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AN APPROACH TO THE ELECTRONIC PROPERTIES OF SULFONYL AND SULFINYL COMPOUNDS BY MEANS OF SULFUR-33 AND OXYGEN-17 NMR

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Abstract. *The trend of variation of sulfur and oxygen shieldings of X-SO₂-Y and X-SO-Y substrates is rationalized in terms of the joint effects of n → σ* conjugative interactions and ligands electronegativity. The relative weight of these effects is different in the two classes of compounds, the former being dominant in the series X-SO₂-Y and the latter in the series X-SO-Y.*

In principle, the overall information on the electronic configuration of a molecule, including that on excited energy states, is contained in the chemical shifts of all its nuclei taken together (1). In fact, decoding all the information which can be obtained by use of modern nuclear magnetic resonance instruments is not an easy task, given the present state of development of theoretical NMR. The chemical shifts depend upon a complex balance of factors and only when one of them is dominant within a related series of compounds, the observed variations are amenable to meaningful correlations with molecular electronic features (1).

We have analyzed the sulfur-33 and oxygen-17 shielding variations within the two classes of compounds X-SO₂-Y and X-SO-Y, where X and Y are ligands covering a wide range of group electronegativities (2-4). For both classes of compounds extensive studies on their structure have been carried out (5). Our data provide evidence for the existence of n → σ* conjugative interactions of the oxygen lone pairs of -SO₂- and -SO- moieties with the vacant antibonding σ*(S-Y) and/or σ*(S-X) molecular orbitals.

Owing to the relatively narrow sulfur and oxygen NMR lines, a large number of

relationship for δ_S vs. δ_O or for δ_S or δ_O vs. the sum of group electronegativities of X and Y, although as a general trend both δ_S and δ_O decrease when the ligands electronegativity increases. We have shown that when X is held constant while Y varies, conjugative interactions manifest themselves as a progressive *deshielding* of oxygen and *shielding* of sulfur as the atom next to sulfur varies down the same column of the periodic table. In this case there is a linear correlation between δ_O and χ_Y but the negative slope of the regression line indicates that the effect of $n \rightarrow \sigma^*$ interactions on δ_O , i.e. the so called 'chlorine effect' (2,3), overwhelms that of ligands electronegativities (3). A negative slope of δ_O vs. χ_Y is also found for the series Cl-SO₂-Y where the electronegativity of Y increases in the order CH₃ < N(CH₃)₂ < OCH₃ (figure 1b). This finding, which appeared at the beginning of our work rather puzzling (2), can be explained assuming that the amount of charge transfer from the terminal oxygens to the S-Cl bond, due to the conjugative interactions between the oxygen lone pairs and the vacant $\sigma^*(S-Cl)$ MO, decreases regularly as the electron withdrawing ability of Y increases.

For the series of sulfinyl compounds X-SO-Y only a few sulfur-33 NMR data are available, owing to the fact that sulfur NMR lines of an -SO- moiety may be so broad to be undetectable (6). Moreover, sulfur shifts may be strongly affected by changes of the average excitation energy (7). The oxygen chemical shifts of several of these compounds have already been reported, although the trend of variation of δ_O on changing X and Y was not fully understood (7). That $n \rightarrow \sigma^*$ interactions are also important in an X-SO-Y series is shown by the fact that a chlorine atom next to sulfur always deshields the terminal oxygen by several tens of ppm, *cf.* compounds CH₃-SO-Cl and CH₃-SO-OCH₃, where the terminal oxygen of the former is deshielded by 50 ppm compared to that of the latter compound, despite the fact that Cl and OCH₃ have quite similar group electronegativities (7,4). It is worth noting that the magnitude of this 'chlorine effect' is nearly the same as that for the corresponding sulfonyl compounds (2,3). However, the effect of ligands electronegativity is more important in sulfinyl than in the

corresponding sulfonyl compounds. This is clearly shown by figure 1 which gives the plots of δ_{O} vs. χ_{Y} for the series $\text{CH}_3\text{-SO}_2\text{-Y}$ and $\text{CH}_3\text{-SO-Y}$ (figure 1b) and the series $\text{Cl-SO}_2\text{-Y}$ and Cl-SO-Y (figure 1a), with $\text{Y} = \text{CH}_3, \text{N}(\text{CH}_3)_2, \text{OCH}_3$. For methane sulfonyl and sulfinyl series conjugative interactions are negligible because of the high energy gap between the occupied orbitals and the σ^* (S-Y) MO, as the atoms next to sulfur belong to the first row of the periodic table. For the other two series, where the methyl group is replaced by chlorine, the effect of ligands electronegativity on oxygen electronic

