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THEORETICAL STUDIES OF FLUOROCARBONS
PART III. PRIMARY, SECONDARY, TERTIARY AND QUATERNARY CENTRES

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SUMMARY

Quantum chemical calculations are used to examine the differences between fully fluorinated alkanes with primary, secondary, tertiary and quaternary centres. Systems studied include $C(CF_3)_nF_{4-n}$ (n=0-4), $CF_3[C(CF_3)_2]_pCF_3$ (p=1-5), $(CF_3)_2CF[C(CF_3)_2]_qCF(CF_3)_2$ (q=0-3) and $CF_3CF_2[C(CF_3)_2]_rCF_2CF_3$ (r=0-3).

In addition we compare systems which react with arenethiolate nucleophiles under mild conditions (e.g. cis-perfluorodecalin and perfluoro(methylcyclohexane)) and those which do not (e.g. perfluorohexane and perfluorocyclohexane). A crude "lattice energy" model is used to investigate the likelihood of electron transfer, which is one possible mechanism for the unexpected reactivity.

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INTRODUCTION

In this paper we extend our previous ab initio studies of small fluorine and chlorine substituted alkanes [1,2,3] to investigate the differences between primary, secondary, tertiary and quaternary centres in larger perfluoroalkanes. This study was prompted by the unexpected reactivity of systems such as perfluorodecalin [4], and by intriguing charge distributions observed in our previous work [1]. It is evident that the electronic structure and reactivity even of fairly small, fully fluorinated saturated systems are not fully understood.

We have found for fluorine substituted alkanes that variations in carbon-fluorine bond length can be rationalized using a simple electrostatic model [1,2]. The Mulliken populations on fluorine vary very little, but the corresponding charges for carbon, q(C), show a much wider range of values, with more positive charges corresponding to shorter C-F bonds. For example, successive substitution of H by F in $\underline{C}H_4$ or $CF_3\underline{C}H_3$ leads to a more positive q($\underline{C}$) and a shortening of the $\underline{C}$-F bond length(s).

Similarly, Mulliken population analyses for perfluoroalkanes [1] suggest that the $-CF_3$ group is less electron withdrawing than is the fluorine atom itself. Thus, we can expect the positive charge on carbon to be ordered tertiary < secondary < primary and the C-F bond lengths to follow the order tertiary > secondary > primary. In this work, we compare tertiary, secondary and primary centres, and we examine the charge distributions for molecules which do react with arenethiolate nucleophiles under mild conditions [4] (e.g. perfluoro(methylcyclohexane)) with those for molecules which do not (e.g. perfluorocyclohexane).

Our interest also in quaternary sites arises, to a large extent, from the unusual Mulliken populations calculated for perfluorospiro[2.2]pentane, according to which the central carbon atom appears to carry a small net negative charge [1]. In addition to $C(CF_3)_4$, we investigate systems with adjacent quaternary sites. We consider three series of perfluoroalkane systems with a backbone of -$C(CF_3)_2$- units:

$CF_3[C(CF_3)_2]_pCF_3$ (p=1,2,3,4,5)
$(CF_3)_2CF[C(CF_3)_2]_qCF(CF_3)_2$ (q=0,1,2,3)
$CF_3CF_2[C(CF_3)_2]_rCF_2CF_3$ (r=0,1,2,3)

We show in Figure 1 the systems with p=3, q=1, and r=1.

RESULTS

Results of geometry optimizations for CF_4, C_2F_6, $CF_2(CF_3)_2$, $CF(CF_3)_3$ and $C(CF_3)_4$ are summarized in Table 1. Semi-empirical results using the AM1 method, which we have found to be more reliable for perfluoroalkanes than MNDO or MINDO/3 [1], are given together with ab initio SCF results using STO-3G and 3-21G+d_F basis sets. Full details of the ab initio and semi-empirical computational methods are given in Ref. 1. Based on our previous experience, we expect the most appropriate basis sets to be those that include polarization functions on fluorine ("d_F") but not on carbon. Our computational resources were not sufficient for a full geometry optimization of the largest system, $C(CF_3)_4$, using a 3-21G+d_F basis set.

It is clear from the Mulliken populations in Table 1 that the charge on fluorine is essentially independent of its environment. Consequently, we observe the orders anticipated above, namely

q(C): quaternary < tertiary < secondary < primary

and

r(C-F): tertiary > secondary > primary.

The differences between the C-F bond lengths are of the order of 0.02Å. The C-C bond lengths and the primary C-F bond lengths do not vary significantly from molecule to molecule.

