SOLVENT EFFECTS ON THE CIRCULAR DICHROISM OF α-CHLORO-SULPHOXIDES.

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Molecules having methylene groups between an asymmetric center and a chromophore often show chiroptical properties different from those of the corresponding molecules where the asymmetric center is directly bonded to the chromophore (1). The RD and CD curves of some benzyl alkyl sulphoxides have been shown to be strongly dependent on the polarity of the solvent (2,3). This characteristic is closely connected to the nature of the alkyl-group (2) and is also found in other sulphoxides structurally related to benzyl alkyl sulphoxides (4).

The CD spectrum of benzyl methyl sulphoxide (1) ($[\alpha]_D^{20}$ +96°, EtOH; −55°, CHCl$_3$) (5) (see Fig. 1) shows in ethanol two positive Cotton effects in the region from 300 to 200 mμ (2b): a weak band containing fine structure in the 250-270 mμ region, associated with the ^1L_b transition of the aromatic chromophore (6), and a more intense band at 223 mμ, which probably involves contributions from both the ^1L_a transition of aromatic compounds and the n-π* transition of the sulphoxide* (7). When isooctane is used as solvent, this last transition is split into its components, and inversion of all the three Cotton effects, ^1L_b at 250-270 mμ, ^1L_a at 220 mμ, n-π* at 233 mμ, is observed. The nature of this last transition at 233 mμ is displayed in the CD and UV spectra by the red shift characteristic of n-π* bands.

It has been reported (3) that steroidal benzyl sulphoxides show in ethanol positive Cotton effects in the region 229-236 mμ and negative Cotton effects centered below 220 mμ. However, when hexane was used as solvent red shifts in both Cotton effects were observed, indicating that the associated transitions were n-π* in type (3). No definite optical activity

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* Both contribution should be of the same sign, since it is well established that two overlapping Cotton effects of similar amplitude but with opposite sign produce a spectrum made up by two separate bands with maxima differing of about 30 mμ (8).

corresponding to aromatic transitions was observed in this case (3). These results show that the extrapolation of the chiroptical properties of certain kinds of benzylic systems is very uncertain.
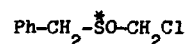
To gain further information about these systems we have now examined the solvent effect on the optical properties of α-chloro benzyl methyl sulphoxide (II) ($[α]_D^{20}$ -27,9, EtOH; +10,8, CHCl$_3$) and of benzyl chloromethyl sulphoxide (III) ($[α]_D^{20}$ +36, EtOH; -23, CHCl$_3$)[*], obtained by chlorination of (I) with iodobenzene dichloride (9).

$$Ph-CH_2-\overset{*}{S}O-CH_3 \qquad Ph-\overset{*}{C}HCl-SO-CH_3 \qquad Ph-CH_2-\overset{*}{S}O-CH_2Cl$$
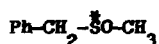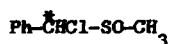
$$(I) \qquad\qquad (II) \qquad\qquad (III)$$

UV and CD spectra of (II) and (III) are reported in Fig. 2 and 3 respectively. Like the spectra of the parent compound (I), the spectra of α-chloro sulphoxides (II) and (III) exhibit two optically active transitions at 250-270 mμ both in ethanol and isooctane. These bands are probably still related to the ^1L_b and ^1L_a transitions of aromatic chromophore. A third Cotton effect is observed at 236-238 mμ in ethanol and at 243-246 mμ in isooctane. This Cotton effect, probably due to a n-π[*] transition of the S=O group, is strongly red--shifted (13-15 mμ) compared to the corresponding effect observed in benzyl methyl sulphoxide (I), and in both α-chlorosulphoxides does not change its sign in passing from ethanol to isooctane. Inversion is, on the contrary, observed for both (II) and (III) in the case of the ^1L_a transition at 220 mμ, and for sulphoxide (III) also in the case of the ^1L_b transition.

Benzyl alkyl sulphoxides and other similar benzylic compounds represent a very simple conformationally mobile system. Any change in the equilibrium position between the conformers may modify the chiroptical properties of these compounds. The inversion of sign of the Cotton effect corresponding to the ^1L_b aromatic transition which is observed in the CD spectra of benzyl methyl sulphoxide (I) but not in the spectra of benzyl t-butyl sulphoxide (2b) has been analyzed in terms of a conformational equilibrium change related to rotation around the benzyl-S bond (2b). The inversion of the ^1L_a Cotton effect has been attributed to a difference in asymmetric solvation of the aromatic chromophore and/or to variations in conformational equilibria associated with rotation around C-phenyl bond (2b). The constancy

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[*] The CD spectra reported in Fig. 2,3 correspond to α-chlorosulphoxides (II), (III) with the maximum of optical purity obtained. A study on the optical purity and the absolute configuration of (II) and (III) is in progress.

