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N-QUATERNARY COMPOUNDS—XXVI[1]

CD CURVES FOR SULPHOXIDES

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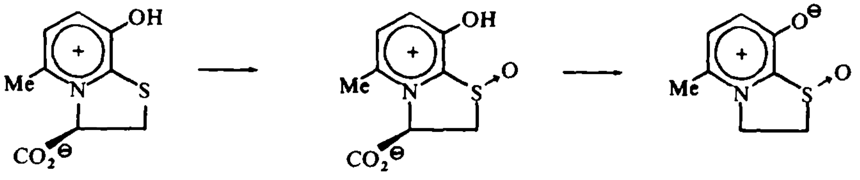
Abstract—The (1S)-sulphoxide from 5-methyldihydrothiazolo[3,2-a]pyridinium-8-oxide shows positive Cotton effects at 355 and 229 mμ in alkaline solution and at 315 and 223 mμ in acid solution. The sign of an intermediate band is pH dependent. The CD curves for (3R)-8-hydroxy-5-methyldihydro[3,2-a]pyridinium-3-carboxylate and a derived diastereomeric sulphoxide with absolute (1S,3R)-configurations are also discussed.

PERACID OXIDATION of sulphide I gives mainly the diastereoisomer sulphoxide II with the sulphinyl oxygen *cis* to the 3-carboxy group.[2,3] The sulphoxide II from the (3R)-sulphide therefore has the (1S,3R)-configuration. Decarboxylation leads to the sulphoxide (1S)-enantiomer (III).[2]



I II III

In alkyl aryl sulphoxides a relationship has been established between absolute chirality on sulphur and the sign of the relevant Cotton effect.[4] Pyridyl alkyl sulphoxides will also give rise to Cotton effects in polarized light. We therefore have recorded CD curves for the sulphoxides II and III. These substances have the properties of internal salts so the curves were recorded in 0·1 N HCl (Fig 1) and 0·1 N NaOH (Fig 2). For comparative purposes the CD curves for the sulphide are reproduced.[5]

From Fig 1 it is seen that in acid solution chirality at C-3 in I results in pyridyl absorption in polarized light with a negative maximum at 340 mμ correlating well with the UV band at 343 mμ. The 268 and 255 mμ optically active transitions are weak in the UV and not apparent from the UV spectrum. The strong positive CD maximum at 234 mμ corresponds well to the 238 mμ UV band. These absorption all arise from the pyridyl chromophore. The strong negative CD maximum at 219 mμ corresponds to the UV band at 213 mμ. It is probably caused by interaction between the pyridyl ring and the n → π* excitation of the carboxyl group.

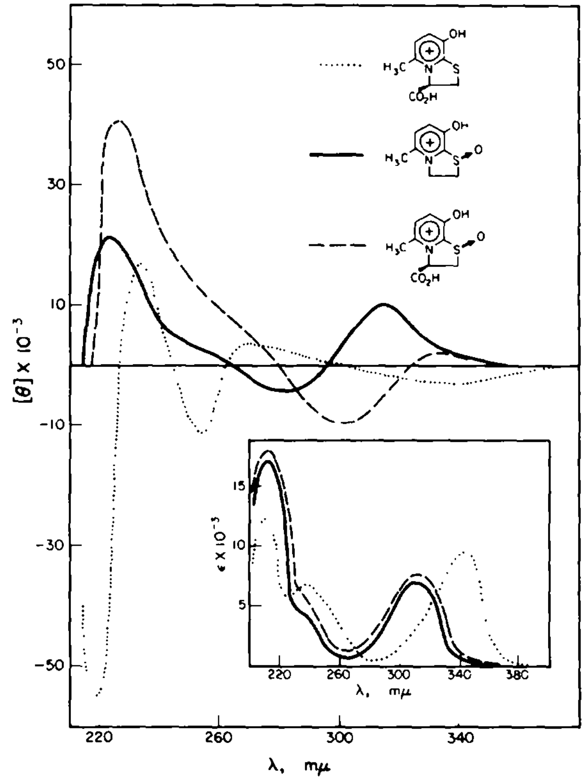


Fig 1. CD curves recorded in 0·1 N HCl

We then shall consider the sulphoxide enantiomer (III). The polarized light absorption in this molecule is caused by chirality at sulphur and arises as a result of perturbation from the sulphinyl chromophore on the substituted pyridyl system. The oxidation leads to a blue shift. A positive Cotton effect is observed at 315 mμ while the UV maximum is at 309 mμ. There is a negative CD maximum at 283 mμ not seen in the UV spectrum and a positive maximum at 223 mμ. The UV spectrum has a shoulder at 230 mμ and a maximum at 212 mμ.