Our results for $C(CF_3)_4$ are consistent with our previous findings for perfluorospiro[2.2]pentane [1], in that the central carbon atom in both of these molecules carries a net negative Mulliken charge. Although, at first sight, this is not what might be expected for a carbon atom attached to four electron-withdrawing groups, it is in keeping with the trend

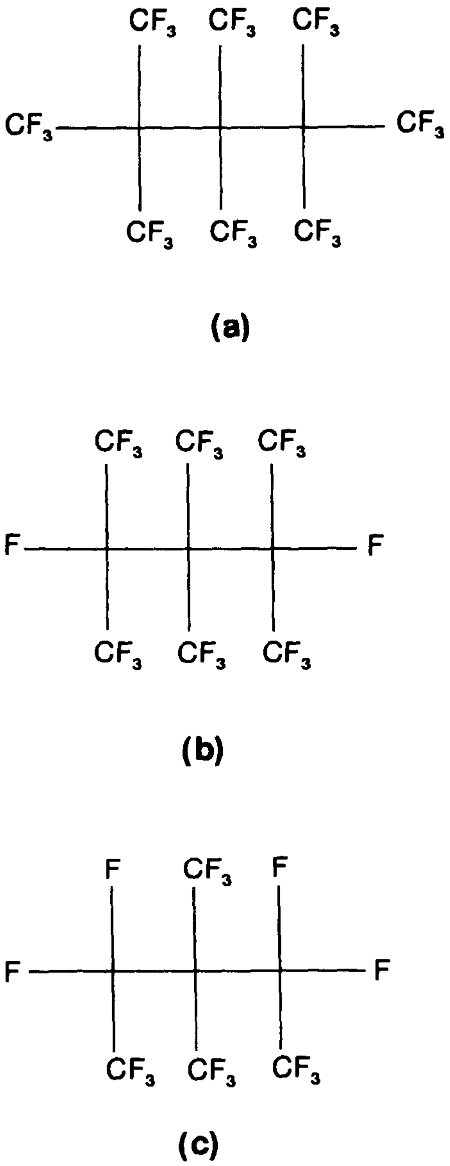

Fig. 1. Representative members of the three series $CF_3[C(CF_3)_2]_pCF_3$, $(CF_3)_2CF[C(CF_3)_2]_qCF(CF_3)_2$ and $CF_3CF_2[C(CF_3)_2]_rCF_2CF_3$: (a) $p=3$, (b) $q=1$ and (c) $r=1$.

TABLE 1

Results for CF_4, for C_2F_6 and for molecules of general formula $\underline{C}(CF_3)_n\underline{F}_{4-n}$ (n=1 to 4)

	AM1	STO-3G	3-21G+d_F	experiment
$(CF_3)F$				
r(C-F)/Å	1.36	1.37	1.31	1.319[a]
q(C)	+0.58	+0.57	+1.40	
q(F)	-0.14	-0.14	-0.35	
$(CF_3)_2$				
r(C-F)/Å	1.36	1.37	1.32	1.326[b]
r(C-C)/Å	1.62	1.62	1.51	1.545[b]
q(C)	+0.39	+0.41	+1.00	
q(F)	-0.13	-0.14	-0.33	
$\underline{C}(CF_3)_2\underline{F}_2$				
r(C-F)/Å	1.36	1.37	1.32	
r($\underline{C}$-$\underline{F}$)/Å	1.37	1.38	1.34	
r($\underline{C}$-C)/Å	1.61	1.61	1.52	
q(C)	+0.39	+0.41	+1.09	
q($\underline{C}$)	+0.20	+0.24	+0.46	
q(F)	-0.13	-0.14	-0.33	
q($\underline{F}$)	-0.11	-0.13	-0.32	
$\underline{C}(CF_3)_3\underline{F}$				
r(C-F)/Å	1.36	1.37	1.32	
r($\underline{C}$-$\underline{F}$)/Å	1.37	1.38	1.36	
r($\underline{C}$-C)/Å	1.61	1.60	1.52	
q(C)	+0.42	+0.42	+1.17	
q($\underline{C}$)	-0.03	+0.08	-0.23	
q(F)	-0.13	-0.14	-0.33	
q($\underline{F}$)	-0.07	-0.12	-0.31	
$\underline{C}(CF_3)_4$				
r(C-F)/Å	1.37	1.37		1.325[c]
r($\underline{C}$-C)/Å	1.58	1.59		1.562[c]
q(C)	+0.45	+0.43		
q($\underline{C}$)	-0.29	-0.09		
q(F)	-0.13	-0.14		

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[a] Ref. 5 [b] Ref. 6 [c] Ref. 7

in the primary→tertiary series. It would be very interesting to investigate the charge distributions in these compounds experimentally using nmr or using the core-level shifts observed in X-ray PES (ESCA). ESCA studies have been reported for some of the smaller systems we considered in previous work [1,2]. Siegbahn and co-workers [8] found a very large shift of the carbon 1s level from CF_4 to CF_3H, in keeping with our calculated values of q(C) in these two systems. In the case of the series CH_4-CH_3Cl-CH_2Cl_2-$CHCl_3$-CCl_4, there is an approximately linear correlation between our calculated values of q(C) and the experimentally observed positions [9] of the corresponding C(1s) peak. It is regrettable that so few haloalkanes have been studied using this technique.