Fig. 1

Fig. 2

Fig. 3
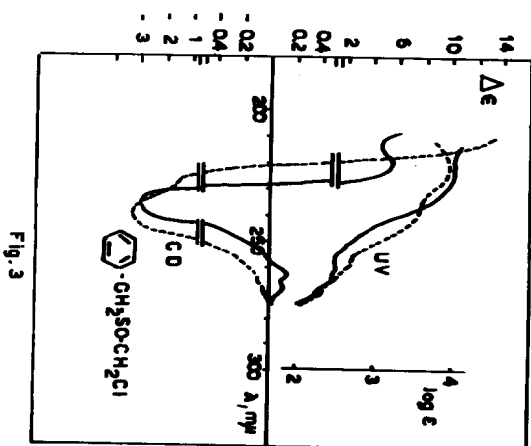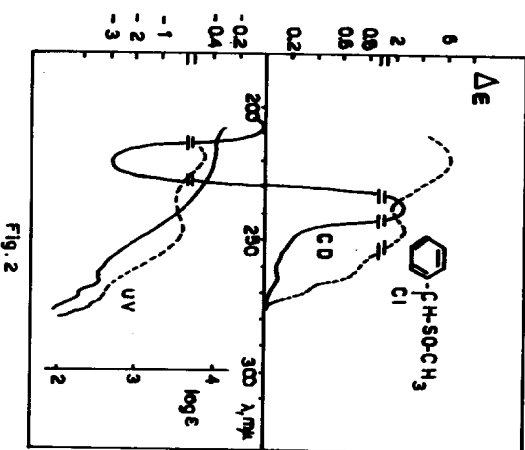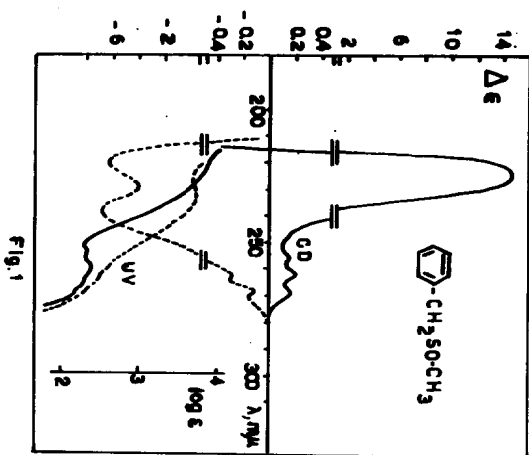
Captions of Figures

Fig. 1 – CD curves and ultraviolet spectra of benzyl methyl sulphoxide (I) in ethanol solution (——) and in isooctane solution (————).

Fig. 2 – CD curves and ultraviolet spectra of α-chloro benzyl methyl sulphoxide (II) in ethanol solution (——) and in isooctane solution (————).

Fig. 3 – CD curves and ultraviolet spectra of benzyl chloromethyl sulphoxide (III) in ethanol solution (——) and in isooctane solution (————).

of sign of the ^1L_b Cotton effect to changes of the solvent which is found in the CD spectra of compound (II) strongly suggest that rotation around the $C_{(halogenated)}$-S bond is noticeably restricted. The existence of a preferential conformation around this bond is confirmed by the PMR spectra in $CDCl_3$ of compound (III) which shows for the CH_2Cl group a quartet in the range 20-80°. The assignment of this quartet centered at 5.78 τ | J_{AB} | = 11 cps at 20° (TMS internal standard) to the CH_2Cl group and not to the benzylic protons which also are magnetically non equivalent has been made on the basis of the PMR spectrum in $CDCl_3$ of the dideutero derivative (IV) (9).

$$Ph-CD_2-SO-CH_2Cl$$
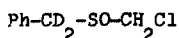
(IV)

Particular attention should be paid to the dramatic change in the spectra of chlorosulphoxide (II) and (III) compared to (I) for the n-π^* transition of the sulphoxide group.* This change indicates that the optical properties of the sulphinyl chromophore in (II) and (III) depend not only on conformational equilibria around the benzyl-S bond, but also on electronic effects due to the chlorine atom: these effects derive from the different polarity of the molecule and probably from the different solvation of the SO group. This suggests that also in simple benzylic derivatives such as (I) an important role is played by dipole-dipole interactions and by hydrogen bonds between the S=O group and the solvent molecules.

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* It should be noted that an α-halogen atom in acyclic ketones does not have a large effect on the carbonyl n-π^* transition. In cyclic ketones however, α-halogen atoms do influence this transition; the influence is greater for axial than for equatorial halogen (10).

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