Journal of Fluorine Chemistry, *46* (1990) 317–337

Received March 20, 1989; accepted May 23, 1989

THEORETICAL STUDIES OF FLUOROCARBONS.
PART I. SMALL PERFLUOROALKANE MOLECULES

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SUMMARY

Ab initio SCF geometry optimizations are reported for perfluoromethane (CF_4), perfluoroethane (C_2F_6), perfluoropropane (C_3F_8), perfluorocyclopropane (C_3F_6) and perfluorospiro[2.2]pentane (C_5F_8) in order to establish a reliable methodology for calculations on such systems. We discuss in detail results obtained using different s/p basis sets and the effects of including polarization functions on carbon and/or fluorine. The small rings need to be treated differently from the acyclic molecules, and this is linked to the hybridization of the carbon atoms.

Systematic structural variations from system to system are noted, and these are interpreted using a very simple model which incorporates the charge on carbon as indicated by Mulliken population analyses.

0022-1139/90/$3.50

INTRODUCTION

It is probably fair to say that the heyday for research into fully-fluorinated saturated molecules occurred some twenty years ago. However, the last decade has seen a significant resurgence of commercial interest in these systems. This has been prompted, in particular, by their increasing use in the electronics industry for etching chips, testing components, cooling computers, and as the basis for so-called artificial blood. The new and unexpected reactivity of some saturated fluorocarbons, whereby, for example, the fluorine atoms in perfluorodecalin are displaced by arenethiolate nucleophiles in dipolar aprotic solvents [1], clearly demonstrates that our understanding of the electronic structure of such compounds is deficient.

Respectable theoretical studies of fluorocarbons tend to be rather scarce, with the obvious exception of the work of Dixon, Smart and co-workers [2]. The experimental situation is not much better, although geometries are available for some of the smaller species, mostly from electron diffraction studies [3]. Semi-empirical schemes such as MNDO tend to produce large errors for highly fluorinated compounds, probably because of overestimating the F-F repulsions [4].

Advances in theoretical methods and in computer hardware mean that we can now envisage fairly sophisticated *ab initio* studies of reasonably large fluorocarbon molecules, although such calculations will necessarily still entail a compromise between accuracy and cost. Unfortunately, the folklore relating to geometry optimizations for saturated neutral fluorocarbons is very limited. With this in mind, the current paper is devoted mainly to a systematic study of the reliability of different *ab initio* calculations for small fluorocarbon molecules. We assess the reliability of different basis sets for systems as large as perfluorospiro[2.2]pentane C_5F_8 (see Figure 1(b)).

One aim is to establish guidelines for the level of accuracy that can be expected from similar calculations on larger systems. Another is to examine the relationships

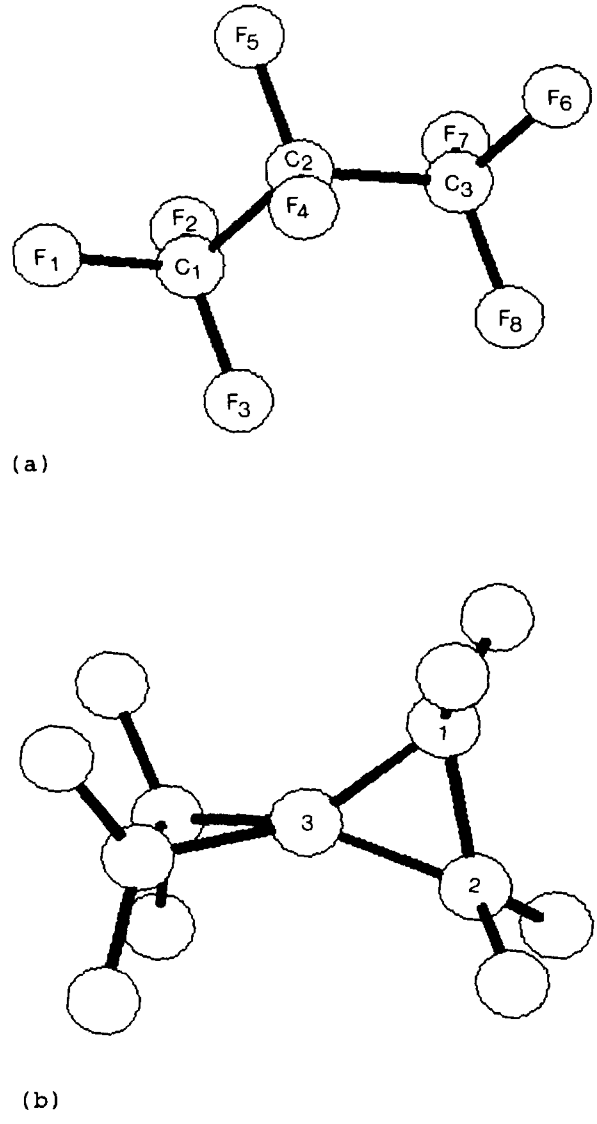

Fig. 1. Structural formulae and atom labels for (a) perfluoropropane (C_3F_8) and (b) perfluorospiro[2.2]pentane (C_5F_8).

between the geometries and the charge distribution in these molecules. This will allow us to make some qualitative predictions concerning the chemical behaviour of larger systems.

