluoro cage effect (PCE), indeed appears to be general, with only a handful of exceptions. Several new examples of the PCE are predicted.

RESULTS AND DISCUSSION

Sixteen perfluorinated polyhedral and/or cage molecules were examined with three well-tested[11−15] exchange-correlation functionals, OLYP,[16,17] B3LYP,[18,19] and B3LYP*,[20,21] augmented with D3[22] dispersion corrections, and large STO-QZ4P basis sets. Table 1 presents their calculated adiabatic EAs, while Figure 1 presents graphical representations of their LUMOs and the spin densities of their anion-radicals. In pretty much every

case examined, the LUMO belongs to the totally symmetric irreducible representation of the point group in question. The vast majority of the molecules also exhibit a significant electron-encapsulating ability, as measured by the adiabatic EAs, which, by and large, are mutually consistent across the three functionals.

All the perfluorinated prismanes exhibit sizable electron affinities, with the following order across all three functionals (the values in eV shown within parentheses are for OLYP): hexaprismane[23,24] (2.15) > pentaprismane[25,26] (1.98) > cubane[27−29] (1.55) > prismane[30,31] (0.97). The ordering suggests a pronounced size effect on the PCE: larger fluorinated cages result in greater stabilization of the encapsulated electron.

The three asteranes[32−36] examined also exhibit relatively large electron affinities, with that of perfluoro[5]asterane (OLYP: 2.43 eV) and perfluoro[4]asterane (2.03 eV) greatly exceeding that of perfluoro[3]asterane (1.36 eV). Again, there appears to be a pronounced size effect.

The two T_d systems examined, tetrafluorotetrahedrane[37,38] and perfluoroadamantane,[39−43] exhibit dramatically different electron affinities. For the former, the value is near zero, suggesting that the relatively tiny tetrahedral cage cannot effectively encapsulate an electron. The same also holds for perfluorinated bicyclo[1.1.1]pentane.[44,45] In contrast, perfluori-
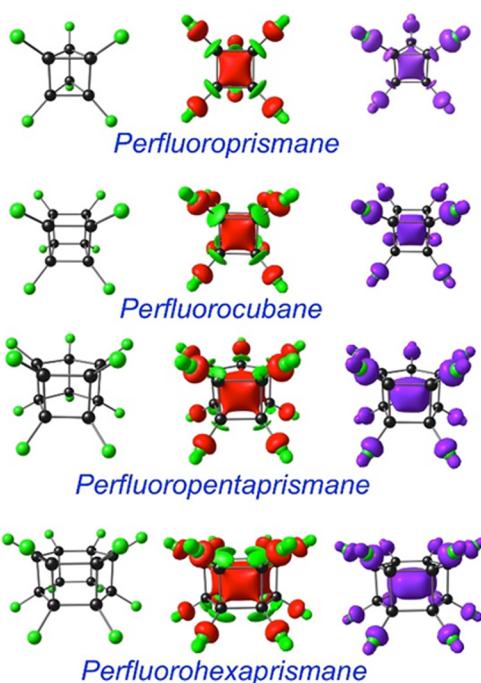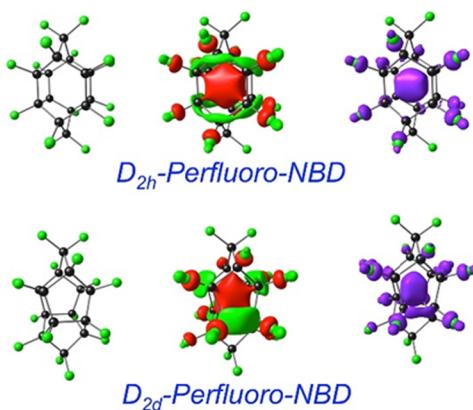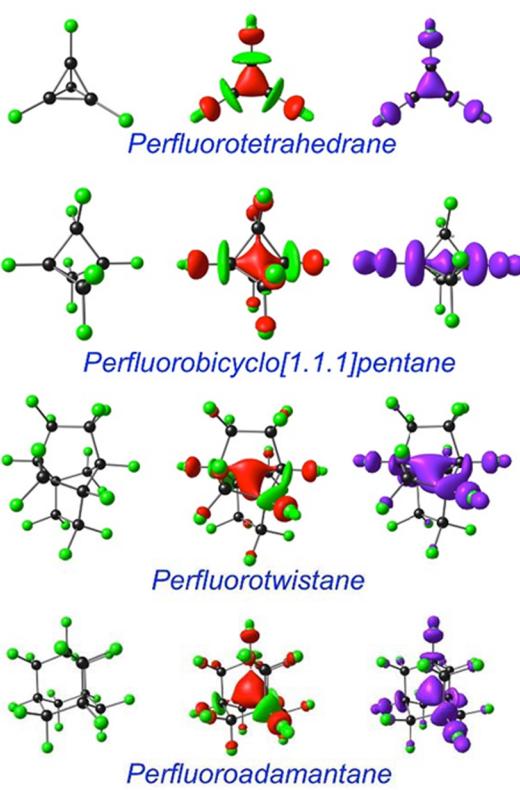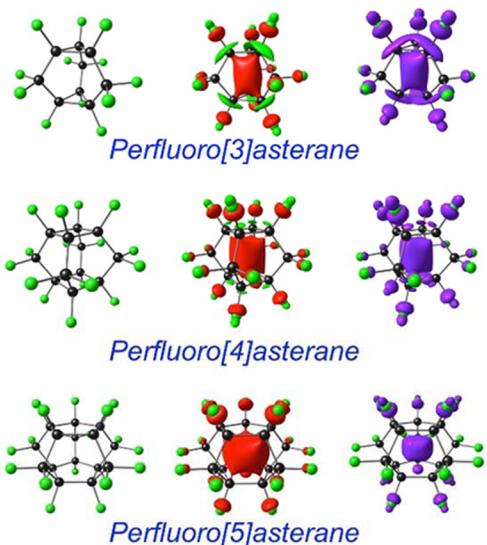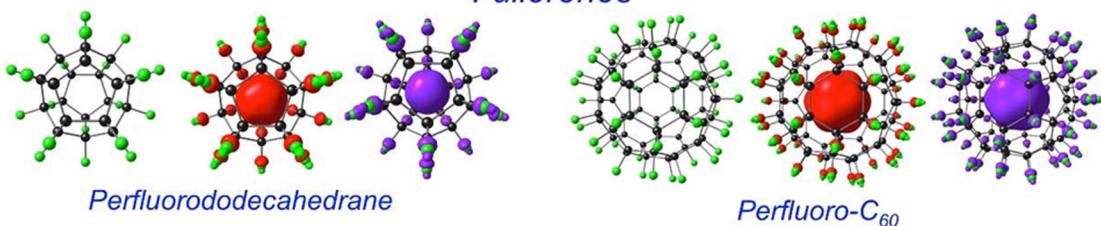
Figure 1. Ball-and-stick structures, neutral LUMOs, anion spin densities of the perfluorinated cage molecules studied.

