On the Structural Differences between Trifluoromethyl Sulphonyl Chloride (CF$_3$SO$_2$Cl) and Methane Sulphonyl Chloride (CH$_3$SO$_2$Cl)

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CNDO/2 MO calculations show the elektron withdrawing ability of the CF$_3$ group versus the electron releasing of the CH$_3$ group to be the primary source of the considerable S-C bond lengthening in CF$_3$SO$_2$Cl as compared with CH$_3$SO$_2$Cl.

The molecular geometries of trifluoromethyl sulphonyl chloride and methane sulphonyl chloride have been determined by electron diffraction [1] and [2] (see also [3]), respectively. The structural variations in the bond configuration around the sulphur atom upon the changing electronegativities of the ligands have been discussed in detail [4]. The geometries of the two mentioned sulphonyl chloride molecules are consistent with the general observations. There is however a strikingly large (0.09 Å) difference between the two S–C bond lengths, much larger than would have been expected on the basis of the other known structural changes caused by CH$_3$/CF$_3$ substitution [5]. Considering the short C–S bond (1.759 ± 0.006 Å) in CH$_3$SO$_2$F [6], Robinson and Aroca [7] called attention to the hyperconjugative release of electrons from the C–H bonds into the S–C bond. To further examine the origin of this large variation in the S–C bond length upon CH$_3$/CF$_3$ substitution, we decided to carry out some CNDO/2 MO calculations.

We used the standard CNDO/2 method and parametrization [8], including d orbitals on the sulphur and chlorine atoms [9]. Although the semiempirical character of the CNDO/2 procedure makes difficult to assess the reliability of the quantitative results obtained for a given individual molecule, we anticipated useful qualitative information concerning the differences between the two similar systems in question. For this reason we did not try to perform a complete geometry optimization, but used the experimental electron diffraction data for both molecules except that the S–C bond lengths were varied.

The minimum energies of CH$_3$SO$_2$Cl and CF$_3$SO$_2$Cl were achieved at the S–C bond lengths of 1.759 Å and 1.807 Å, respectively. Thus a large (0.05 Å) difference was indicated by the theoretical calculations too [10]. Although this difference was smaller than obtained from the experimental data, it was considered to be large enough to yield qualitative information as to its origin.

Some selected numerical results are shown in Tables 1 and 2. In the case of CH$_3$SO$_2$Cl they correspond to the experimental S–C bond length which is practically equal to the calculated one. For CF$_3$SO$_2$Cl the results obtained at two different bond lengths are given: r(S–C) = 1.807 Å is the bond length corresponding to the calculated energy minimum, while the results for r(S–C) = 1.763 Å are added to compare the data for both molecules at the same S–C distance.

Table 1. Valence-electron charges, group charges and dipole moments of CH$_3$SO$_2$Cl and CF$_3$SO$_2$Cl as calculated by the CNDO/2 technique.

	CH$_3$SO$_2$Cl	CF$_3$SO$_2$Cl	
r(S—C), Å	1.763	1.807	1.763
S	5.62	5.71	5.72
Cl	7.06	6.99	6.99
O	6.22	6.17	6.17
O	6.22	6.17	6.17
C	4.08	3.42	3.42
X(=H, F)	0.92	7.17	7.17
X	0.94	7.18	7.18
X	0.94	7.18	7.18
group charges			
CX$_3$	+ 0.132	+ 0.053	+ 0.054
SO$_2$Cl	− 0.132	− 0.053	− 0.054
dipole moments			
	5.11	3.10	3.10

Table 2. Some quantities (in atomic units) referring to the S—C bond from the energy partitioning (see text and Refs. [8, 11]).

	CH$_3$SO$_2$Cl	CF$_3$SO$_2$Cl	
r(S—C), Å	1.763	1.807	1.763
S—C two-center terms:			
$\varepsilon_{el\cdot st\cdot}$	0.05	0.10	0.12
ε_{res}	− 0.92	− 0.82	− 0.86
$\varepsilon_{SC} = \varepsilon_{el\cdot st\cdot} + \varepsilon_{res}$	− 0.87	− 0.72	− 0.73
Molecular binding energy	− 2.282	− 2.502	− 2.499

According to Table 1 there is only one drastic change in the atomic charges of the CSO_2Cl fragment which is common for both molecules, viz. the carbon atom becomes strikingly positive upon the CH_3/CF_3 substitution. (For CF_3SO_2Cl the valence electron population on the carbon decreases by about 2/3 as compared with CH_3SO_2Cl.) The consequences of this charge redistribution may be best seen by considering the results of the energy partitioning [8, 11]. The largest differences in the quantities comparable for the two molecules were found in the two-center terms referring to the S–C bond. In Table 2 $\varepsilon_{el.st.}$ is the sum of the nuclear-nuclear repulsion, electron-nuclear attraction and electron-electron repulsion (including exchange) energy terms between the sulphur and carbon atoms. As the decrease of the electron charge on the carbon leads to the decrease of all these contributions, except, of course, the nuclear repulsion, the net electrostatic interaction between the S and C atoms becomes strongly out of balance for CF_3SO_2Cl. Roughly speaking: the screening of the carbon nuclear charge considerably decreases and the nuclear repulsion in the S–C bond becomes less compensated.