COMPUTATIONAL DETAILS

All the calculations reported in this work were performed using implementations of a general electronic structure program known as GAMESS. The program is based on the GAMESS package of Dupuis, Spangler, and Wendoloski [5] but has been substantially modified and extended in the U.K., mostly by the Computational Science Group of the Daresbury Laboratory (SERC) [6]. The single-configuration self-consistent field (SCF) calculations used the same set of orbitals for α and β spin (restricted Hartree-Fock, RHF) and the geometry optimizations employed quasi-Newton analytical gradient techniques.

Various different qualities of basis sets of contracted gaussian-type orbitals were used during the course of this work. The smallest of these is the split valence 3-21G basis set of Pople and co-workers (see, for example, Ref. 7). We also use the 4-31G and 6-31G basis sets from the same authors. Next in size are the split-valence (SV) sets due to Dunning and Hay in the contraction <9s5p/3s2p> [8]. The most expensive calculations were based on triple-zeta (TZV) basis sets in the contraction <10s6p/5s3p> [9]. All these basis sets are stored internally in the GAMESS program.

In order to investigate the effects of polarization functions on optimized geometries, we augmented these s/p basis sets with d functions (six components) with exponents d_C=0.72 and d_F=1.62 [10]. We use the letter P (e.g. 6-31G+P) to denote the addition of polarization functions on all atomic centres. For some calculations the TZV basis was augmented with two sets of polarization functions. We refer to this basis as TZV+2P, where the exponents [11] are d_C=0.3, 1.0 and d_F=0.85, 3.4.

BASIS SET EFFECTS FOR C_nF_{2n+2}

For each system, four types of basis sets are considered: (1) no polarization functions ('none'); (2) polarization functions only on carbon ('d_C'); (3) polarization functions only on fluorine ('d_F'); (4) polarization functions on all centres ('d_C' and 'd_F' or 'P').

CF_4

Full optimizations of all geometrical parameters for perfluoromethane (CF_4), using 3-21G, 4-31G or TZV+P basis sets, resulted in four equivalent C-F bonds and perfect T_d symmetry. All further calculations were then carried out within the constraint of tetrahedral symmetry. The optimized C-F bond lengths are collected in Table 1 and are represented graphically in Figure 2.

Without polarization functions, the calculated C-F bond length in CF_4 is too long and varies considerably. On the other hand, the basis sets with polarization functions on carbon predict bond lengths which are too short. Adding polarization functions only on the fluorine centres leads to results which are intermediate between these two sets of values, except for the TZV basis set where the d_C and d_F results are practically identical. The basis sets of highest quality are those with polarization functions on all centres, but these all predict a very similar C-F bond length which is far too short. It is clear that without the inclusion of the effects of electron correlation, there is convergence to values which differ significantly from the experimental value of 1.32Å [12]. In fact, the basis sets which predict C-F bond lengths closest to the experimental result, are 4-31G+d_F, 6-31G+d_F, and SV+d_F.

For comparison, we have also employed the MNDO [13], MINDO/3 [14] and AM1 [15] semi-empirical methods (see Table 1). Rather than examine the difference from experiment, it is more important to determine whether or not these methods can reproduce the correct trends in geometrical parameters over a range of systems. This is a question to which we return later.

TABLE 1

Results from SCF geometry optimizations of perfluoromethane (CF_4) with various basis sets. We compare with experimental [12] and with semi-empirical values.