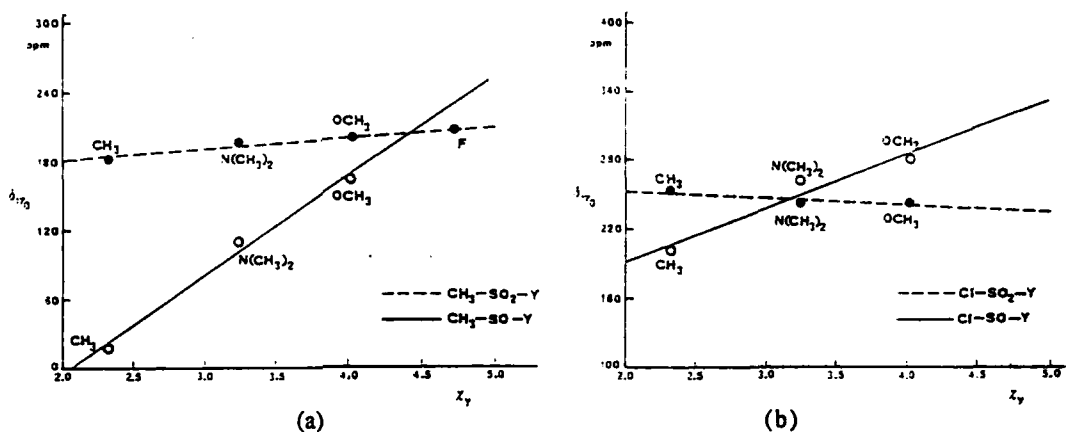


Figure 1. Oxygen-17 chemical shifts of the series $\text{CH}_3\text{-SO}_2\text{-Y}$, $\text{Cl-SO}_2\text{-Y}$ and $\text{CH}_3\text{-SO-Y}$, Cl-SO-Y vs. the group electronegativity of the Y ligands.

density is counteracted by the effect of conjugative interactions between the oxygen lone pair electrons and the σ^* (S-Cl) MO. The figure shows that for the series $\text{Cl-SO}_2\text{-Y}$ the slope of the regression line is negative, indicating that the effect of conjugative interactions on the chemical shift is predominant. On the contrary, in the series Cl-SO-Y the slope of the regression line of δ_{O} vs. χ_{Y} is positive, since the effect of the electronegativity of Y on the chemical shift is more important than that of conjugative interactions. However, conjugative interactions are responsible for the fact that the slope of the regression line for the series Cl-SO-Y is significantly smaller than that for the series $\text{CH}_3\text{-SO-Y}$. That the influence of the Y substituent on the charge distribution of the S-O bond is in X-SO-Y larger

than in X-SO₂-Y is reasonable. Indeed, although the electronic properties of the Y substituent have in both series a direct effect on the polarization of the S-Y bond, in the case of X-SO-Y the nature of Y should have a large influence also on the hybridization of the

Table 1. MNDO calculated atomic charges (q, in millielectrons) and chemical shifts (δ_S and δ_O , in ppm) of selected sulfinyl and sulfonyl compounds

| | q_S | q_O | δ_S^* | δ_O^* |
|---|-------|-------|--------------|--------------|
| CH ₃ -SO ₂ -CH ₃ | 389 | -268 | 315 | 164 |
| CH ₃ O-SO ₂ -OCH ₃ | 505 | -249 | 319 | 140 |
| CH ₃ O-SO ₂ -Cl | 561 | -210 | 311 | 219 |
| Cl-SO ₂ -Cl | 612 | -174 | 287 | 296 |
| CH ₃ -SO-CH ₃ | 307 | -329 | 325 | 15 |
| CH ₃ O-SO-OCH ₃ | 457 | -305 | 510 | 173 |
| CH ₃ O-SO-Cl | 545 | -252 | 600 | 254 |
| Cl-SO-Cl | 621 | -174 | 570 | 287 |

(*) From references 2 and 3

sulfur atom. Consequently, a larger variation on sulfur and oxygen atomic charges is expected in the X-SO-Y series compared to the X-SO₂-Y series, on changing the Y ligand. Table 1, which gives the atomic charges on sulfur and oxygen for a series of sulfoxides, for which both sulfur and oxygen chemical shifts have been measured (7), and the corresponding sulfones shows this to be actually the case.

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