nated twistane[46] (OLYP: 0.73) and adamantane (1.09 eV) exhibit moderate, positive EAs.

Among the molecules examined here, the largest adiabatic EAs have been calculated for perfluorinated dodecahedrane, $C_{20}F_{20}$,[47−49] and buckministerfullerene, $C_{60}F_{60}$,[50−52] the OLYP

Table 1. Adiabatic Electron Affinities (eV) of the Compounds Studied

compound	point group	LUMO irrep	adiabatic EA			
			OLYP	OLYP (ZPE)	B3LYP*	B3LYP
Prismanes						
Perfluoroprismane	D_{3h}	a'_1	0.97	1.04	0.87	0.80
Octafluorocubane	O_h	a_{1g}	1.55	1.67	1.43	1.35
Perfluoropentaprismane	D_{5h}	a'_1	1.98	2.12	1.85	1.77
Perfluorohexaprismane	D_{6h}	a_{1g}	2.15	2.28	2.04	1.96
Asteranes						
Perfluoro[3]asterane	C_{3h}	a'	1.36	1.54	1.18	1.08
Perfluoro[4]asterane	D_{4h}	a_{1g}	2.03	2.19	1.91	1.82
Perfluoro[5]asterane	D_{5h}	a'_1	2.43	2.59	2.39	2.33
Perfluoronorbornadiene dimers						
D_{2d}-Perfluoro-NBD	D_{2d}	a_1	2.02	2.18	1.90	1.81
D_{2h}-Perfluoro-NBD	D_{2h}	a_g	2.05	2.26	1.96	1.87
Miscellaneous						
Perfluorotetrahedrane	T_d	a_1	0.02	0.10	0.07	0.07
Perfluorobicyclo[1.1.1]pentane	D_{3h}	a	−0.03		−0.05	−0.13
Perfluorotwistane	D_2	a	0.73	0.99	0.59	0.48
Perfluoroadamantane	T_d	a_1	1.09	1.29	0.93	0.81
Fullerenes						
Perfluorododecahedrane	I_h	a_{1g}	3.44	3.54	3.52	3.46
Perfluoro-C_{60}	I_h	a_{1g}	3.87		4.53	4.50

values being 3.44 and 3.87 eV, respectively. In each case, the spin density of the anion radical has the shape of a spheroidal shell within the interior of the polyhedral skeletons.

CONCLUDING REMARKS

Given the large number of polyhedral or cage-shaped molecules that have been synthesized and the vastly greater number that are theoretically possible, a clear conclusion from the present study is that electron encapsulation by their perfluorinated counterparts should be widely prevalent — indeed more the rule than the exception — and limited only by the accessibility of the compounds in question. The only exceptions appear to be the smallest cages such as tetrahedrane and bicyclo[1.1.1]pentane.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c07374.

Optimized Cartesian coordinates (10 pages) (PDF)

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Notes

The authors declare no competing financial interest.

The data underlying this study are available in the published article and its online Supplementary Material.

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