	Basis set	Energy/hartree	r(C-F)/Å
No d functions:	3-21G	-433.29631	1.32
	4-31G	-435.07441	1.33
	6-31G	-435.48702	1.34
	SV	-435.58784	1.35
	TZV	-435.67157	1.33
d_C only:	3-21G+d_C	-433.39343	1.30
	4-31G+d_C	-435.17254	1.30
	6-31G+d_C	-435.58755	1.30
	SV+d_C	-435.71188	1.31
	TZV+d_C	-435.76047	1.31
d_F only:	3-21G+d_F	-433.52552	1.31
	4-31G+d_F	-435.16602	1.32
	6-31G+d_F	-435.55449	1.32
	SV+d_F	-435.65881	1.32
	TZV+d_F	-435.74560	1.31
d_C and d_F:	3-21G+P	-433.59722	1.30
	4-31G+P	-435.24250	1.30
	6-31G+P	-435.63529	1.30
	SV+P	-435.76126	1.30
	TZV+P	-435.81053	1.30
	TZV+2P	-435.82863	1.30
Semi-empirical:	MNDO		1.35
	AM1		1.36
	MINDO/3		1.30
Experiment:			1.319

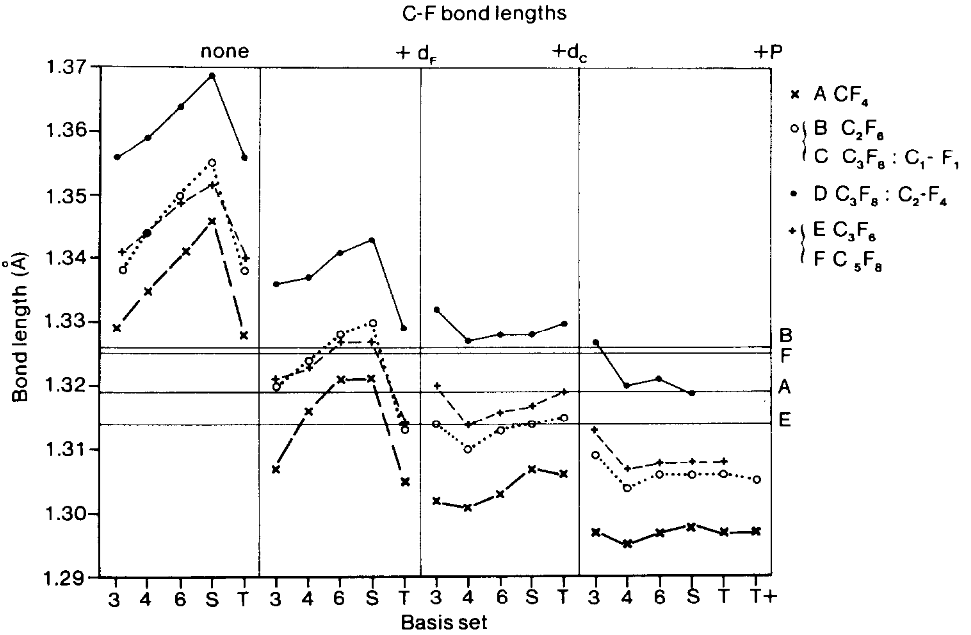

Fig. 2. Variation with basis set of the C-F bond lengths in the systems studied. The basis sets 3-21G, 4-31G, 6-31G, SV and TZV are labelled 3, 4, 6, S and T, respectively. 'none', '+d_F', '+d_C' and '+P' denote, respectively, no polarization functions, polarization functions only on fluorine, polarization functions only on carbon, and polarization functions on all centres. 'T+' denotes TZV+2P - further details are given in the text. Horizontal lines denote experimental measurements as indicated.

C_2F_6

The results for perfluoroethane (C_2F_6) are more informative than those for CF_4 as there is now more than one geometrical variable to be considered. Geometry optimization of all independent parameters using either 3-21G or 4-31G basis sets produced structures with six equivalent C-F bonds and perfect D_{3d} symmetry. All subsequent calculations were carried out within the constraint of D_{3d} symmetry.

TABLE 2

Results from SCF geometry optimizations of perfluoroethane (C_2F_6) with various basis sets. We compare with semi-empirical and with experimental [22] values.

Basis set	Energy/hartree	r(C-F)/Å	r(C-C)/Å	Θ(CCF)/°
STO-3G	-663.05949	1.37	1.62	110.0
3-21G	-668.74489	1.34	1.50	109.8
4-31G	-671.50343	1.34	1.51	109.8
6-31G	-672.14596	1.35	1.52	109.9
SV	-672.30170	1.36	1.54	110.0
TZV	-672.42364	1.34	1.53	109.8
3-21G+d_C	-668.91431	1.31	1.52	109.9
4-31G+d_C	-671.65525	1.31	1.53	109.8
6-31G+d_C	-672.29727	1.31	1.53	109.9
SV+d_C	-672.48926	1.31	1.54	109.8
TZV+d_C	-672.56374	1.32	1.54	110.0
3-21G+d_F	-669.07949	1.32	1.51	109.5
4-31G+d_F	-671.63709	1.32	1.52	109.7
6-31G+d_F	-672.24421	1.33	1.52	109.7
SV+d_F	-672.40406	1.33	1.55	109.8
TZV+d_F	-672.52843	1.31	1.54	109.6
3-21G+P	-669.21429	1.31	1.53	109.8
4-31G+P	-671.75828	1.30	1.53	109.8
6-31G+P	-672.36778	1.31	1.53	109.8
SV+P	-672.56229	1.31	1.54	109.7
TZV+P	-672.63629	1.31	1.54	109.9
TZV+2P	-672.66451	1.31	1.54	109.8
MNDO		1.35	1.67	110.7
AM1		1.36	1.62	112.1
MINDO/3		1.33	1.48	107.6
Experiment		1.326	1.545	109.8

