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# THEORETICAL STUDIES OF FLUOROCARBONS
# PART II. FLUORINE AND CHLORINE SUBSTITUTED ALKANES

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## SUMMARY

*Ab initio* SCF and semi-empirical geometry optimizations are carried out for fluoromethanes and chloromethanes, for fluorochloromethanes, and for fluorine or chlorine substituted ethane. We also examine the charge distributions inferred from Mulliken population analyses.

In order to establish a reliable foundation for calculations on systems such as these, we discuss in detail the effects of using different s/p basis sets and of including polarization functions on different centres. We find significant differences between fluorine and chlorine substituted alkanes. Apparent correlations between the Mulliken charge on carbon and the reaction enthalpy for hydrogen-atom abstraction by chlorine atoms are noted for F and Cl substituted methane.

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## INTRODUCTION

Halogen-containing materials have physical and chemical properties which have made them of considerable importance as anaesthetics, fire-fighting and fire-retarding chemicals, refrigerants, solvents, and propellants. Polymeric halocarbons are known, amongst things, for their important barrier properties. However, despite the evident industrial significance of these materials, the origins of the physical characteristics imparted by chlorine are poorly understood. Better understanding is needed to guide the development of new halogen-containing products which are environmentally more benign but which still possess the desired properties.

In Part I of this series [1], we reported the results of ab initio geometry optimizations for a series of small perfluoroalkane molecules, in order to establish a reliable methodology for calculations on such systems. In the current paper, Part II, we extend this work to consider the differences between fluorine and chlorine substituted alkanes. We consider the geometries and charge distributions of partially halogenated alkanes and of fluorochlorocarbons. We find considerable differences between fluorine and chlorine.

The computational details and basis sets are as discussed in Part I of this study [1]. Some of the ab initio calculations reported here use basis sets that include polarization functions on some or all of the atomic centres. The exponents of these functions are $p_H$=1.0, $d_C$=0.72, $d_F$=1.62, and $d_{Cl}$=0.619. Because of its position in the second row of the periodic table, we expect that the inclusion of d polarization functions for chlorine will be especially important.

Particularly for systems containing many chlorine atoms, there is a restrictive compromise between the accuracy and cost of ab initio calculations. Consequently, we also examine in some detail the predictions of much cheaper semi-empirical methods such as MINDO/3 [2], MNDO [3], and AM1 [4]. In a sense, the absolute differences between experiment and theory are less important in this context than the ability to reproduce the correct trends. This should provide some indication of the utility of such calculations for studies of larger systems.

## FLUOROMETHANES

We report in Table 1 optimized bond lengths and bond angles for the series $CH_4$, $CH_3F$, $CH_2F_2$, $CHF_3$ and $CF_4$ from ab initio SCF calculations with 3-21G and TZVP basis sets. We also tabulate the results from semi-empirical methods. All the experimental values in this paper are taken from standard compilations [5].

Both the 3-21G and TZVP results reproduce the decrease in the C-F bond length observed experimentally with increasing fluorine substitution. For each system, the 3-21G basis set overestimates the C-F bond length, while the TZVP set underestimates it. As discussed previously for fully-fluorinated alkanes [1], this indicates that without the inclusion of the effects of electron correlation, there is convergence to values which differ considerably from the experimental C-F bond lengths.

As expected, differences between theory and experiment are much larger for the semi-empirical methods. MINDO/3 and AM1 reproduce the successive shortening of the C-F bond(s) on multiple substitution of H by F. MNDO does not reproduce the correct trend. It is well known that this method tends to produce large errors for highly fluorinated compounds, probably because of overestimating the fluorine-fluorine repulsions [3c].

The change in bond length is consistent with a simple electrostatic argument [1], based on Mulliken population analyses. As the charge on carbon becomes more positive, as a result of the introduction of more fluorine atoms, the C-F bond contracts. Although the absolute values of the charges from Mulliken population analyses differ considerably from method to method, the qualitative variation of these charges from molecule to molecule is the same. However, the semi-empirical techniques suggest a uniform increment in the carbon

TABLE 1

Results for fluoromethanes $CH_nF_{4-n}$. Bond lengths are quoted in Å and angles in degrees.