The unusual character of the quaternary carbon atoms in $C(CF_3)_4$ and perfluorospiro[2.2]pentane has prompted us to consider the charges in larger perfluoroalkanes. The size of such molecules has precluded *ab initio* calculations, and so we investigate the charge distributions using the AM1 semi-empirical method. The AM1 charges listed in Table 1 and in our previous work [1] reproduce the qualitative trends established from the *ab initio* studies.

The results for the three series $CF_3[C(CF_3)_2]_pCF_3$, $(CF_3)_2CF[C(CF_3)_2]_qCF(CF_3)_2$ and $CF_3CF_2[C(CF_3)_2]_rCF_2CF_3$ are listed in Table 2. Our results for the $CF_3[C(CF_3)_2]_pCF_3$ series suggest that a quaternary carbon atom bonded to four CF_3 groups (p=1) has a slightly more negative charge than a quaternary carbon connected to three CF_3 groups and to a larger perfluoroalkyl group (p=2-5). Carbon atoms which are separated by more than two positions from the end carry only very small charges.

The results for the other two series, $(CF_3)_2CF[C(CF_3)_2]_qCF(CF_3)_2$ and $CF_3CF_2[C(CF_3)_2]_rCF_2CF_3$, in which the second carbon atom from each end is no longer quaternary, show that the charge distributions at the ends of these molecules can be altered significantly by the substitution of CF_3 by F. The alpha carbon atom, bonded to the fluorine atom(s), becomes more positively charged: the adjacent quaternary (beta) carbon atom becomes more negatively

TABLE 2

Semi-empirical (AM1) estimates of the charges on the backbone carbon atoms for the series $CF_3[C(CF_3)_2]_pCF_3$, $(CF_3)_2CF[C(CF_3)_2]_qCF(CF_3)_2$ and $CF_3CF_2[C(CF_3)_2]_rCF_2CF_3$. See also Figure 1, where we show the molecules with p=3, q=1, and r=1

System	Charges on carbon
$CF_3[C(CF_3)_2]_pCF_3$	
p=1	+0.45 -0.29 +0.45
p=2	+0.43 -0.21 -0.21 +0.43
p=3	+0.42 -0.21 -0.09 -0.21 +0.42
p=4	+0.42 -0.21 -0.09 -0.09 -0.21 +0.42
p=5	+0.42 -0.22 -0.09 -0.09 -0.09 -0.22 +0.42
$(CF_3)_2CF[C(CF_3)_2]_qCF(CF_3)_2$	
q=0	+0.41 +0.00 +0.00 +0.41
q=1	+0.41 +0.03 -0.17 +0.03 +0.41
q=2	+0.41 +0.02 -0.14 -0.14 +0.02 +0.41
q=3	+0.41 +0.02 -0.13 -0.09 -0.13 +0.02 +0.41
$CF_3CF_2[C(CF_3)_2]_rCF_2CF_3$	
r=0	+0.40 +0.20 +0.20 +0.40
r=1	+0.40 +0.25 -0.26 +0.25 +0.40
r=2	+0.40 +0.23 -0.18 -0.18 +0.23 +0.40
r=3	+0.40 +0.23 -0.18 -0.09 -0.18 +0.23 +0.40

charged. A CF_3 group appears to lead to a more negative charge on an attached quaternary carbon atom than does a larger perfluoroalkyl group, such as C_2F_5. The systems with p=2, q=2 and r=2 all have adjacent carbon atoms with significant negative charges.

The perfluoroalkane systems which have been reported to react readily with arenethiolate nucleophiles under mild conditions [4] all possess a tertiary centre. Molecules such as perfluorohexane and perfluorocyclohexane, which have only primary or secondary centres, do not appear to react under these conditions. It is tempting to link the difference in reactivity to the very different charge distributions in the two sets of molecules. With this in mind, we have carried out semi-empirical (AM1) calculations on cis-perfluorodecalin and perfluoro(methylcyclohexane), and on perfluorohexane and perfluorocyclohexane. Results are listed in Table 3.