For comparison simple alkyl aryl sulphoxides show an intense optically active band at 235–255 mμ. This transition is thought to arise from the interaction of the weak forbidden phenyl $\pi \rightarrow \pi^*$ (L_b) band with allowed sulphoxide $n \rightarrow \pi^*$ transitions.[4] Another Cotton effect of opposite sign occurs in the 220 mμ region.[4] In diaryl sulphoxides a red shift occurs especially in the presence of auxochromic groups such as in (—)-*p*-N,N-dimethylaminophenyl *p*-tolyl sulphoxide where the long wave band occurs at 293 mμ with Cotton effect at 298 mμ.[6] The above observations for the pyridyl chromophore with its auxochromic substituents is in keeping with this.

The CD curve for the diastereoisomeric sulphoxide (II) is caused by polarized absorption due to both chiral centres. The curve represents a modification arising by couplings between the chiral chromophores, and the final curve appears almost

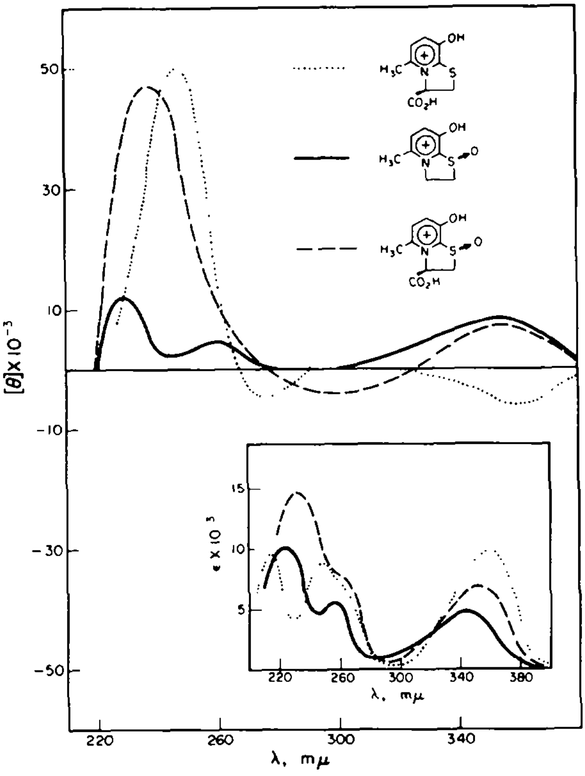


FIG 2. CD curves recorded in 0·1 N NaOH

additive of the two separate absorptions. Thus the curve displays a weak positive extremum at 333 mμ, a negative band at 300 mμ and a strong positive maximum at 227 mμ. The latter correlates with the UV absorption at 230 mμ while the strong long-wave is at 312 mμ and must obscure the weak transition resonsible for polarized light absorption at 333 mμ.

In alkaline solution the pyridyl ring is in the phenolate form as seen by a marked red shift (Fig 2). Polarized absorption of I occurs at 360 mμ (negative), 275 mμ (negative) and 247 mμ (strongly positive) with UV bands at 360, 248 and 214 mμ.

The CD curve for the sulphoxide enantiomer (III) exhibits three positive maxima. The long-wave band is at 355 mμ while the maximum of the absorption band in this region lies at 343 mμ. The polarized band at 260 mμ correlates with the UV absorption at 258 mμ. The next UV band is at 224 mμ with CD maximum at 229 mμ.

The diastereoisomeric sulphoxide (II) again has a CD curve resulting from interaction of both chiral chromophores. At high wavelength a positive Cotton effect is observed at 355 mμ. This could be interpreted as if the pyridyl sulphinyl chromophore is the stronger but could also be a net result of electronic interference between the chromophores. At low wavelength all maxima are positive and an increase in amplitude for II could perhaps be expected. The polarized absorption of II, however, was found to follow closely the strong absorption of the sulphide (I) in this region but with a maximum at 237 mμ which lies between that of the sulphide (247) and that of the sulphoxide (229).