| | | | MNDO | MINDO/3 | AM1 | 3-21G | TZVP | Experiment |
|---|---|---|---|---|---|---|---|---|
| $CH_4$ | ($T_d$) | r(C-H) | 1.10 | 1.10 | 1.11 | 1.08 | 1.08 | 1.0870 |
| | | q(C) | +0.07 | +0.04 | -0.27 | -0.79 | -0.45 | |
| | | q(H) | -0.02 | -0.01 | +0.07 | +0.20 | +0.11 | |
| $CH_3F$ | ($C_{3v}$) | r(C-H) | 1.12 | 1.10 | 1.12 | 1.08 | 1.08 | 1.100 |
| | | r(C-F) | 1.35 | 1.37 | 1.38 | 1.40 | 1.37 | 1.383 |
| | | Θ(HCH) | 108.3 | 111.2 | 109.4 | 109.6 | 110.1 | 110.62 |
| | | q(C) | +0.26 | +0.51 | -0.04 | -0.18 | -0.01 | |
| | | q(F) | -0.25 | -0.33 | -0.18 | -0.41 | -0.30 | |
| | | q(H) | -0.01 | -0.06 | +0.07 | +0.20 | +0.10 | |
| $CH_2F_2$ | ($C_{2v}$) | r(C-H) | 1.13 | 1.10 | 1.13 | 1.07 | 1.08 | 1.084 |
| | | r(C-F) | 1.35 | 1.34 | 1.37 | 1.37 | 1.34 | 1.3508 |
| | | Θ(HCH) | 108.2 | 114.5 | 111.0 | 111.8 | 112.9 | 112.8 |
| | | Θ(FCF) | 106.8 | 104.9 | 103.9 | 108.9 | 108.3 | 108.49 |
| | | q(C) | +0.44 | +0.97 | +0.17 | +0.41 | +0.35 | |
| | | q(F) | -0.24 | -0.38 | -0.18 | -0.41 | -0.27 | |
| | | q(H) | +0.02 | -0.11 | +0.09 | +0.20 | +0.09 | |
| $CHF_3$ | ($C_{3v}$) | r(C-H) | 1.14 | 1.10 | 1.13 | 1.07 | 1.08 | 1.091 |
| | | r(C-F) | 1.35 | 1.31 | 1.37 | 1.35 | 1.31 | 1.3284 |
| | | Θ(FCF) | 107.4 | 109.8 | 105.7 | 108.3 | 108.4 | 108.58 |
| | | q(C) | +0.62 | +1.38 | +0.37 | +0.96 | +0.60 | |
| | | q(F) | -0.23 | -0.42 | -0.17 | -0.39 | -0.23 | |
| | | q(H) | +0.09 | -0.13 | +0.15 | +0.22 | +0.10 | |
| $CF_4$ | ($T_d$) | r(C-F) | 1.35 | 1.30 | 1.36 | 1.33 | 1.30 | 1.3193 |
| | | q(C) | +0.82 | +1.73 | +0.58 | +1.51 | +0.82 | |
| | | q(F) | -0.20 | -0.43 | -0.14 | -0.38 | -0.20 | |

charge upon successive fluorine substitution. The large basis set (TZVP) ab initio calculations show a large change for the first fluorine atom, and successively smaller changes thereafter.

The HCH and FCF angles predicted by the ab initio calculations are in good agreement with experiment. The same is not true of the semi-empirical techniques. The ab initio charges on hydrogen, and the ab initio and experimental C-H bond lengths do not show significant changes for this series of molecules.

## CHLOROMETHANES

Results for the chloromethanes are listed in Table 2. It can be seen that there are marked differences between the geometries and charge distributions obtained using the 3-21G and TZVP basis sets. In particular, the SCF calculations with the 3-21G basis set significantly overestimate the C-Cl bond length, whereas the TZVP predictions are in good agreement with experiment. However, the TZVP values are still slightly too large, in contrast to the analogous calculations for fluoromethanes. The semi-empirical C-Cl bond lengths are in better agreement with experiment than are those from the 3-21G basis set. None of the semi-empirical techniques reproduces the observed contraction in the C-Cl bond length along the series $CH_3Cl$, $CH_2Cl_2$, and $CHCl_3$. In contrast to the case of $CF_4$ and $CHF_3$, the C-Cl bond length appears to be fractionally longer in $CCl_4$ than in $CHCl_3$. This different behaviour is presumably due to the much larger size of the chlorine atom and its smaller electronegativity, so that our simple electrostatic model for fluoroalkanes is no longer applicable.

The Mulliken charges from the SCF calculations with 3-21G and TZVP basis set are very different. The charge on carbon predicted with the TZVP basis set follows the order

$CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl > CH_4$

which is consistent with chemical intuition. The 3-21G charges, on the other hand, show a very different order which

TABLE 2

Results for chloromethanes $CH_nCl_{4-n}$. Bond lengths are quoted in Å and angles in degrees.

