Optically Active Absorption Bands in Open-chain Sulphides

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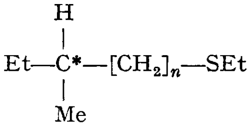
ALTHOUGH the u.v. absorption spectra of aliphatic sulphides have been extensively studied,[1] there is a lack of agreement on the number and position of their absorption bands. The o.r.d. spectra of some cyclic sulphides,[2] have been studied in detail, but despite the similar framework in the vicinity of sulphide chromophore, these cyclic compounds show a different number of optically active absorption bands.[2]

To clarify the problem we have studied the u.v., o.r.d., and c.d.† properties of some optically active sulphides with structure (I) and an *S* absolute configuration.‡



$$\mathrm{Et{-}\overset{\displaystyle H}{\underset{\displaystyle Me}{C^{*}}}{-}[CH_2]_{\mathit{n}}{-}SEt}$$

(I), $n = 0, 1, 2$

The u.v. spectrum in heptane solution of each of the compounds examined shows (Table) an absorption maximum at 198 mμ, which corresponds in the c.d. spectrum to a negative maximum at 201 mμ for (I; $n = 1$ or 2) and a shoulder at 193—197 mμ for (I; $n = 0$); the sign of the band corresponding to this shoulder, which is in the positive zone of the c.d. spectrum (Figure A), cannot be determined. The transition at 198 mμ therefore seems to be optically active in the sulphides (I; $n = 0$, 1, or 2).

The shoulder present in the u.v. spectrum for all cases between 208 and 212 mμ also corresponds to an optically active transition. In fact the c.d. spectrum of (I; $n = 0$) shows a negative maximum at 213 mμ and those of both (I; $n = 1$) and (I; $n = 2$) a negative shoulder between 206 and 210 mμ (Table and Figure A).

A second shoulder in the u.v. absorption spectrum is present at 225—232 mμ; the corresponding transition seems also to be optically active, the sign of the Cotton effect being positive in all three cases. In fact for (I; $n = 1$ or 2) a positive c.d. maximum at 229—230 mμ has been found and for (I; $n = 0$) we attribute the c.d. negative minimum at 227 mμ (Figure A) (between the low intensity negative c.d. maximum at 236 mμ and the high intensity negative c.d. maximum at 213 mμ) to a low intensity positive band corresponding to that found in the same region for (I; $n = 1$ or 2).

Finally we note in the u.v. spectrum a region of

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† The u.v. measurements were performed by Dr. E. Belgodere of the Institute of Organic Chemistry of Florence University with a Cary 14 spectrophotometer. The o.r.d. and c.d. measurements were made with a Cary 60 spectropolarimeter and a Roussel-Jouan Dichrograph II respectively.

‡ The samples of (I) were of comparable optical purity (>95%); the preparation, the purification, and the relationship between rotatory power and optical purity has been recently discussed (P. Salvadori, L. Lardicci, and M. Stagi, *Gazzetta*, in the press).