A positive Cotton effect at higher wavelength and an opposite effect approximately equal in amplitude at shorter wavelengths have been reported to characterize the absolute (R)-configuration in alkyl aryl sulphoxides.[4] This is in contrast to the finding in the above series where the absolute (S)-configuration at sulphur in the cyclic sulphoxide (III) is associated with both long wavelength and short wavelength positive CD maxima in both acid and alkaline solution. The sign of the intermediate band is pH dependent.

EXPERIMENTAL

The CD measurements were made on a Cary model 60 spectropolarimeter in 0·1 N HCl aq and 0·1 NaOH aq at 27°, cell length 1 mm.

(3R)-8-*Hydroxy-5-methyldihydrothiazolo*[3,2-a]*pyridinium-3-carboxylate* (I)
$[\alpha]_D^{20} = -130°$ (*c* 0·6 in 0·1 N NaOH). CD in 0·1 N NaOH: *c* 0·43 g/l: $[\theta]_{390}$ −1·100, $[\theta]_{360}$ −5·800, $[\theta]_{320}$ 0, $[\theta]_{290}$ 0, $[\theta]_{275}$ −4·500, $[\theta]_{268}$ 0, $[\theta]_{247}$ +50·000, $[\theta]_{230}$ +15·000. CD in 0·1 N HCl: *c* 0·43 g/l: $[\theta]_{380}$ −800, $[\theta]_{340}$ −3·000, $[\theta]_{300}$ 0, $[\theta]_{268}$ +3·000, $[\theta]_{262}$ 0, $[\theta]_{255}$ −11·500, $[\theta]_{245}$ 0, $[\theta]_{234}$ +16·500, $[\theta]_{277}$ 0, $[\theta]_{219}$ −55·000, $[\theta]_{204}$ −13·500. UV in 0·1 N NaOH: 360 mμ (log ε 4·00), 248 (3·95), 215 (3·98). UV in 0·1 N Hcl: 343 mμ (log ε 3·98), 238 (3·81), 213 (4·10).

(1S,3R)-8-*Hydroxy-5-methyl-1-oxo-dihydrothiazolo*[3,2-a]*pyridinium-3-carboxylate* (II)
$[\alpha]_D^{20} = +169°$ (*c* 0·2 in water). CD in 0·1 N NaOH: *c* 0·45 g/l: $[\theta]_{380}$ +1·700, $[\theta]_{355}$ +7·000, $[\theta]_{325}$ 0, $[\theta]_{303}$ −4·000, $[\theta]_{277}$ 0, $[\theta]_{237}$ +47·000, $[\theta]_{215}$ −20·000. CD in 0·1 N HCl: *c* 0·45 g/l: $[\theta]_{340}$ +400, $[\theta]_{333}$ +1·500, $[\theta]_{324}$ 0, $[\theta]_{300}$ −9·500, $[\theta]_{280}$ 0, $[\theta]_{227}$ +40·500, $[\theta]_{215}$ +20·000. UV in 0·1 N NaOH: 352 mμ (log ε 3·85), 255 sh (3·91), 232 (4·18). UV in 0·1 N HCl: 312 mμ (log ε 4·00), 230 sh (3·85), 213 (4·25).

(1S)-8-*Hydroxy-5-methyl-1-oxo-dihydrothiazolo*[3,2-a]*pyridinium perchlorate* (III)
$[\alpha]_D^{20} = +260°$ (*c* 1·9 in H_2O). CD in 0·1 N NaOH: *c* 0·60 g/l: $[\theta]_{380}$ +1·600, $[\theta]_{355}$ +8·300, $[\theta]_{300}$ 0, $[\theta]_{260}$ +4·500, $[\theta]_{246}$ +1·900, $[\theta]_{229}$ +12·000, $[\theta]_{220}$ +3·000. CD in 0·1 N HCl: *c* 0·60 g/l: $[\theta]_{340}$ +1·300, $[\theta]_{315}$ +10·000, $[\theta]_{296}$ 0, $[\theta]_{283}$ −4·100, $[\theta]_{265}$ 0, $[\theta]_{223}$ +21·100, $[\theta]_{216}$ +15·800. UV in 0·1 N NaOH: 343 mμ (log ε 3·70), 258 (3·74), 224 (4·00). UV in 0·1 N HCl: 309 mμ (log ε 3·85), 230 sh (3·68), 212 (4·24).

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