Stereospecific Transmission of Electronic Effects by a Sulphoxide Bridge

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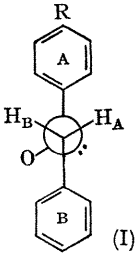
Summary Stereospecific transmission of electronic effect across the sulphoxide bridge in α-methylbenzyl *p*-substituted phenyl sulphoxides is attributed to the relative geometry of the proton and the lone pair, in which the difference in the hybridization states is important.

DIFFERENCES between S, SO, and SO_2 in the transmission of electronic effects is a subject of current interest.[1] The substituent effect on the pK_a of the acids $RCH:CH\cdot CO_2H$[2] and $RCH_2\cdot CO_2H$[3] (R = $Y\cdot C_6H_4SO_n$; n = 0, 1, and 2) was studied, and it was found that the effect of the substituent Y is more efficiently transmitted in the case of S than in the case of SO or SO_2. This was substantiated by a recent investigation by Hyne and Greidanus[1] on the n.m.r. spectra of 4,4′-disubstituted diphenyl sulphides, sulphoxides, and sulphones.

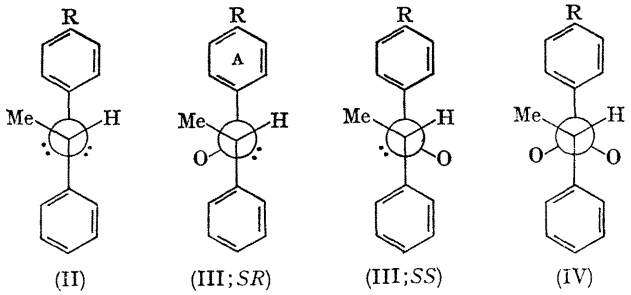
In a recent study of magnetic nonequivalence of the methylene protons of benzyl *p*-substituted phenyl sulphoxides (I), it was found that the peaks corresponding to the proton *gauche* to the lone pair on sulphur (H_A) are more sensitive to a substituent change.[4] This phenomenon was tentatively attributed to the conformational preference of the ring-A phenyl group[5] and has been applied to configurational assignment of some diastereomeric sulphoxides.[6]



(I)

I now report n.m.r. data relevant to the transmission of electronic effects by some sulphur-containing bridges, and present some considerations on the stereospecific transmission of electronic effects observed in α-methylbenzyl phenyl sulphoxides.

The Table lists chemical shifts of methine protons of α-methylbenzyl *p*-substituted phenyl sulphides (II), sulphoxides (III; *RR/SS* and III; *RS/SR*), and sulphones (IV).



(II) (III;*SR*) (III;*SS*) (IV)

TABLE

R	(II)	(III; *RS/SR*)	(III; *RR/SS*)	(IV)
Me	5·75[a]	5·99	6·23	5·80
H	5·70	5·98	6·22	5·77
Cl	5·75	5·94	6·23	5·78
NO_2	5·46	5·77	6·18	5·71
Δ[b]	−0·29	−0·22	−0·05	−0·09

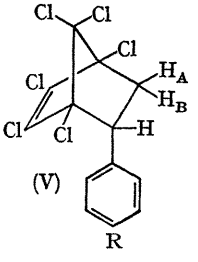
Preparation and assignment of relative configuration of these sulphoxides were reported in a previous paper.[6]

[a] τ (in $CDCl_3$); spectra were taken at 100 MHz. on a JEOL JNM-4H-100 spectrometer at 24° using 5% solutions, the accuracy of the measurements being within ±0·01 p.p.m.

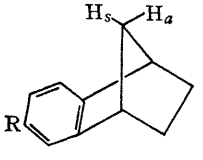
[b] τ (R NO_2) − τ (R Me).

Substituent shifts induced by replacement of methyl by a nitro-group (Δ) are −0·29 p.p.m. for sulphides (II) and −0·09 p.p.m. for sulphones (IV). This is wholly compatible with the previous results[1-3] establishing the sulphide as the most effective transmitter in this series, and suggests that some kind of electronic interaction (such as *d*-orbital involvement in the hybridization states of covalently bonded sulphur) occurs even in the ground state.

Another interesting feature shown in Table is the stereospecific transmission of the electronic effect observed in sulphoxides [Δ for (III; *RS/SR*) −0·22 p.p.m., Δ for (III; *RR/SS*) −0·05 p.p.m.]. A possible interpretation for the larger Δ in (III; *RS/SR*) may be a preferred conformation of the ring-A phenyl group and the variation of the ring-current effect (magnetic anisotropy) with the substituent. However, this possibility can be ruled out, since chemical shifts of methyl protons in *p*-substituted ethylbenzenes, of methylene protons (H_A and H_B) in *p*-substituted 5-phenylhexachlorobicyclo[2,2,1]heptenes (V)[7] and of *syn*-C-9 protons (H_S) in 6-substituted benzonorbornenes (VI)[8] do not show such a remarkable shift on substitution.† To account for the larger ρ_{anti} values‡ in systems such as (VI), Inamoto



(V)



(VI)

and his co-workers[8] concluded that hyperconjugation occurs through an interaction of the *p*-orbitals of the aromatic ring with the rear-side lobe of the sp^3 orbital of the C-9–H_{anti} bond.[9] An analogous argument may be used to interpret the present results. A simple analogy does not apply in this case, however, since this requires the proton *anti* to the lone pair [α-H in (III; *RR/SS*) and H_B in (I)] to be more sensitive to a substituent change.[4,5] This is probably because, in sulphur, the valence electrons occupy

† ρ Values in the Hammett relationship $\Delta\tau = \rho\sigma$ are 0·14, 0·13, and 0·12 p.p.m./σ for H_A, H_B of (V), and H_s of (VI), respectively.[8]

‡ 0·16 ~ 0·19 p.p.m./σ.

the third shell and can easily use *d*-orbitals (which is not so with carbon or oxygen), thus influencing the geometry of the system. We therefore conclude that an interaction of the π-orbital system in the aromatic ring occurs with the antibonding orbital of C–H through the agency of the lone pair and a *d*-orbital on the sulphur atom, where the steric requirement favours interaction with the proton *gauche* to the unshared pair and is unfavourable for the proton *anti* to it.§ The detailed mechanism of this stereospecific interaction, however, is not certain.

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§ The present result does not conflict with the previous finding[10] that H_B in (I) is exchanged more rapidly than H_A, since this concerns the relative stabilities of the excited states irrespective of the bonding structure in the ground state.

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