We find that the tertiary centres in cis-perfluorodecalin and perfluoro(methylcyclohexane) have charges which are very similar to that for the tertiary site in $CF(CF_3)_3$, whereas perfluorohexane and perfluorocyclohexane have the charge distributions expected for systems with primary and secondary centres. A possible mechanism for the reactivity of the compounds with a tertiary centre involves electron transfer to form a radical anion which then loses F^-. Some support for this idea comes from anionic polymerization of perfluorinated alkenes, which provides only products of low molecular weight [10]. This has been interpreted in terms of the facile loss of a beta fluoride ion from perfluorinated carbanions.

Accordingly, we have considered how the different charge distributions in the neutral molecules might affect the likelihood of electron transfer. First of all, we examined the HOMO and LUMO energies from our AM1 calculations (see Table 3), but could see no significant differences between the reactive and non-reactive systems. As an alternative, we investigated a very crude "lattice energy" model. Motivated by the well known result that an electron moving in the field of a fixed dipole moment exceeding 1.625 Debye may in principle have an infinite number of bound states [11] (within the Born-

TABLE 3

Semi-empirical (AM1) estimates of charges on carbon, q(C), and SCF orbital energies, ε_{HOMO} and ε_{LUMO}. ΔE_L is the change in "lattice energy" on adding an electron, as described in the text

	net Mulliken q(C)	SCF orbital energy		ΔE_L/eV
		ε_{HOMO}/eV	ε_{LUMO}/eV	
cis-perfluorodecalin				
tertiary-C	+0.01	-12.53	-1.27	-2.4
secondary-C	+0.21‡	"	"	+0.3 to +0.7
perfluoro(methylcyclohexane)				
tertiary-C	-0.02	-12.60	-1.16	-3.3
secondary-C	+0.21‡	"	"	+0.2 to +0.6
primary-C	+0.42	"	"	+3.5
perfluoro(methylpropane) $(CF_3)_3CF$				
tertiary-C	-0.03	-13.49	-0.89	-3.7
primary-C	+0.42	"	"	+3.5
perfluorocyclohexane				
secondary-C	+0.21	-12.36	-1.09	+0.2
perfluorohexane				
secondary-C	+0.21‡	-12.41	-1.29	+0.0 to +0.2
primary-C	+0.40	"	"	+3.2

‡ There are small differences between the different secondary sites.

Oppenheimer approximation), we estimate the binding energy of an electron in the electrostatic field defined by the Mulliken charges of the neutral molecule.

One major source of error in this simple model is the neglect of penetration effects, so that the "extra" electron experiences larger effective nuclear charges than are suggested by the Mulliken population analysis. Furthermore, no account has been taken of the Pauli principle or of electron correlation.

Using the AM1 optimized geometries and Mulliken population analysis, we constructed an array of point charges for each system. The "lattice energy" of these arrays was calculated using classical electrostatics. We then investigated the change in "lattice energy" ΔE_L on placing an extra negative charge (to represent an electron) at each of the different lattice sites in turn.

The quantity ΔE_L differs markedly for the tertiary, secondary and primary sites, with values of ≈ -3, ≈ 0 and $\approx +3$ eV, respectively (see Table 3). We caution that these numbers are not meant to be realistic estimates of the electron affinities, but our crude model does appear to predict that the transfer of an electron is much more favourable for systems that possess tertiary sites than for those which do not. These very simple arguments would appear to suggest that $(CF_3)_3CF$ will also react with arenethiolate nucleophiles, as do perfluorodecalin and perfluoro(methylcyclohexane), but we are unaware of any experimental results for this system.

CONCLUSIONS

We have presented results of quantum chemical calculations for larger perfluoroalkane systems than in our previous work [1]. Our calculations for the series CF_4 to $C(CF_3)_4$ predict geometries and charge distributions that are consistent with the idea that the CF_3 group can be considered less electron-withdrawing than a fluorine atom.

Quaternary sites in perfluorocarbons appear to be particularly unusual, in that they can exhibit negative

Mulliken charges. In some of the molecules with more than one quaternary centre, it appears that adjacent carbon atoms may carry significant negative charges. It would be very interesting to examine how the different charge distributions in the $CF_3[C(CF_3)_2]_pCF_3$, $(CF_3)_2CF[C(CF_3)_2]_qCF(CF_3)_2$ and $CF_3CF_2[C(CF_3)_2]_rCF_2CF_3$ series might modify their properties. Nmr and X-ray PES experiments on all of the systems we have studied would be particularly useful.

Perfluorodecalin and perfluoro(methylcyclohexane), which react with arenethiolate nucleophiles under mild conditions, both contain tertiary centres. Unreactive systems, such as perfluorohexane and perfluorocyclohexane, do not. A crude, electrostatic, 'lattice energy' model was used to consider electron transfer to these systems and highlighted the special properties of tertiary sites. Our calculations suggest that $C(CF_3)_3F$ will also be reactive with arenethiolate nucleophiles.

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