Furthermore, the strong decrease in the absolute value of the S–C "resonance energy" [11]

$$\varepsilon_{res} = \sum_{\mu \in S} \sum_{\nu \in C} 2\,P_{\mu\nu}\,\beta_{\mu\nu}$$

as going from CH_3SO_2Cl to CF_3SO_2Cl (see Table 2) can be attributed to the fact that the S–C bond of the fluorinated derivative becomes poorer in electrons due to the loss of electrons on the carbon. Accordingly, the S–C bond becomes more compliant as it is well shown by the differences in curvature of the energy vs. bond length plots of Figure 1. This is also consistent with the values of the Wiberg indices [12] giving a measure for the bond order between the atoms in question:

$$H_3C \xrightarrow{1.089} SO_2Cl\,, \qquad F_3C \xrightarrow{0.925} SO_2Cl\,.$$

Thus, there are two main effects of the CH_3/CF_3 substitution which are closely related to each other both leading to the decrease in the absolute value of the total contribution ε_{SC} of the S–C bond to the molecular binding energy: the increase of the electrostatic repulsion between C and S and the partial removal of the electrons from the bond.

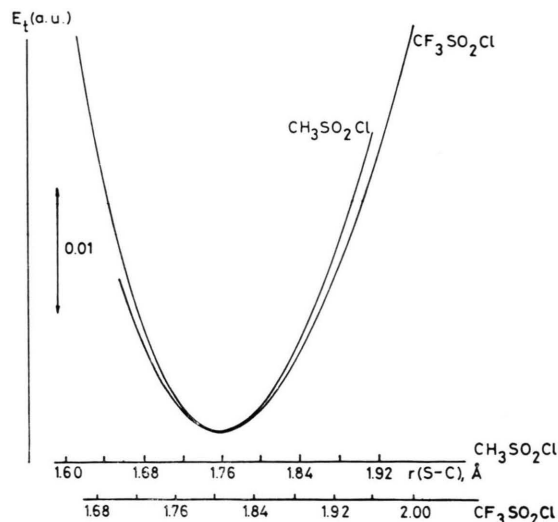The results of Table 2 obtained for CF_3SO_2Cl at two different S–C distances show that in the vicinity

Fig. 1. Calculated total CNDO/2 molecular energy *vs.* bond length curves for CH_3SO_2Cl and CF_3SO_2Cl molecules.

of the energy minimum the individual terms $\varepsilon_{el.st.}$ and ε_{res} vary much more with the bond length than the total two-center contribution ε_{SC}: their changes almost entirely compensate each other. The overall molecular energy changes significantly less than the S–C two-center contribution and in the opposite direction: ε_{SC} is more negative at the bond length 1.763 Å than at 1.807 Å though the latter corresponds to the calculated energy minimum. (An analogous example has been described in [11].) This behaviour may be connected with a slightly larger electron population on the sulphur atom at r(S–C) $= 1.763$ Å which leads to an increased sulphur one-center electron-electron repulsion, overweighting the change in the ε_{SC} contribution. Considering these variations one has to keep in mind that the two-center energy contributions are static characteristics corresponding to a given nuclear configuration only and are not immediately related to the bond dissociation energies [11].

Returning to the question of the S–C bond length variation upon the CH_3/CF_3 substitution, it may be attributed in simple terms to the difference between the electron releasing ability of the CH_3 group and the electron withdrawing ability of the CF_3 group. The direction of the changes in the group charges and dipole moments (Table 1) are also consistent with this notion [13].

It seems, however, that for correct interpretation of the change in the bond length it is not sufficient

to consider the SO_2Cl and CX_3 groups as whole entities but one has to take into account also the effects of the charge alternation within these groups, which perhaps may be a general tendency for similar systems. Thus, among others, one expects effects quite similar to those discussed above for CF_3SO_2Cl in the case of CCl_3SO_2Cl, in which, though determined with a larger uncertainty, the S–C bond has a similar length (1.87 ± 0.03 Å) [14]. It is also hoped that some day accurate *ab initio* calculations can throw more light on the structures discussed in the present paper.

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[8] J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory. McGraw-Hill, New York 1970.
[9] For both CH_3SO_2Cl and CF_3SO_2Cl relatively large sulphur d populations (1.96 and 1.99, resp.) and relatively small chlorine d populations (0.136 and 0.144, resp.) were obtained. The CNDO/2 method probably exaggerates the d populations. However, this hardly influences the conclusions concerning the comparison of CH_3SO_2Cl and CF_3SO_2Cl as the numerical values of the d population are almost the same for the two systems.
[10] The bond lengths corresponding to the minimum energies were found by fitting a fourth-order polinom to five calculated points spaced by 0.05 Å around the experimental bond length. The fact that for CH_3SO_2Cl the experimental and calculated bond lengths coincide within the experimental error should be considered as fortiutous.
[11] H. Fischer and H. Kollmar, Theor. Chim. Acta Berlin **16**, 163 (1970).
[12] K. A. Wiberg, Tetrahedron **24**, 1083 (1968).
[13] The fact that the signs of the group charges remain the same indicates the electron-withdrawing force of the SO_2Cl group to be larger than that of the CF_3 group.
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Erratum

A. Graovac, O. E. Polansky, N. Trinajstić, and N. Tyutyulkov, Graph Theory in Chemistry. II. Graph-Theoretical Description of Heteroconjugated Molecules [Z. Naturforsch. **30 a**, 1696 – 1699 (1975)].

On page 1698 the following part of the sentence: "However, a real virtue of the method is in providing..." should read: "However, when appropriately modified [1] the method could provide...".

[1] N. Trinajstić, Croat. Chem. Acta **49**, 593 (1977).