

CHEMISTRY OF SULFINES XI¹

NMR SPECTRA OF AROMATIC SULFINES

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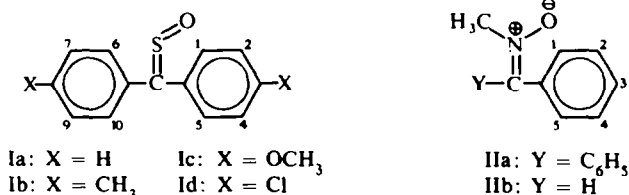
Abstract— The NMR spectra of 4,4'-disubstituted diphenylsulfines are discussed in terms of the deshielding effect of the bent CSO system on the *ortho*- and *meta* protons of either phenyl ring. The data presented reveal that the deshielding effect of the CSO group is directed to one side of the molecule and is mainly caused by the S=O part rather than by the C=S moiety.

The NMR spectra of the fused aromatic sulfines V-X show one proton at lower field. The shift of this proton relative to the remaining aromatic protons is discussed by taking into account the angles α and β , and the electronic effect of the fusing group.

For comparison the spectra of some nitrones, which have a bent structure analogous to sulfines, are considered.

THE CSO group in sulfines² is rigid and non-linear as indicated by the isolation of two geometrical isomers of chloro-phenyl-sulfine³ as well as of *thiono*-oxides of dithio-carboxylic esters.⁴ An X-ray analysis of ethylene trithiocarbonate *thiono*-oxide⁵ reveals that the sulfine carbon atom is sp²-hybridized, that the sulfine oxygen atom lies almost in this sp²-plane and that the CSO-angle amounts to 109.4°.

The NMR spectrum of diphenylsulfine (Ia) shows absorptions corresponding to two protons at considerably lower field than the remaining eight protons, whereas in benzophenone and thiobenzophenone four protons are shifted downfield. Hence, the bent CSO group directs its deshielding effect only to one side of the molecule. A similar deshielding effect was observed for nitrones which have a bent structure comparable with sulfines.



The aromatic pattern of IIa is almost identical with that of Ia. In the nitron IIb which has the phenyl ring in the *cis* position with respect to the oxygen atom, the *ortho* protons H-1 and H-5 are shifted downfield.⁶

Because of this analogy it is evident that in the sulfines I the protons situated closest to the sulfine oxygen atom, e.g. H-1 and H-5, are shifted to lower field. In accordance herewith *trans*-chloro-phenyl-sulfine shows the two *ortho* protons shifted to lower field, while the *cis*-isomer gives the aromatic protons as one multiplet.^{2, 3}

TABLE 1. SUBSTITUENT CONSTANTS OF SOME CSO, CO AND CS CONTAINING GROUPS, IN CPS, RELATIVE TO BENZENE IN THE SAME SOLVENT (CCl₄).

I : X		II : X		III : X		IV : X	
a : X = H							
Substituent	S _o	S _m	Substituent	S _o ^M	S _m ^M	Substituent	S _o ^t
	-36,4	-		-	-		-23,5
H ₃ C	-37,0	-5,8		-2,4	-7,8	H ₃ C	-24,7
H ₃ CO	-42,2	-1,9		-3,1	-3,6	H ₃ CO	-29,0
Cl	-35,4	-4,8		-4,2	-7,3	Cl	-28,7
b : X = CH ₃							
Substituent	S _o ^k	S _m ^k	Substituent	S _o ^k	S _m ^k	Substituent	S _o ^k
	-29,0	-		-29,7	-9,1		-32,5
H ₃ C	-29,7	-9,1		-	-	H ₃ CO	-28,7
H ₃ CO	-32,5	-4,6		-	-	Cl	-
Cl	-28,7	-9,0		-	-		
c : X = OCH ₃							
Substituent	S _o ^t	S _m ^t	Substituent	S _o ^k	S _m ^k	Substituent	S _o ^k
	-	-		-	-		-
H ₃ C	-	-		-	-	H ₃ CO	-
H ₃ CO	-	-		-	-	Cl	-
Cl	-	-		-	-		

The substituent constants S_o and S_m of CH₃, OCH₃ and Cl, necessary for evaluating the above substituent constants are taken from N. van Meurs, *Rec. Trav. Chim.* **87**, 145 (1968).