| | | | MNDO | MINDO/3 | AM1 | 3-21G | TZVP | Experiment |
|---|---|---|---|---|---|---|---|---|
| $CH_4$ | ($T_d$) | r(C-H) | 1.10 | 1.10 | 1.11 | 1.08 | 1.08 | 1.0870 |
| | | q(C) | +0.07 | +0.04 | -0.27 | -0.79 | -0.45 | |
| | | q(H) | -0.02 | -0.01 | +0.07 | +0.20 | +0.11 | |
| $CH_3Cl$ | ($C_{3v}$) | r(C-H) | 1.10 | 1.10 | 1.11 | 1.08 | 1.08 | 1.0872 |
| | | r(C-Cl) | 1.79 | 1.74 | 1.74 | 1.89 | 1.80 | 1.7756 |
| | | θ(HCH) | 110.8 | 110.8 | 110.6 | 112.5 | 110.8 | 110.35 |
| | | q(C) | +0.15 | +0.29 | -0.18 | -0.70 | -0.26 | |
| | | q(Cl) | -0.21 | -0.20 | -0.12 | -0.11 | -0.18 | |
| | | q(H) | +0.02 | -0.03 | +0.10 | +0.27 | +0.15 | |
| $CH_2Cl_2$ | ($C_{2v}$) | r(C-H) | 1.10 | 1.00 | 1.11 | 1.07 | 1.07 | 1.085 |
| | | r(C-Cl) | 1.79 | 1.74 | 1.74 | 1.85 | 1.78 | 1.767 |
| | | θ(HCH) | 112.3 | 110.8 | 112.1 | 114.4 | 111.8 | 111.51 |
| | | θ(ClCCl) | 111.2 | 114.9 | 113.0 | 110.8 | 112.6 | 112.03 |
| | | q(C) | +0.21 | +0.50 | -0.10 | -0.70 | -0.13 | |
| | | q(Cl) | -0.16 | -0.20 | -0.08 | +0.02 | -0.11 | |
| | | q(H) | +0.05 | -0.05 | +0.13 | +0.33 | +0.18 | |
| $CHCl_3$ | ($C_{3v}$) | r(C-H) | 1.11 | 1.10 | 1.12 | 1.07 | 1.07 | 1.100 |
| | | r(C-Cl) | 1.78 | 1.74 | 1.75 | 1.84 | 1.77 | 1.758 |
| | | θ(ClCCl) | 110.3 | 112.0 | 111.2 | 110.5 | 112.2 | 111.3 |
| | | q(C) | +0.25 | +0.66 | -0.04 | -0.75 | -0.04 | |
| | | q(Cl) | -0.11 | -0.20 | -0.04 | +0.12 | -0.06 | |
| | | q(H) | +0.09 | -0.07 | +0.16 | +0.38 | +0.22 | |
| $CCl_4$ | ($T_d$) | r(C-Cl) | 1.78 | 1.75 | 1.76 | 1.83 | 1.77 | 1.7667 |
| | | q(C) | +0.28 | +0.79 | +0.03 | -0.80 | +0.06 | |
| | | q(Cl) | -0.07 | -0.20 | -0.01 | +0.20 | -0.02 | |

does not make much chemical sense. As we discuss later, this is linked to the lack of polarization functions on chlorine.

In spite of the fact that the charge on an atomic fragment is not an experimental observable, such quantities have proved very useful in discussions of electronic structure and of reactivity. The Mulliken scheme [6] employed here is one of the most widely used theoretical procedures, but suffers from a somewhat arbitrary partitioning of the 'overlap' charge density in the regions between the different nuclei. Moreover, the Mulliken charges derived from closed-shell SCF wavefunctions are not invariant to unitary transformations of the orbitals. In addition, even if two SCF wavefunctions calculated with different basis sets define exactly the same electron density distribution, the Mulliken population analysis may still suggest different atomic charges. However, whereas the absolute values of the populations might be suspect, we do expect that the <u>variation</u> of the charges from molecule to molecule will be meaningful, particularly if we compare SCF calculations of the same quality for a range of systems.

An important experimental measure of the C-H bond energy is provided by the reaction enthalpies $\Delta H_R$ for hydrogen-atom abstraction by chlorine atoms

$$RH + Cl \rightarrow R + HCl$$

These are ordered [7]
$CHCl_3 < CH_2Cl_2 < CH_3Cl$

and
$CHF_3 > CH_2F_2 > CH_3F$

where the process is most exothermic for $CHCl_3$ and is in fact endothermic for $CHF_3$. We plot in Figure 1 the variation of the experimental reaction enthalpy (at 298K) with the calculated Mulliken charge on carbon (TZVP basis set). The values of $\Delta H_R$, and their large error bars, are taken from the work of