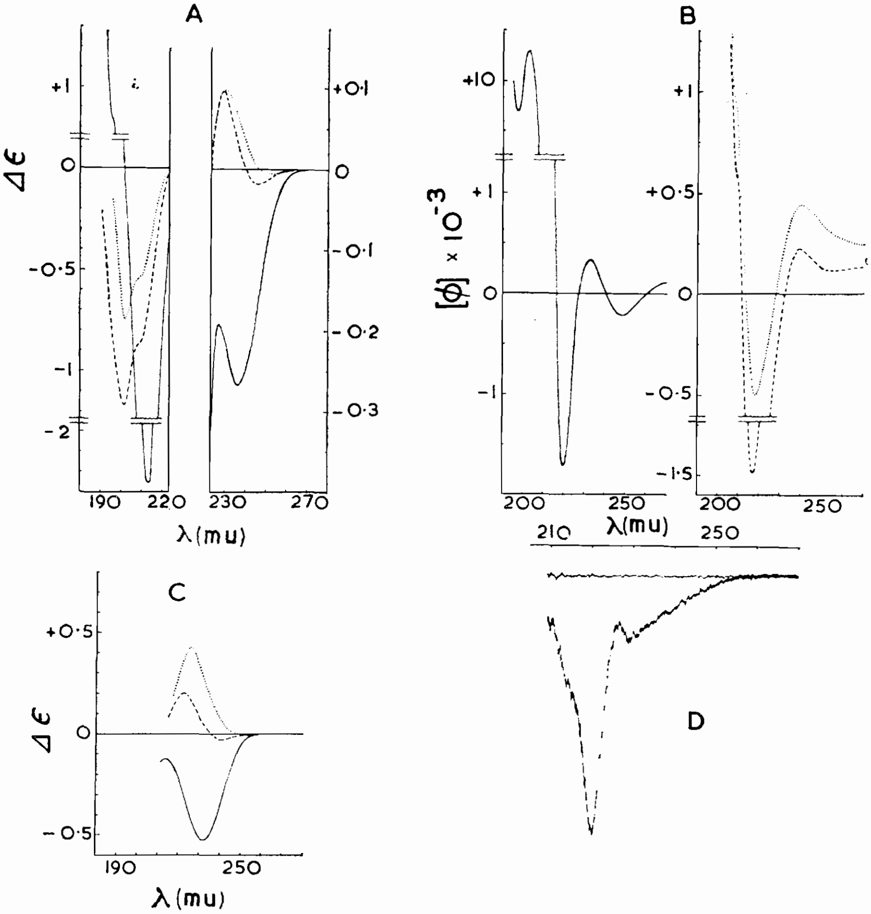


FIGURE. (I; $n = 0$) ———, (I; $n = 1$) -----, (I; $n = 2$) .....
(A) *C.d. curves in heptane solution at* 27°; (c 0·2—0·4 g. %).
(B) *O.r.d. curves in n-heptane solution at* 27°; (c 0·5—0·9 g. %).
(C) *C.d. curves in methylcyclohexane–isopentane* (1 : 3) *solution at* ca. −180°; (c 0·03—0·05 g. %).
(D) *C.d. curve of* (I; $n = 0$); *vapour phase in the presence of the liquid at* 27°.

weak absorption between 235—255 mμ to which corresponds a weak c.d. negative band (Table).

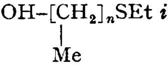
In view of its low intensity, the last band could be interpreted as follows: (*a*) an optically active electronic transition exists also in this region; (*b*) the band derives from the overlap of two preceding bands having opposite sign; (*c*) the band is a so-called "hot band";[3] (*d*) only one optically active transition exists in the range 227—251 mμ and the two c.d. bands in this region derive from conformational and/or solvation equilibria.[4]

Since, for the sulphides (I) the o.r.d. spectrum (Figure B) clearly shows a Cotton effect at almost the same wavelength as the c.d. maximum for the longest wavelength, hypothesis (*b*) seems therefore rather improbable.

Hypothesis (*c*) is also unlikely in view of the remarkable intensity increase in the c.d. band at the longest wavelength which is found on lowering the temperature to −180° for (I; $n = 0$ or 1) (Figure C). The apparent intensity decrease of the same band‡ for (I; $n = 2$) is probably due to the large intensity increase of the band at about 230 mμ which has the opposite sign (Figure A).

Furthermore the presence of both the last two bands in the c.d. vapour-phase spectrum (Figure D) and the intensity increase of both upon lowering the temperature (Figure C) rule out hypothesis (*d*).

‡ This band, which does not appear in Figure C, is still detectable at −180° by using rather concentrated solutions.



U.v. and c.d. characteristics of sulphides $EtOH\text{–}[\underset{\substack{|\\ Me}}{C}H_2]_nSEt$ *in heptane solution*

	Uv.		C.d.	
n	λ (mμ)	log ε	λ (mμ)	Δε
0	198m	3·45	197—193sh	(?)
	208—212sh	3·2	213m	−2·25
	225—232sh	2·1	227(m)	(+)
	235—255	⩽1·9	236m	−0·26
1	198m	3·43	201m	−1·16
	208—212sh	3·2	206—210sh	−0·9
	225—232sh	2·1	229m	+0·09
	235—255	⩽1·9	246m	−0·02
2	198m	3·48	201m	−0·74
	208—212sh	3·2	206—210sh	−0·5
	225—232sh	2·1	230m	+0·09
	235—255	⩽1·9	251m	−0·005

m = maximum; sh = shoulder.

At present the best way to interpret the c.d. band at the longest wavelength for the aliphatic sulphides is to admit, according to hypothesis (*a*) that an optically active transition is also present in the range 235—255 mμ (Table). In the o.r.d. spectrum down to 200 mμ (Figure B), two Cotton effects corresponding to the transitions at *ca.* 210 and 245 mμ are detectable.

Owing to overlap in the intermediate region, it is very difficult to determine if the positive o.r.d. extremum at 230—240 mμ and the negative one at 215—220 mμ correspond respectively to the peak and trough of the positive Cotton effect at 227—230 mμ, which is clearly shown in the c.d. spectra (Figure A).

In general the intensity of the c.d. bands decreases with increasing distance between the sulphur atom and the asymmetric carbon atom; the corresponding electronic transitions are influenced in different ways by the asymmetric field variations connected with the structure of the compounds. The shift towards the visible observed in c.d. bands at 227—230 and 236—246 mμ upon lowering the temperature shows that the hydrocarbon solvents cannot be considered "inert solvents" with respect to the sulphide chromophore, as has been observed for the carbonyl-chromophore.[4,5]

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