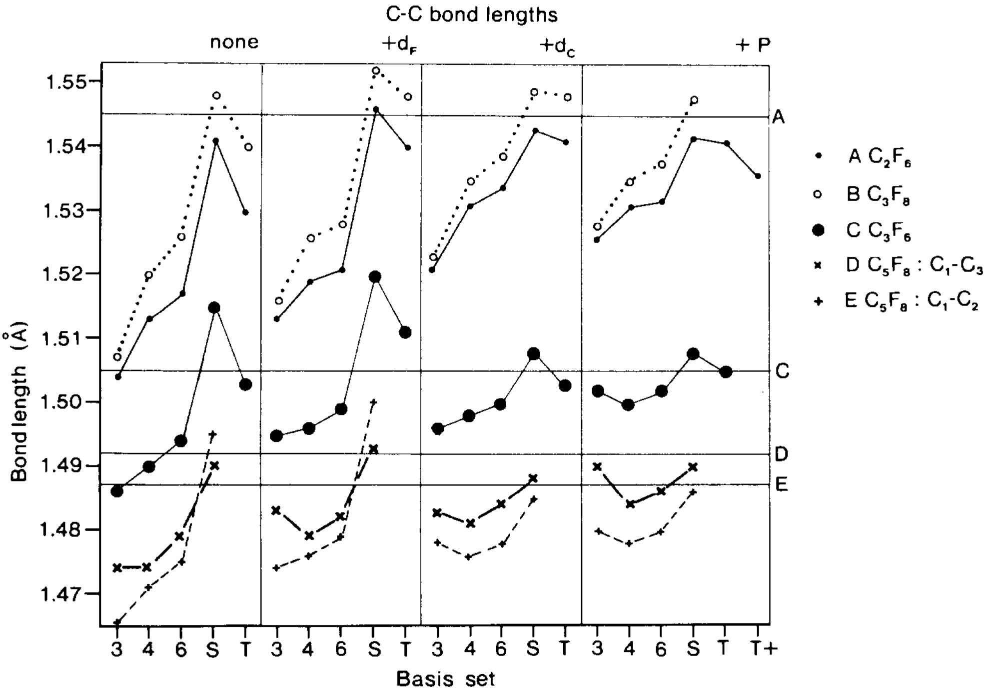

Fig. 3. Variation with basis set of the C-C bond lengths in the systems studied. See also the caption to Fig. 2.

As can be seen from Table 2 and Figure 2, the variation of the C-F bond length with basis set is very similar indeed to that described above for CF_4. Our calculations indicate that the C-F bond in C_2F_6 is slightly longer than that in CF_4, as is found experimentally.

As is clear from Table 2 and Figure 3, the calculated C-C bond length shows a basis set dependence which is rather different from that of C-F. Except for the STO-3G basis set, which predicts a value which is far too long, all the basis sets without polarization functions yield a C-C bond which is too short. The addition of polarization functions on carbon lengthens this bond in all cases, but the calculated value is still too short. The addition of polarization functions on fluorine also lengthens the C-C bond to an extent which varies considerably with the s/p basis set. The effect of adding polarization functions on all centres also varies considerably from basis set to basis set, as can be seen from Table 2. In general, however, the C-C bond is still too short.

Taking into account all of the geometrical parameters for C_2F_6, the basis set which gives the best overall structure is SV+d_F. This basis set also performed well for CF_4.

C_3F_8

A full optimization of all independent geometrical parameters in C_3F_8 (using a 3-21G basis set) resulted in perfect C_{2v} symmetry. Although all subsequent calculations were carried out assuming only C_s symmetry, where the mirror plane is that which contains C_1, C_2, C_3, F_1 and F_6 (see Figure 1(a)), the C_{2v} symmetry always emerged. In addition, the lengths of the C_1-F_1 and C_1-F_2 bonds never differed by more than 0.002 Å.