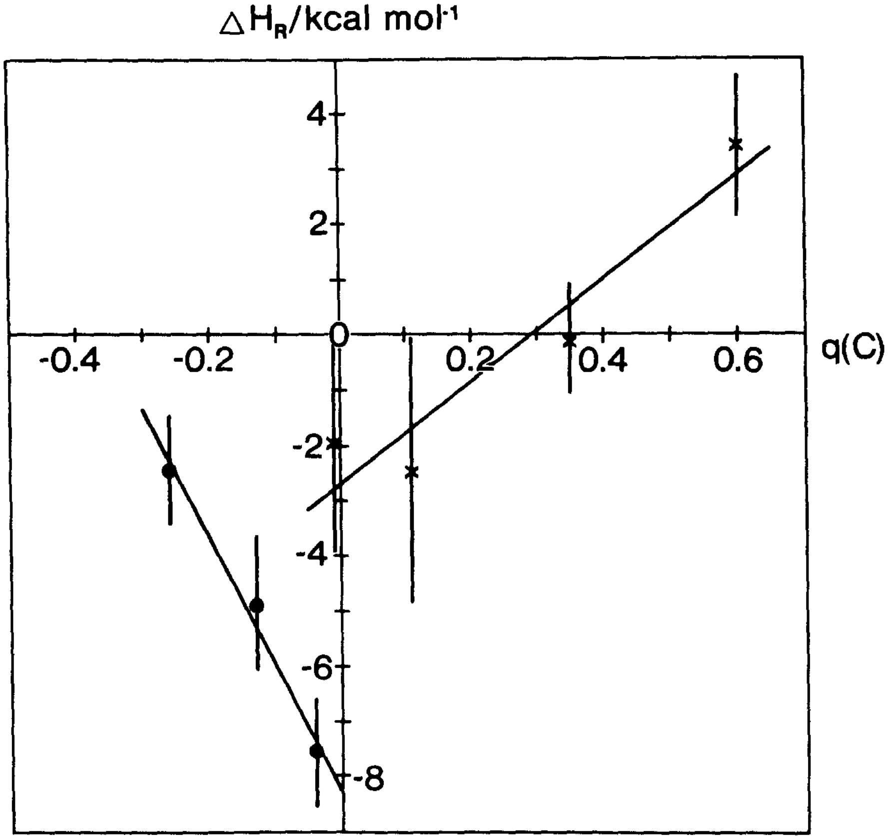

Fig. 1. $\Delta H_R$ versus q(C). Further details are given in the text. From left to right, the molecules marked • are $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$, and those marked × are $CH_3F$, $CH_2ClF$, $CH_2F_2$ and $CHF_3$.

Tschuikow-Roux et al. [7]. Although the fluoromethane and chloromethane series show very different behaviour, there does appear to be a fairly good correlation in each case. $CH_2ClF$, for which we calculate q(C)=+0.11, appears to fit in best with the fluoromethane series, but the experimental value of $\Delta H_R$ is subject to a large uncertainty. The hydrogen-atom abstraction reaction appears to be most exothermic for small values of $|q(C)|$: for the chloromethane series, $|q(C)|$ decreases with increasing Cl substitution, but for the fluoromethane series $|q(C)|$ increases with increasing F substitution. It would be interesting to examine whether these two different trends occur also for other fluorine and chlorine substituted alkanes.

Although the first step in the photochlorination of halogen (F,Cl,Br) substituted methane is hydrogen abstraction, as above, there appears to be no correlation between activation energy and C-H bond strength except, perhaps, for the fluoromethanes [7]. Even for this series, the increasing activation energy on successive fluorine substitution of $CH_3F$ does not vary in a linear fashion with the increasing strength of the C-H bond. It follows that it would be unrealistic to expect a correlation between the rate of photochlorination and any of the quantities listed in Tables 1 and 2.

## TETRAFLUOROMETHANE AND TETRACHLOROMETHANE

We continue our study of fluorine and chlorine substituted alkanes with a comparison of tetrafluoromethane and tetrachloromethane. The results of ab initio and semi-empirical geometry optimizations for these two molecules are collected in Table 3. As was noted in Part I of this work [1], the C-F bond lengths in $CF_4$ calculated without polarization functions are too large and vary considerably with s/p basis set. The closest agreement with experiment occurs for the 4-31G and SV basis sets augmented with polarization functions only on fluorine. The addition of polarization functions also on carbon leads consistently to a C-F bond length that is too short.

The situation for $CCl_4$ is rather different. For the basis sets without polarization functions, the ab initio bond length is too long but fairly constant. The addition of polarization functions on chlorine to any of the s/p basis sets leads to a considerable reduction in the bond length. The further

TABLE 3

Results for tetrafluoromethane and tetrachloromethane $CX_4$ (X=F or Cl). The C-X bond lengths are quoted in Å.

| | Tetrafluoromethane | | | | Tetrachloromethane | | | |
|---|---|---|---|---|---|---|---|---|
| | E/hartree | C-F | q(C) | q(F) | E/hartree | C-Cl | q(C) | q(Cl) |
| STO-3G | -429.5810 | 1.37 | +0.57 | -0.14 | -1855.6785 | 1.82 | +0.16 | -0.03 |
| 3-21G | -433.2963 | 1.32 | +1.51 | -0.38 | -1866.7719 | 1.83 | -0.80 | +0.20 |
| 4-31G | -435.0744 | 1.33 | +1.48 | -0.37 | -1873.7007 | 1.83 | -0.46 | +0.12 |
| SV | -435.5878 | 1.35 | +0.99 | -0.25 | -1875.5976 | 1.82 | -0.43 | +0.11 |
| TZV | -435.6716 | 1.33 | +0.99 | -0.25 | -1875.7621 | 1.82 | -0.35 | +0.09 |
| 3-21G+$d_X$ | -433.5255 | 1.31 | +1.40 | -0.35 | -1867.1467 | 1.78 | -0.27 | +0.07 |
| 4-31G+$d_X$ | -435.1660 | 1.32 | +1.59 | -0.40 | -1873.8433 | 1.78 | +0.09 | -0.02 |
| SV+$d_X$ | -435.6588 | 1.32 | +1.08 | -0.27 | -1875.6834 | 1.78 | +0.09 | -0.02 |
| TZV+$d_X$ | -435.7456 | 1.31 | +1.16 | -0.29 | -1875.8400 | 1.78 | +0.18 | -0.05 |
| 3-21G+P | -433.5972 | 1.30 | +1.05 | -0.26 | -1867.2034 | 1.77 | -0.32 | +0.08 |
| 4-31G+P | -435.2425 | 1.30 | +1.18 | -0.30 | -1873.8811 | 1.77 | -0.05 | +0.01 |
| SV+P | -435.7613 | 1.30 | +0.73 | -0.18 | -1875.7210 | 1.77 | +0.00 | -0.00 |
| TZV+P | -435.8105 | 1.30 | +0.82 | -0.20 | -1875.8700 | 1.77 | +0.06 | -0.02 |
| MINDO/3 | | 1.30 | +1.73 | -0.43 | | 1.75 | +0.79 | -0.20 |
| MNDO | | 1.35 | +0.82 | -0.20 | | 1.78 | +0.28 | -0.07 |
| AM1 | | 1.36 | +0.58 | -0.14 | | 1.76 | +0.03 | -0.01 |
| Experiment | | 1.3193 | | | | 1.7667 | | |

