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CIRCULAR DICHROISM OF CHIRAL EPISULPHOXIDES

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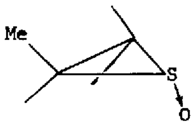
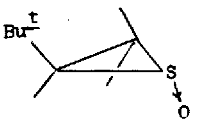
It is well known that the o.r.d. and c.d. tecniques can be used for configurational and conformational problems concerning trigonal-pyramidal tricoordinate sulphur compounds, especially of the sulphoxide family.[1] Nevertheless, until now the rules which seem to govern the chiroptical properties of such compounds are essentially of empirical origin. The reason for this may be ascribed to the lack of theoretical information about electronic transitions of the sulphoxide chromophore and of data on the u.v. and c.d. spectra of simple and conformationally rigid systems of known absolute configuration. In a previous study we carried out an investigation on the excited states of sulphoxides by recording and interpreting, by means of an ab-initio SCF calculation, the c.d. spectra of the simplest optically active sulphoxide with a fixed geometry, i.e. (S,S)-(+) trans-propylene episulphoxide (1).[2]

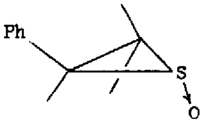
In order to obtain further insight into the influence of steric and electronic factors on the chiroptical properties of episulphoxides we recorded the u.v. and c.d. spectra of the compounds (2)-(4). The optically active derivatives were obtained by oxidation of the corresponding (S)-episulphides[3] with peroxybenzoic acid, following the procedure described by Kondo and Negishi.[4] The synthetic results and the n.m.r. spectra of episulphoxides were in close agreement with those reported in the literature:[4] therefore, following to the Japanese authors we assigne to our compounds the trans-configuration and the (S) absolute chirality at the asymmetric carbon atoms and at the asymmetric sulphur atoms of (1)-(4).[*]



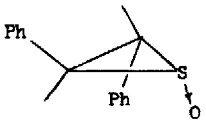
(+)-(1)



(+)-(2)



(+)-(3)



(-)-(4)

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[*] It should be noted that in the optically active trans-diphenyl episulphoxide (4) the sulphur atom is not asymmetric being linked to two carbon atoms of the same (S) configuration.

The absorption and circular dichroism spectra of the episulphoxides (1)-(4) were recorded in cyclohexane and absolute ethanol solutions; the spectra of the compounds (2)-(4) are reported in the Figures 1-3.

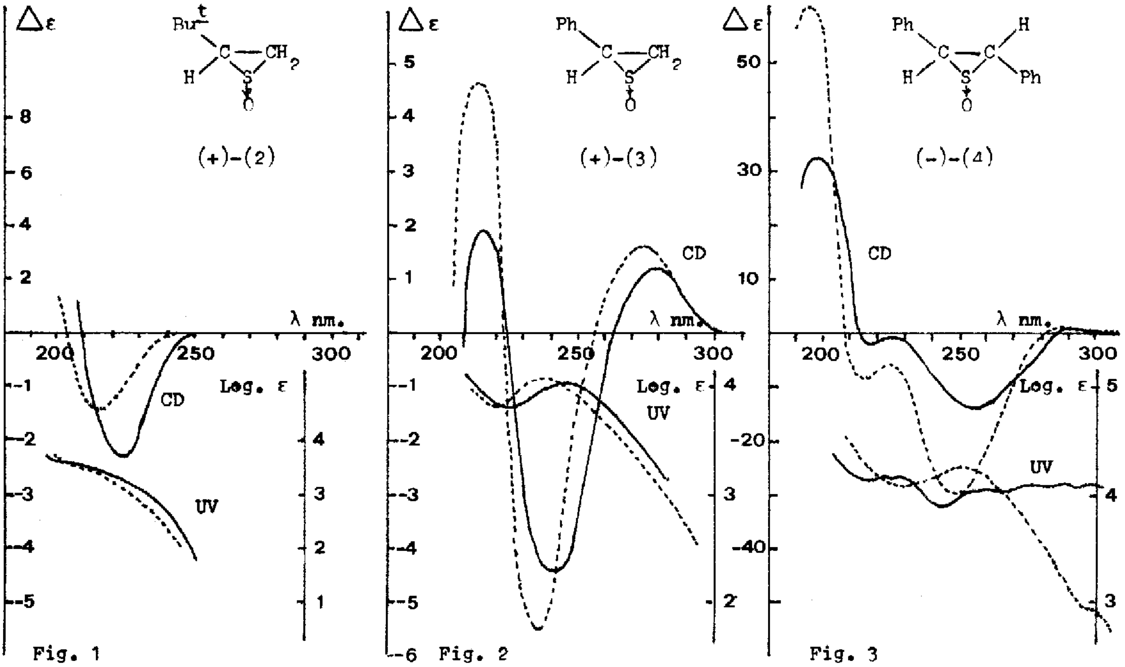

Fig. 1 Fig. 2 Fig. 3

Figures 1-3:UV and CD spectra of episulphoxides (2)-(4) in cyclohexane (——) and ethanol (-----)