Our results for perfluoropropane (C_3F_8) are reported in Table 3, and in Figures 2 and 3. The variation with basis set of the C_1-F_1 and C_2-F_4 bond lengths follows the same pattern as for CF_4 and C_2F_6. Thus, we predict C_1-F_1 and C_2-F_4 bond lengths of 1.33 Å and 1.34 Å, respectively. The primary (terminal) C-F bond is essentially the same length as in C_2F_6, but the secondary (central) C-F bond is approximately 0.01 Å longer. The C-C bond length calculated for C_3F_8 appears to be slightly larger than that for C_2F_6, but we observe essentially the same basis set dependence. We have been unable to find an experimental geometry with which to compare.

As might be expected from the semi-empirical results for CF_4, the corresponding results for C_2F_6 and C_3F_8 are, at best, on a par with those from the STO-3G basis set. Structural variations noted consistently in the *ab initio* calculations are not always reproduced by the semi-empirical calculations. For example, MNDO predicts that the C_2-F_4 bond in C_3F_8 is shorter than any of the terminal C-F bonds.

TABLE 3

Results from SCF geometry optimizations of perfluoropropane (C_3F_8) with various basis sets. We compare with semi-empirical values.

Basis set	Energy (in hartree)	Bond lengths (in Å)			Angles (in °)			
		C_1-C_2	C_1-F_1	C_2-F_4	$C_1C_2C_3$	$C_2C_1F_1$	$C_2C_1F_2$	$C_1C_2F_4$
STO-3G	-896.54679	1.61	1.37	1.38	110.7	109.8	110.3	109.8
3-21G	-904.20507	1.51	1.34	1.36	114.4	109.6	110.1	108.2
4-31G	-907.93444	1.52	1.34	1.36	116.5	109.2	110.4	107.7
6-31G	-908.80527	1.53	1.35	1.36	116.8	109.3	110.5	107.7
SV	-909.01489	1.55	1.35	1.37	117.1	109.1	110.9	107.7
TZV	-909.17498	1.54	1.34	1.36	117.4	109.1	110.7	107.6
3-21G+d_C	-904.44125	1.52	1.31	1.33	114.7	109.4	110.2	108.2
4-31G+d_C	-908.14037	1.53	1.31	1.33	115.9	108.9	110.5	107.9
6-31G+d_C	-909.00854	1.54	1.31	1.33	116.2	109.0	110.5	107.9
SV+d_C	-909.26564	1.55	1.31	1.33	116.5	108.7	110.7	107.7
TZV+d_C	-909.36594	1.55	1.32	1.33	116.6	108.9	110.8	107.8
3-21G+d_F	-904.64790	1.52	1.32	1.34	113.9	109.3	109.8	108.1
4-31G+d_F	-908.11104	1.53	1.32	1.34	115.8	109.0	110.3	107.8
6-31G+d_F	-908.93511	1.53	1.33	1.34	116.2	109.1	110.4	107.8
SV+d_F	-909.15004	1.55	1.33	1.34	116.2	108.8	110.7	107.8
TZV+d_F	-909.31191	1.55	1.31	1.33	116.7	108.7	110.4	107.7
3-21G+P	-904.83849	1.53	1.31	1.33	114.6	109.2	110.1	108.2
4-31G+P	-908.27693	1.54	1.30	1.32	115.8	108.8	110.4	107.9
6-31G+P	-909.10232	1.54	1.31	1.32	115.9	108.8	110.5	107.9
SV+P	-909.36290	1.55	1.31	1.32	116.3	108.5	110.7	107.8
MNDO		1.67	1.35	1.34	114.0	110.3	111.3	108.8
AM1		1.61	1.36	1.37	110.1	111.9	112.5	110.5

BASIS SET EFFECTS FOR C_3F_6 AND C_5F_8

Previous ab initio work on fluorocarbons has concentrated mostly on unsaturated molecules such as fluoroethenes. Dixon et al. [2b] found for such systems that polarization functions on carbon are significantly more important than those on fluorine. The present work shows that the same is not true for saturated molecules. However, we turn now to the strained ring systems perfluorocyclopropane and perfluorospiro[2.2]pentane, in which the carbon atoms will have appreciably more sp^2 character, analogous to the unsaturated systems. Experimental geometries are available for both of these compounds.

C_3F_6

An SCF geometry optimization (3-21G basis set) of perfluorocyclopropane within C_s symmetry produced a structure with D_{3h} symmetry, and so this higher point group was imposed for all subsequent calculations. The electron diffraction studies of Chiang and Bernett [16] assumed D_{3h} symmetry for this molecule.

The variation with basis set of the C-F bond length in C_3F_6 is analogous to that seen for the C_nF_{2n+2} systems, and the calculated values are very similar to those for C_2F_6. Nonetheless, the experimental measurements show that the C-F bond in C_3F_6 is significantly shorter than that in C_2F_6. The basis sets which perform best for C_2F_6 do not produce the best agreement with experiment for C_3F_6, and vice versa. With the exception of the largest basis sets (based on TZV) our optimized geometries for C_3F_6 (Table 4, and Fig. 2 and 3) are consistent with the findings of Dixon et al. [2b]: polarization functions on carbon are significantly more useful than those on fluorine.