To analyze the effect of substituents on the CSO system the NMR spectra of the 4,4'-disubstituted diphenylsulfines Ib–Id were recorded. The substituent constants S_o , S_m , S_o^* and S_m^* of the CSO containing groups are compiled in Table I. For comparison the substituent constants of the corresponding CS and CO containing groups, obtained from the spectra of the thioketones III and ketones IV, are included. (Table I)

The S_o -values indicate that the deshielding effect on H-1 and H-5 decreases with electron withdrawing substituents and increases with electron releasing substituents, presumably because of their effect on the electron density in the CSO group. The deshielding effect on H-6 and H-10 in sulfines (S_o^*) is strongly reduced as compared with that in the corresponding thioketones (S_o'). This indicates that the deshielding of the C=S part in sulfines is almost negligible. Therefore, the downfield shift of H-1 and H-5 (S_o) must be attributed to the influence of the S = O moiety.

Remarkably, S_m^* is more negative† than S_o^* ; apparently the *ortho* protons 6 and 10 experience a small shielding effect superimposed on the usual inductive effect on the deshielding.

The NMR spectra of the fused aromatic sulfines V–X show an absorption corresponding to one proton at lower field than the remaining aromatic protons (Fig. 1). A comparison is made between the position of the perturbed and unperturbed protons, e.g. H-1 and H-8 (expressed by Δ). For this series of sulfines the deshielding effect varies considerably with the nature of the central ring: X < VIII ~ IX < V ~ VII < VI.

By variation of the fusing element (or group) of the two aromatic rings a change takes place in the angle α and the dihedral angle ϑ between the two aromatic rings, which results in a change of the position of the perturbed proton in the deshielding region of the SO group of the CSO system. X-ray studies⁷ reveal that tricyclic hetero compounds derived by replacing the 9- and 10-carbon atom of anthracene by atom A and B are planar if both A and B are any of C or O, but folded if at least one of A and B is S. Therefore, we propose that ϑ for V and VI will be close to 180° and that the molecules VII, VIII and IX are folded with a ϑ of about 130°. The differences in α for VI–IX will be small, probably in V α will be slightly larger than in VI–IX.

Furthermore, the deshielding Δ will be influenced by the electronic effect of the fusing element or group on the CSO system (*cf.* Table I).