addition of polarization functions on carbon has a very minor effect, but serves to improve slightly the agreement between theory and experiment. The *ab initio* calculations appear to converge with improved quality of basis set towards a value that agrees well with experiment, even without the inclusion of electron correlation.

In considering the Mulliken population analyses of tetrachloromethane, we concentrate only on the basis sets with polarization functions on some or all of the centres, since these are the only ones that give accurate bond lengths. After the addition of polarization functions on chlorine, the subsequent addition of polarization functions on carbon appears to have very little effect on the charge distribution (see Table 3). The various calculations suggest that chlorine carries only a small net charge. The contrast with the fluorine atoms in tetrafluoromethane is striking.

## FLUOROCHLOROMETHANES

Our calculations for $CX_4$, $CHX_3$, $CH_2X_2$, $CH_3X$ and $CH_4$ (X=F or Cl) molecules have indicated significant differences between fluorine and chlorine substituted alkanes. With this in mind, we consider also the $CF_nCl_{4-n}$ series of molecules.

Our results for $CF_3Cl$, $CF_2Cl_2$ and $CFCl_3$ are listed in Tables 4-6. The basis sets that include polarization functions on chlorine, but not on carbon or fluorine, appear to give the best overall agreement with experiment for these three molecules. The further addition of polarization functions on the other centres has relatively little effect on the calculated C-Cl bond lengths. We suspect that the same will be true for the other chlorofluoroalkanes.

In each case the variations of the C-F and C-Cl bond lengths with basis set follows the same patterns as for the molecules discussed earlier. Starting with $CF_4$, successive substitution of fluorine by chlorine reduces the charge on carbon and appears to lengthen the C-F bond length, in line with our simple electrostatic argument. In addition, the calculated C-Cl bond lengths increase, in agreement with the experimental data, although the basis sets with polarization functions on all centres barely exhibit this effect.

As was the case for tetrachloromethane, the calculation of chemically meaningful Mulliken charges appears to require large s/p basis sets that include polarization functions on the chlorine centres.

Not only do the semi-empirical methods fail to reproduce accurately the individual geometrical parameters, but they do not necessarily reproduce the consistent trends noted with the

TABLE 4

Results for $CF_3Cl$. Bond lengths are quoted in Å and angles in degrees.

| | E/hartree | C-F | C-Cl | FCCl | q(C) | q(F) | q(Cl) |
|---|---|---|---|---|---|---|---|
| STO-3G | -786.1097 | 1.36 | 1.85 | 109.2 | +0.50 | -0.11 | -0.17 |
| 3-21G | -791.6453 | 1.33 | 1.83 | 109.4 | +0.98 | -0.35 | +0.08 |
| 4-31G | -794.7211 | 1.34 | 1.81 | 110.1 | +0.98 | -0.36 | +0.08 |
| SV | -795.5852 | 1.36 | 1.79 | 110.8 | +0.66 | -0.25 | +0.07 |
| TZV | -795.6869 | 1.34 | 1.80 | 110.4 | +0.68 | -0.25 | +0.05 |
| 3-21G+$d_{Cl}$ | -791.7472 | 1.34 | 1.74 | 110.4 | +1.11 | -0.37 | +0.00 |
| 4-31G+$d_{Cl}$ | -794.7623 | 1.35 | 1.73 | 111.0 | +1.16 | -0.38 | -0.03 |
| SV+$d_{Cl}$ | -795.6110 | 1.36 | 1.73 | 111.4 | +0.81 | -0.26 | -0.02 |
| TZV+$d_{Cl}$ | -795.7107 | 1.34 | 1.73 | 111.1 | +0.84 | -0.26 | -0.05 |
| 3-21G+P | -791.9870 | 1.30 | 1.76 | 109.6 | +0.80 | -0.24 | -0.08 |
| 4-31G+P | -794.8948 | 1.30 | 1.75 | 110.2 | +0.92 | -0.28 | -0.07 |
| SV+P | -795.7458 | 1.30 | 1.75 | 110.2 | +0.62 | -0.18 | -0.09 |
| TZV+P | -795.8202 | 1.30 | 1.76 | 110.2 | +0.64 | -0.19 | -0.07 |
| MNDO | | 1.34 | 1.84 | 110.5 | +0.68 | -0.19 | -0.10 |
| AM1 | | 1.37 | 1.82 | 105.7 | +0.44 | -0.13 | -0.04 |
| Experiment[a] | | 1.328 | 1.74 | | | | |

[a] A value of 108° was assumed for the FCF angle in the fit of the experimental (microwave spectroscopy) data.