The u.v. and c.d. spectra of the simplest chiral episulphoxide (1)^2 are very similar to those of optically active methyl-alkyl sulphoxides having (S) absolute configuration at Sulphur.^{5} In particular, corresponding to well defined maxima of the absorption spectra observed at 205 nm. in cyclohexane and 198 nm. in ethanol, the c.d. spectra of (1) show positive Cotton effects of relatively high optical activity, (R ca. 1x10^{-39} cgs.). On the contrary, quite surprisingly, the c.d. spectra of the t.-butyl derivative (2) show a negative transition which is considerably red-shifted (ca. 16-18 nm.) with respect to the maxima shown by (1) in both solvents used (Fig. 1). The corresponding absorption spectra of (2) exhibit a shoulder at 205 nm. in cyclohexane solution (Log. ε ca. 3.5) and no well-defined maxima or inflections in ethanol.

The u.v. spectra of (S,S) styrene episulphoxide (3) show only one intense maximum (Log. ε ca. 4.0-4.3) at 246 nm. in cyclohexane and 242 nm. in ethanol. On the contrary the c.d. spectra clearly reveal two positive Cotton effects at 276 and 216 nm. which are relatively solvent insensitive, and a stronger optically active negative transition centered at 243 nm. in cyclohexane and 236 nm. in ethanol (Fig. 2). The spectroscopic and optical properties of the (S,S) styrene episulphoxide closely resemble those of optically active (S) alkyl-aryl sulphoxides,[†] with the only exception of the first ^1L_b aromatic transition which is observed at 275 nm. and is positive in the cyclic compound (3) and negative in the acyclic ones.[7]

In compound (4) there is the further complication of the presence of the new phenyl group, therefore more complex spectra are observed. The more interesting feature of these spectra is represented by the strong negative and solvent dependent Cotton effect at 256-248 nm.

In our opinion the chiroptical properties of the compounds (1)-(4) at *ca.* 205, 223, 243, and 256 nm. (cyclohexane) respectively, are very probably dependent on the same electronic transition of the episulphoxide chromophore which is more or less red-shifted by effect of the substituents of the three membered ring.

MO-SCF calculations indicate that the first transition in (1) has a prevalent $\sigma \rightarrow \sigma^*$ character ($A'' \leftarrow A'$ in group C_s), with the σ molecular orbital strongly polarized towards the oxygen atom.[2] This electronic transition is electrically and magnetically allowed with the electric dipole moment μ polarized along the *z* axis of the ring and the magnetic dipole moment *m*, which has a prevalent one center component arising from the $p_z p_y$ transition density of the oxigen atom, oriented along the S→O bond, as depicted in the Figure 4-a.

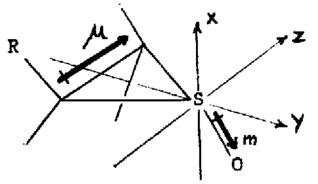

Fig. 4-a

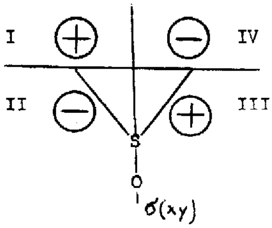

Fig. 4-b

The optical activity of the alkyl-episulphoxides could originate mainly from two mechanisms:[8]

i) The electric-electric dipole coupling of the substituents with the electric transition moment of the episulphoxide chromophore.

ii) The coupling of the substituent transition dipole moments with the magnetic moment of the episulphoxide.

In both cases the coupling energy is given by the interactions between the charge density of the $\sigma \rightarrow \sigma^*$ transition and the dipole induced in the polarizable perturber. The contributions given from mechanism *ii*) for *trans*-substituted episulphoxides are roughly depicted in the Figure 4-b. On the other hand it is difficult to give a sector-type picture of the contributions given by mechanism *i*).

[†] It is noteworthy that the spectra of the rigid sulphoxides (1)-(4) do not show the marked solvent dependence of the Cotton effects shown by alkyl-benzyl sulphoxides.[6]

Nevertheless, in our opinion, contributions in region II should be stronger than in I with both mechanisms i) and ii); therefore the sign inversion of the derivative (2) with respect to (1) is likely to be caused by the strong negative effect given by the methyl group of the *t*-butyl substituent lying in region II.

In phenyl-derivatives the shifts of both episulphoxide and benzene transitions indicate stronger interactions, probably of conjugative type. In this case mechanisms i) and ii) are likely to display smaller effects.

Dipole-dipole and electric-magnetic coupling calculations are in progress in order to put the contribution of the two mechanisms to the optical activity of these systems on a quantitative basis.

Acknowledgements.

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