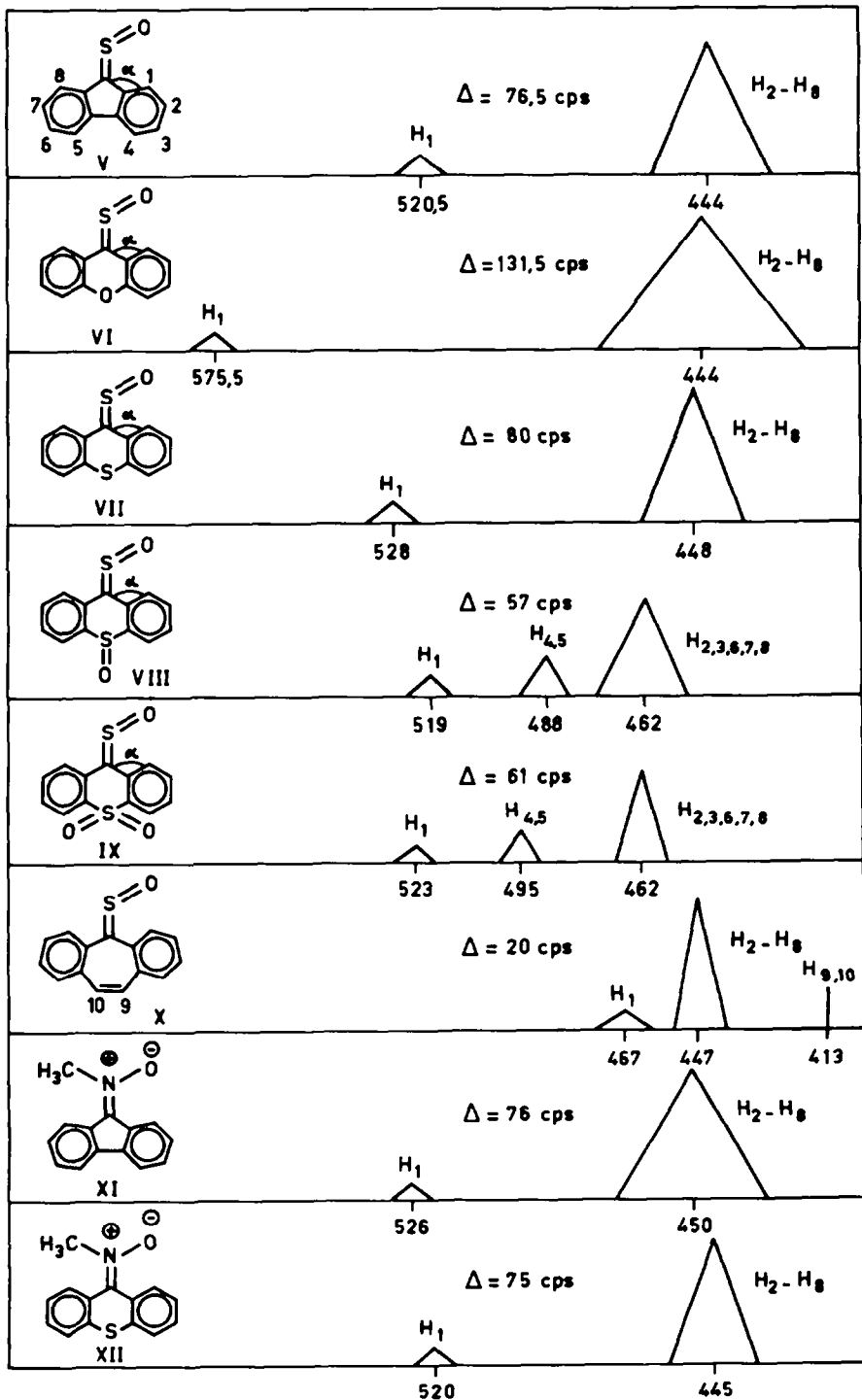
The Δ -value in xanthione-S-oxide (VI) is much larger than that in thiofluorenone-S-oxide (V). Possibly, the somewhat smaller α in VI causes a more favourable position of H-1 in the deshielding region. However, the main difference in Δ may be attributed to the electronic effect of the fusing O-atom in VI, since contribution of zwitter-ionic resonance structures will enhance the electron density in the CSO system considerably.

The Δ -value for VII is substantially smaller than for VI. This will partly be due to a difference in ϑ and presumably also to a diminished contribution of zwitter-ionic resonance structures.

The sulfoxide- and sulfone sulfines VIII and IX have a smaller Δ -value than VII. The change in α and ϑ will be negligible, hence the difference will be caused by the change in electronic effects: the thioether function being a slightly donating group whereas the sulfoxide and sulfone group are strongly electron withdrawing.

To explain the small Δ -value for X as compared to V differences in ϑ and α must be

† Usually, the reverse is the case.

FIG. 1. NMR spectra of V-XII in CDCl₃.

invoked. Molecular models clearly show that in the folded molecule X H-1 is rather far out of the effective deshielding region of the CSO group.

The $\Delta\omega$ value for the "fused" nitrones XI and XII are very close to those of the corresponding sulfines.

EXPERIMENTAL

The NMR spectra were recorded with a Varian Associates A-60 spectrometer (60 Mc/sec). For compounds I, III and IV spectro-grade CCl_4 was used as solvent (TMS as an internal standard). Sample concentrations were 3-5% by weight. Line positions were found by using the side band technique with a precision of ± 0.2 cps. The ultimate standard was pure C_6H_6 in CCl_4 (ca. 5%) referenced against TMS (435.6 cps). The compounds Ib-d, IIb, c and IVb-d all gave A_2B_2 type spectra. The chemical shift of the respective protons was calculated with the formula

$$\delta_A - \delta_B = \sqrt{(v_4 - v_1)(v_3 - v_2)}$$

The substituent constants S were obtained according to the method of Diehl.⁸ The NMR spectra of V-XII were recorded in CDCl_3 -solutions (3-5% by weight).

The sulfines Ia, Ic, V-IX were prepared as described previously.² The sulfines Ib, Id and X were prepared by peracid oxidation of the corresponding thioketones. (Ib: 70%, m.p. 92-93; Id: 74%, m.p. 86-89; X: 84%, m.p. 102-103).

The nitrones† were prepared according to Smith and Robertson.⁹

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† The compounds were prepared by Mr. T. Hibma.