*ab initio* calculations. For example, MNDO and AM1 both predict that the C-Cl bond length increases on successive fluorination of tetrachloromethane, in some case substantially, and MNDO does not predict the expected shortening of the C-F bond length. There are particularly large discrepancies between the semi-empirical and *ab initio* predictions of the ClCCl angles for this series of molecules.

TABLE 5

Results for $CCl_2F_2$. Bond lengths are quoted in Å and angles in degrees.

| | E/hartree | C-F | C-Cl | ClCCl | FCCl | FCF | q(C) | q(F) | q(Cl) |
|---|---|---|---|---|---|---|---|---|---|
| 3-21G | -1150.0067 | 1.34 | 1.84 | 110.5 | 109.1 | 110.0 | +0.42 | -0.33 | +0.12 |
| 4-31G | -1154.3736 | 1.35 | 1.82 | 111.7 | 109.2 | 108.4 | +0.51 | -0.34 | +0.09 |
| SV | -1155.5862 | 1.37 | 1.80 | 112.7 | 109.2 | 107.2 | +0.30 | -0.24 | +0.09 |
| TZV | -1155.5862 | 1.37 | 1.80 | 112.7 | 109.2 | 107.2 | +0.37 | -0.25 | +0.06 |
| 3-21G+$d_{Cl}$ | -1150.2046 | 1.35 | 1.75 | 112.1 | 109.2 | 108.0 | +0.68 | -0.36 | +0.02 |
| 4-31G+$d_{Cl}$ | -1154.4519 | 1.36 | 1.75 | 112.9 | 109.3 | 106.8 | +0.83 | -0.38 | -0.03 |
| SV+$d_{Cl}$ | -1155.6341 | 1.38 | 1.75 | 113.7 | 109.2 | 105.9 | +0.59 | -0.27 | -0.02 |
| TZV+$d_{Cl}$ | -1155.7512 | 1.36 | 1.75 | 113.4 | 109.2 | 106.5 | +0.66 | -0.27 | -0.06 |
| 3-21G+P | -1150.3831 | 1.30 | 1.76 | 111.1 | 109.2 | 109.1 | +0.50 | -0.22 | -0.02 |
| 4-31G+P | -1154.5511 | 1.30 | 1.76 | 111.6 | 109.3 | 108.1 | +0.63 | -0.27 | -0.04 |
| SV+P | -1155.7336 | 1.31 | 1.76 | 111.9 | 109.2 | 107.9 | +0.44 | -0.17 | -0.05 |
| TZV+P | -1155.8328 | 1.31 | 1.76 | 111.8 | 109.2 | 108.0 | +0.46 | -0.18 | -0.05 |
| MNDO | | 1.34 | 1.83 | 106.8 | 110.6 | 107.6 | +0.56 | -0.17 | -0.11 |
| AM1 | | 1.37 | 1.80 | 106.7 | 111.9 | 102.5 | +0.32 | -0.11 | -0.05 |
| Experiment | | 1.345 | 1.744 | 112.6 | | 106.2 | | | |

The results of *ab initio* SCF geometry optimizations for $CH_2ClF$, $CHCl_2F$ and $CHClF_2$ are summarized in Table 7. The trends in the various bond lengths and Mulliken charges are consistent with those that we have described previously, and so do not require further comment. A limited range of basis sets has been considered for these molecules, prompted by our expectation that basis sets with polarization functions only on chlorine will be the most appropriate. The TZV+$d_{Cl}$ calculations do indeed appear to give good overall agreement with experiment. However, these comparisons are complicated by the values assumed by the experimentalists for those parameters that could not be determined from the microwave data.

TABLE 6

Results for $CCl_3F$. Bond lengths are quoted in Å and angles in degrees.