The difference in the experimental C-F bond length for C_3F_6 and CF_4 accords with the greater electronegativity of an sp^2 carbon atom (c.f. C_3H_6 and CH_4). From similar considerations, we would expect the C-C bond length in

TABLE 4

Results from SCF geometry optimizations of perfluorocyclopropane (C_3F_6) with various basis sets. We compare with experimental [16] and with semi-empirical values.

Basis set	Energy/hartree	r(C-F)/Å	r(C-C)/Å	θ(FCF)/°
STO-3G	-700.38404	1.37	1.55	111.5
3-21G	-706.28240	1.34	1.49	113.2
4-31G	-709.21012	1.34	1.49	112.7
6-31G	-709.89627	1.35	1.49	112.3
SV	-710.06330	1.35	1.52	111.6
TZV	-710.18497	1.34	1.50	112.0
3-21G+d_C	-706.48576	1.32	1.50	112.8
4-31G+d_C	-709.37327	1.31	1.50	112.4
6-31G+d_C	-710.05369	1.32	1.50	112.2
SV+d_C	-710.25514	1.32	1.51	111.9
TZV+d_C	-710.33341	1.32	1.50	111.8
3-21G+d_F	-706.60949	1.32	1.50	113.7
4-31G+d_F	-709.33748	1.32	1.50	113.1
6-31G+d_F	-709.98857	1.33	1.50	112.8
SV+d_F	-710.16031	1.33	1.52	112.1
TZV+d_F	-710.28120	1.31	1.51	112.5
3-21G+P	-706.78268	1.31	1.50	112.7
4-31G+P	-709.47389	1.31	1.50	112.6
6-31G+P	-710.12195	1.31	1.50	112.4
SV+P	-710.32607	1.31	1.51	112.2
TZV+P	-710.40297	1.31	1.50	112.0
MNDO		1.33	1.61	108.8
AM1		1.35	1.56	106.6
MINDO/3		1.35	1.50	104.4
Experiment		1.314	1.505	112.2

perfluorocyclopropane to be shorter than that in perfluoroethane. This is confirmed both by the experimental and theoretical results.

The effect on the calculated C-C bond length of polarization functions depends on the quality of the s/p basis. For the 3-21G, 4-31G and 6-31G cases, the C-C bond length varies according to $P>d_C>d_F>$none, but the bond length is still too short. For the SV and TZV cases, $d_F>$none$>d_C\approx P$, where the d_C and P values differ least from experiment.

The semi-empirical results for C_3F_6 are not particularly impressive. For example, all of the methods predict an FCF angle which is too small. Furthermore, MINDO/3 predicts a large increase in C-F bond lengths relative to CF_4, rather than the anticipated decrease, and a C-C bond length which is much longer than that in C_2F_6.

C_5F_8

All of our calculations for perfluorospiro[2.2]pentane assumed equivalent C_3F_4 rings. Each unit was assumed to possess C_{2v} symmetry, but there were no constraints on the relative orientation about C_3 (see Fig. 1(b)). Nonetheless, D_{2d} symmetry emerged from all of the geometry optimizations. This is the point group symmetry suggested by the electron diffraction experiments of Dolbier *et al*. [17].

The calculated C-F bond lengths for perfluorospiro[2.2]pentane (see Table 5 and Fig. 2) are virtually identical to those for perfluorocyclopropane. However, the electron diffraction studies show that the C-F bond in C_5F_8 is 0.01 Å longer than that in C_3F_6. The best agreement with the experimental C-F bond length is achieved for C_5F_8 with the d_F basis sets, as was the case for the C_nF_{2n+2} molecules. The C-F bond in C_5F_8 is virtually the same length as that in C_2F_6, but it is shorter than our calculations predict for the secondary bond (C_2-F_4) in C_3F_8.

Theory and experiment agree that there is very little difference in length between the C_1-C_2 and C_1-C_3 bonds in C_5F_8, and that both are shorter than in C_3F_6. The variation

TABLE 5

Results from SCF geometry optimizations of perfluorospiro[2.2] pentane (C_5F_8) with various basis sets. The results are compared with semi-empirical values and with experiment [17].