| | E/hartree | C-F | C-Cl | ClCCl | q(C) | q(F) | q(Cl) |
|---|---|---|---|---|---|---|---|
| STO-3G | -1499.1570 | 1.35 | 1.83 | 109.8 | +0.29 | -0.07 | -0.07 |
| 3-21G | -1508.3817 | 1.35 | 1.83 | 110.4 | -0.17 | -0.31 | +0.16 |
| 4-31G | -1514.0332 | 1.35 | 1.82 | 110.6 | +0.02 | -0.33 | +0.10 |
| SV | -1515.5902 | 1.38 | 1.81 | 110.9 | -0.06 | -0.23 | +0.10 |
| TZV | -1515.7320 | 1.36 | 1.81 | 111.0 | +0.02 | -0.25 | +0.07 |
| 3-21G+$d_{Cl}$ | -1508.6707 | 1.36 | 1.76 | 110.8 | +0.22 | -0.35 | +0.04 |
| 4-31G+$d_{Cl}$ | -1514.1452 | 1.38 | 1.76 | 111.0 | +0.47 | -0.38 | -0.03 |
| SV+$d_{Cl}$ | -1515.6580 | 1.39 | 1.76 | 111.3 | +0.34 | -0.27 | -0.02 |
| TZV+$d_{Cl}$ | -1515.7941 | 1.37 | 1.77 | 111.2 | +0.44 | -0.28 | -0.05 |
| 3-21G+P | -1508.7880 | 1.31 | 1.76 | 110.4 | +0.12 | -0.21 | +0.03 |
| 4-31G+P | -1514.2128 | 1.31 | 1.76 | 110.5 | +0.31 | -0.26 | -0.01 |
| SV+P | -1515.7251 | 1.32 | 1.76 | 110.6 | +0.24 | -0.16 | -0.03 |
| TZV+P | -1515.8491 | 1.31 | 1.77 | 110.6 | +0.27 | -0.17 | -0.03 |
| MNDO | | 1.33 | 1.81 | 108.1 | +0.43 | -0.15 | -0.09 |
| AM1 | | 1.38 | 1.79 | 108.2 | +0.18 | -0.09 | -0.03 |
| Experiment | | 1.362 | 1.754 | 111 | | | |

## FLUORINE AND CHLORINE SUBSTITUTED ETHANE

We concentrate on fluorine substitution of $CF_3CH_3$ and on chlorine substitution of $CCl_3CH_3$. Semi-empirical results are compared with experiment in Table 8. The two carbon atoms are labelled $C_a$ and $C_b$, where $C_a$ occurs in the $CX_3$ group (X=F or Cl). We report here only the quantities which change most significantly from molecule to molecule. We are unaware of any

TABLE 7

Results for $CH_2ClF$, $CHCl_2F$ and $CHClF_2$. Bond lengths are quoted in Å and angles in degrees.

| | r(C-H) | r(C-Cl) | r(C-F) | Θ(XCX) | Θ(FCCl) | q(C) | q(H) | q(Cl) | q(F) |
|---|---|---|---|---|---|---|---|---|---|
| $CH_2ClF$ (X=H) | | | | | | | | | |
| 3-21G | 1.07 | 1.89 | 1.37 | 114.1 | 108.7 | -0.10 | +0.27 | -0.08 | -0.36 |
| SV+$d_{Cl}$ | 1.07 | 1.77 | 1.41 | 112.9 | 110.0 | +0.07 | +0.22 | -0.14 | -0.36 |
| TZV+$d_{Cl}$ | 1.07 | 1.77 | 1.39 | 112.6 | 110.0 | +0.14 | +0.18 | -0.15 | -0.35 |
| TZV+P | 1.08 | 1.78 | 1.34 | 112.5 | 110.0 | +0.11 | +0.14 | -0.14 | -0.25 |
| experiment | 1.078 | 1.759 | 1.378 | 111.9[a] | 110.0 | | | | |
| $CHCl_2F$ (X=Cl) | | | | | | | | | |
| 3-21G | 1.07 | 1.85 | 1.35 | 110.2 | 108.9 | -0.12 | +0.33 | +0.06 | -0.34 |
| SV+$d_{Cl}$ | 1.07 | 1.76 | 1.40 | 112.8 | 108.7 | +0.22 | +0.26 | -0.08 | -0.31 |
| TZV+$d_{Cl}$ | 1.07 | 1.76 | 1.38 | 112.6 | 108.9 | +0.29 | +0.21 | -0.09 | -0.31 |
| TZV+P | 1.07 | 1.77 | 1.32 | 111.8 | 109.3 | +0.18 | +0.18 | -0.08 | -0.20 |
| experiment | 1.10[a] | 1.758 | 1.346 | 111.4 | 109.5 | | | | |
| $CHClF_2$ (X=F) | | | | | | | | | |
| 3-21G | 1.07 | 1.87 | 1.34 | 109.8 | 108.3 | +0.46 | +0.28 | -0.02 | -0.36 |
| SV+$d_{Cl}$ | 1.07 | 1.75 | 1.38 | 106.8 | 110.2 | +0.46 | +0.23 | -0.08 | -0.31 |
| TZV+$d_{Cl}$ | 1.07 | 1.75 | 1.36 | 107.2 | 110.0 | +0.52 | +0.18 | -0.10 | -0.30 |
| TZV+P | 1.07 | 1.77 | 1.32 | 108.2 | 109.7 | +0.39 | +0.14 | -0.11 | -0.22 |
| experiment | 1.09[a] | 1.747 | 1.350 | 107.0 | 110.1 | | | | |

[a] This value was assumed in the fit of the experimental (microwave spectroscopy) data.

experimental geometry for $CF_3CFH_2$, and so we have carried out *ab initio* calculations for this molecule using SV basis sets augmented with polarization functions on some or all of the centres. It is reasonable to expect that the most reliable prediction of the $C_b$-F bond length in $CF_3CFH_2$ is the one provided by the SV+$d_F$ basis set.