Basis set	Energy (in hartree)	Bond lengths (in Å)			Angles (in °)		
		C_1-C_2	C_1-C_3	C-F	FCF	C_3C_1F	C_2C_1F
3-21G	-979.34754	1.46	1.47	1.34	111.7	118.6	119.5
4-31G	-983.40612	1.47	1.47	1.35	111.6	118.9	119.4
6-31G	-984.36171	1.48	1.48	1.35	111.3	119.0	119.5
SV	-984.58700	1.50	1.49	1.36	110.8	119.3	119.6
3-21G+d_C	-979.65736	1.47	1.48	1.32	111.6	118.6	119.5
4-31G+d_C	-983.64534	1.48	1.48	1.31	111.5	118.9	119.5
6-31G+d_C	-984.59004	1.48	1.48	1.32	111.3	118.9	119.5
SV+d_C	-984.86233	1.49	1.49	1.32	111.1	119.1	119.5
3-21G+d_F	-979.78085	1.47	1.48	1.32	112.0	118.5	119.3
4-31G+d_F	-983.57384	1.48	1.48	1.32	111.9	118.7	119.3
6-31G+d_F	-984.48312	1.48	1.48	1.33	111.6	118.9	119.3
SV+d_F	-984.71408	1.50	1.49	1.33	111.2	119.1	119.5
3-21G+P	-980.05102	1.48	1.49	1.31	111.5	118.7	119.5
4-31G+P	-983.77807	1.48	1.48	1.31	111.6	118.8	119.4
6-31G+P	-984.68020	1.48	1.49	1.31	111.5	118.9	119.4
SV+P	-984.95570	1.49	1.49	1.31	111.3	119.0	119.5
MNDO		1.60	1.55	1.33	108.7	120.3	120.7
AM1		1.56	1.51	1.35	106.0	121.4	121.7
MINDO/3		1.46	1.51	1.34	98.5	122.3	125.8
Experiment		1.487	1.492	1.325	110.8	118.6	120.0

with basis set of the calculated C-C bond lengths in these two molecules is very similar, and it is the same basis sets which give the best agreement with experiment (see Table 5 and Figure 3). Unfortunately, these are not the basis sets which give the best values for the C-F bond length in C_5F_8. Moreover, none of the basis sets gives good agreement with experiment for all of the bond lengths and angles.

As is clear from Table 5, the semi-empirical methods are not very successful for perfluorospiro[2.2]pentane. All three methods predict significant differences between the C_1-C_2 and C_1-C_3 bond lengths, and give poor values for the angles.

DISCUSSION

The variation in structural parameters from molecule to molecule can be rationalized to a large extent simply by considering the charge distributions. In line with simple electrostatic arguments, we assume that the shorter the C-F bond, the larger the positive charge on C (for a given basis set) as indicated by a Mulliken population analysis.

For the basis sets based on SV, the Mulliken populations for the unique atoms in each molecule are listed in Table 6. For a given basis set, it can be seen that the charge on fluorine remains essentially constant, whereas the charge on carbon is very sensitive to environment and varies considerably. It would be particularly interesting to try and investigate the effect of the environment on the charge distribution around carbon using ^{13}C nmr and X-ray PES.

Our general argument can be illustrated using the series CH_3F, CH_2F_2, CF_3H and CF_4, which have experimental C-F bond lengths of 1.383 Å [18], 1.351 Å [19], 1.328 Å [20] and 1.319 Å [12], respectively. It can be seen that multiple substitution of H by F leads to successive shortening of the C-F bond(s). This change in bond length is consistent with the increasing positive charge on carbon as more fluorine atoms are introduced.

We now consider the substitution of a fluorine atom by a CF_3 group. As our example, we compare CF_4 and C_2F_6. The Mulliken population analyses confirm that the $-CF_3$ group is

TABLE 6

Mulliken population analyses with selected basis sets.

		Basis set			
		SV	SV+d_C	SV+d_F	SV+P
Perfluoromethane	C	5.01	5.41	4.92	5.27
CF_4	F	9.25	9.15	9.27	9.18
Perfluoroethane	C	5.22	5.50	5.14	5.39
C_2F_6	F	9.26	9.17	9.29	9.20
Perfluoropropane	C_1	5.22	5.48	5.14	5.38
C_3F_8	C_2	5.49	5.69	5.44	5.62
	F_1	9.25	9.16	9.28	9.20
	F_2	9.26	9.16	9.28	9.20
	F_4	9.27	9.18	9.30	9.22
Perfluorocyclopropane	C	5.47	5.66	5.43	5.60
C_3F_6	F	9.26	9.17	9.29	9.20
Perfluorospiro[2.2]pentane	C_1	5.46	5.62	5.39	5.54
C_5F_8	C_3	6.06	6.19	6.11	6.21
	F	9.26	9.17	9.29	9.20

less electron withdrawing than -F, as we should expect. This is not to be confused with the different behaviour of these two groups when attached to a benzene ring, where the fluorine atom uses its lone pairs to stabilize transition states leading to ortho and para substitution. For a given basis set, the positive charge on the C atoms in C_2F_6 is less than that in CF_4, and the C-F bond in C_2F_6 is longer.

It is now relatively straightforward to extend this argument to perfluoropropane. For a given basis set, the central carbon atom (secondary site) has a smaller positive charge than a terminal carbon atom (primary site). The primary C-F bonds in C_3F_8, which are of the same length as in perfluoroethane, are shorter than the secondary C-F bonds in C_3F_8. The C-C bonds in C_3F_8 and C_2F_6 have very similar lengths, suggesting that this distance is relatively insensitive to the changes in the positive charges on carbon, although it is slightly longer in C_3F_8.

This very simple model, in which C-F bond length is related to the charge on C, can be used to predict that tertiary C-F bonds will be longer than secondary C-F bonds. In that we expect the positive charge on carbon to follow the order tertiary < secondary < primary, the C-F bond lengths should be ordered according to tertiary > secondary > primary. Work is in progress on larger fluorocarbons, and results for these systems will be reported in due course. It is interesting in this context to note that MacNicol and Robertson [1] report on the importance of a tertiary centre in controlling reactivity. Whereas perfluorodecalin and perfluoro(methylcyclohexane) react with certain nucleophiles under relatively mild conditions, perfluorohexane and perfluorocyclohexane do not.

It is necessary to use a modified argument when considering systems with very small rings. The C-F bond in perfluorocyclopropane is considerably shorter than the secondary C-F bond in C_3F_8, and it is even shorter than the bond in CF_4. In addition, the C-C bond in the ring is shorter than that in C_2F_6. These observations can be rationalized in terms of the increased sp^2 character of a ring carbon atom, and thus its increased electronegativity. It is not useful to compare directly the Mulliken populations of the ring atoms with those in the acyclic molecules.

Comparing the Mulliken population analyses of perfluorocyclopropane and perfluorospiro[2.2]pentane (see Table 6), we notice an unusual feature. The central carbon atom (C_3) in C_5F_8 appears to carry a small net negative charge, but the charges on the other carbon atoms are much more similar to those in C_3F_6. The C_1-C_2 and C_1-C_3 distances in C_5F_8 are both shorter than the C-C bond in C_3F_6, while the C-F bond is longer. It is useful to note that the experimentally determined C-F bond length in perfluoro(2,2-dimethylpropane) C_5F_{12} [21] is much the same as that in perfluorospiro[2.2]pentane.

CONCLUSIONS

We have carried out a large number of _ab_ _initio_ SCF geometry optimizations for various fully-fluorinated saturated molecules in order to establish a reliable foundation for calculations on these and larger systems. Our work indicates that more care is required in the choice of basis set than has been implied in the literature. The effects of the addition of polarization functions on carbon or fluorine (or both) may differ significantly from molecule to molecule.

The effect of polarization functions also varies from one s/p basis set to another, as is clear from Figures 2 and 3. The role of d functions is likely to be much more important for negative ions and for calculations which incorporate some of the effects of electron correlation.

Basis sets which perform well at the SCF level for acyclic systems (sp^3 carbon) do not do so well for small rings, with increased sp^2 character. Much of the folklore in the literature has been based on SCF calculations on perfluoroalkenes. Assuming that all the experimental data are correct, the most useful basis set for saturated acyclic molecules is SV+d_F. For the ring compounds, medium-sized s/p basis sets with d functions only on carbon provide SCF optimized geometries which agree best with experiment. Of course, this agreement with experiment must be due to a fortuitous cancellation of errors: larger basis sets give 'poorer' results.

We have noted small, but probably significant, structural variations in the small fluorocarbons we have studied here. For example, secondary C-F bonds are longer than primary C-F bonds. Changes such as these can be rationalized in terms of a model based on Mulliken populations which indicate that a $-CF_3$ group is less electron-withdrawing than a fluorine atom. For the ring systems it is important to take into account the increased sp^2 character of some of the carbon atoms. The significance of the unusual character of the central carbon atoms in perfluorospiro[2.2]pentane and perfluoro(2,2-dimethylpropane) will be discussed in a forthcoming publication.

We are currently exploring the implications of all of our results for the structure and reactivity of larger systems.

ACKNOWLEDGEMENTS

Calculations were carried out on the CRAY-XMP/48 at RAL and were supported by SERC grant GR/F 15793. Computational resources were also made available as part of a joint ICI-Daresbury Laboratory collaboration, and we are grateful to Dr J.E. Inglesfield for a generous allocation of computer time on an FPS 264.

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