TABLE 8

Results for $CX_3CX_nH_{3-n}$ (X=F or Cl). The carbon atom of the $CF_3$ group is labelled $C_a$. Bond lengths are quoted in Å.

| | | $C_a$-$C_b$ | $C_b$-X | $C_b$-H | q($C_a$) | q($C_b$) |
|---|---|---|---|---|---|---|
| $CF_3CF_3$ | experiment | 1.55 | 1.33 | | | |
| | MNDO | 1.67 | 1.35 | | +0.59 | +0.59 |
| | AM1 | 1.62 | 1.38 | | +0.39 | +0.39 |
| $CF_3CF_2H$ | experiment | 1.52 | 1.36 | (1.10)[a] | | |
| | MNDO | 1.66 | 1.35 | 1.13 | +0.55 | +0.42 |
| | AM1 | 1.60 | 1.37 | 1.13 | +0.36 | +0.20 |
| $CF_3CFH_2$ | SV+$d_F$ | 1.52 | 1.38 | 1.08 | +0.11 | +0.00 |
| | SV+$d_C$ | 1.52 | 1.36 | 1.08 | +0.56 | -0.11 |
| | SV+$d_F$+$d_C$ | 1.52 | 1.35 | 1.08 | +0.66 | -0.09 |
| | SV+P | 1.52 | 1.35 | 1.08 | +0.67 | +0.03 |
| | MNDO | 1.62 | 1.34 | 1.12 | +0.55 | +0.23 |
| | AM1 | 1.57 | 1.37 | 1.12 | +0.38 | -0.01 |
| $CF_3CH_3$ | experiment | 1.53 | | 1.09 | | |
| | MNDO | 1.59 | | 1.11 | +0.57 | +0.01 |
| | AM1 | 1.54 | | 1.11 | +0.41 | -0.26 |
| $CCl_3CCl_3$ | experiment | 1.56 | 1.77 | | | |
| | MNDO | 1.57 | 1.79 | | +0.19 | +0.19 |
| | AM1 | 1.56 | 1.76 | | +0.00 | +0.00 |
| $CCl_3CH_3$ | experiment | 1.54 | | 1.09 | | |
| | MNDO | 1.54 | | 1.11 | +0.22 | +0.02 |
| | AM1 | 1.52 | | 1.12 | +0.04 | -0.23 |

[a] This value was assumed in the fit of the experimental data.

We would expect successive fluorination of $CF_3CH_3$ to show the same effects as for the fluoromethanes, and as rationalized by our simple electrostatic model. We find that the experimental (or SV+$d_F$) $C_b$-F bond length does indeed decrease. Sadly, this effect is not reproduced by the semi-empirical calculations, although these do manifest the expected increase in the positive charge on the $C_b$ atom.

We turn now to the analogous chlorine substituted alkanes, but examine only the first and last members of the series, i.e. $CCl_3CH_3$ and $CCl_3CCl_3$. The substitution by chlorine of all the hydrogen atoms in $CCl_3CH_3$ results in a slight increase in the C-C bond length, analogous to that seem experimentally for the $CF_3H_3/CF_3CF_3$ pair. The semi-empirical calculations do suggest that the charge on $C_b$ becomes more positive on fully-chlorinating $CCl_3CH_3$, but the absolute values do not seem very meaningful.

## CONCLUSIONS

We have carried out ab initio and semi-empirical geometry optimizations for a range of fluorine and chlorine substituted alkanes. The main aims were to establish a reliable methodology for SCF calculations on such systems, and to examine the accuracy of cheaper semi-empirical schemes.

The results of our SCF calculations strengthen the comments in Part I of this work [1] that considerable care is required in the choice of basis set. For fluorocarbons, the inclusion of polarization functions only on fluorine leads to C-F bond lengths in good agreement with experiment. On the other hand, the inclusion of polarization functions on all centres leads to the most accurate C-Cl bond lengths in chlorocarbons. For $CCl_3F$, the best overall agreement with experiment is provided by basis sets that include polarization functions only on chlorine. It seems likely that this will also be true for other fluorochloroalkanes.

Our simple electrostatic model for fluorocarbons does not appear to be applicable to chlorocarbons, presumably because of the larger size and smaller electronegativity of chlorine relative to fluorine. We find that polarization functions on chlorine are essential for chemically meaningful Mulliken charges. For fluorine and chlorine substituted methane, the reaction enthalpy for hydrogen-atom abstraction by chlorine atoms appears to correlate with the Mulliken charge on carbon.

Unfortunately, the various semi-empirical techniques are not sufficiently reliable to reproduce the structural variations observed experimentally for the various systems studied in this work.

For fluorocarbons, our work suggests that *ab initio* SCF calculations with relatively small basis sets give accurate geometries and realistic Mulliken charges, provided that polarization functions have been included on the fluorine centres. There are insufficient experimental data to make a definitive judgement for the fluorochloromethanes, but all of the indications are that small s/p basis sets augmented with polarization functions only on chlorine constitute the most appropriate choice for geometry optimizations.

We are now in a strong position to apply appropriate theoretical techniques to the study of the structure and reactivity of fluorine and chlorine substituted hydrocarbons.

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