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O.R.D. OF SOME SATURATED ALIPHATIC ETHERS, SULFIDES AND OF THEIR COMPLEXES WITH Al($\underline{i}$.C_4H_9)$_3$.

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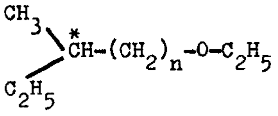
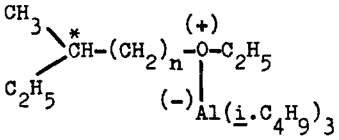
Investigating the O.R.D. of the dialkylethers I and of their complexes with Al($\underline{i}$.C_4H_9)$_3$, II, between 300 and 589 mμ, it was hypothesized (1) that for the compounds in which $n>0$ two of the chromophoric systems present in I gave contributions of opposite sense to the optical rotation. On the contrary, to explain the lower optical rotation of IIa with respect to Ia, it was admitted that in the compound Ia, contributions of the same sign to the optical rotation were given by the chromophoric systems influencing optical rotation between 300 and 589 mμ.

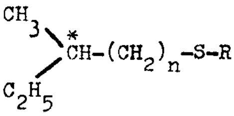


Ia n=0
Ib n=1
Ic n=2



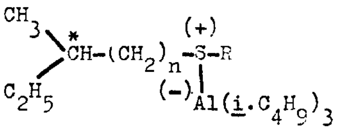
IIa n=0
IIb n=1
IIc n=2

We report now the results of a similar investigation of dialkylsulfides, III, and their complexes with Al($\underline{i}$.C_4H_9)$_3$, IV, as well as a reinvestigation of O.R.D. of ethers I, between 589 and 200 mμ (2) which show that the hypothesis we have proposed (1) for ethers



IIIa n=0, $R=C_2H_5$

IIIb n=1, $R=CH_3$



IVa n=0, $R=C_2H_5$

IVb n=1, $R=CH_3$

I having $n>0$ is valid also for the ether Ia (n=0) as well as for the dialkyl sulfides investigated.

IIIa was prepared from (R)-2-bromobutane both by reaction with thiourea and ethylbromide in alcaline solution (3) and through the (S)-*sec.*butylmercaptan (4) by reaction of the last compound with ethyl bromide in alcaline solution. In both cases ethyl-*sec.* butylsulfide was obtained, showing positive rotation at 589 mμ, to which (S) absolute configuration was assigned on the basis that no inversion of configuration should occur in the reaction between ethyl bromide and the (S)-*sec.*butylmercaptan ($[\alpha]_D^{25}$ + 18.13) (4).

The U.V. spectra in heptane of the sulfides IIIa and IIIb (5) show two shoulders respectively at about 235 mμ and at about 210 mμ in agreement with literature data for other aliphatic sulfides (6)(7)(8). The transition around 235 mμ is optically active as shown by O.R.D. curves (9) which show a negative Cotton effect in this region (Fig.1 and 2). The amplitude of the Cotton effect decreases by increasing the distance between the asymmetric carbon atom and the sulfur atom.

By complexing the sulfides with $Al(\underline{i}.C_4H_9)_3$ (10) the Cotton effect completely disappears in the region above 235 mμ (Fig. 1 and 2) as shown by the Drude plot of the complexes between 589 and 235 mμ. Correspondingly the molar rotatory power of the complexes

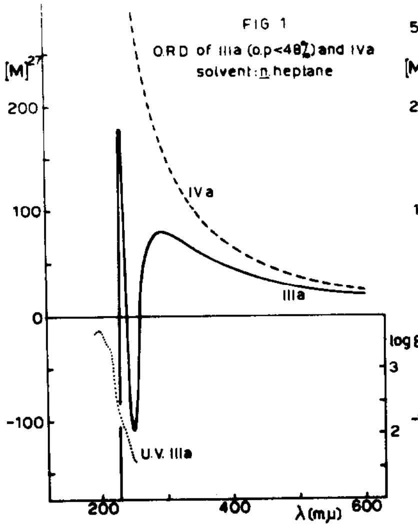


FIG 1

ORD of IIIa (o.p<48%) and IVa solvent: n.heptane

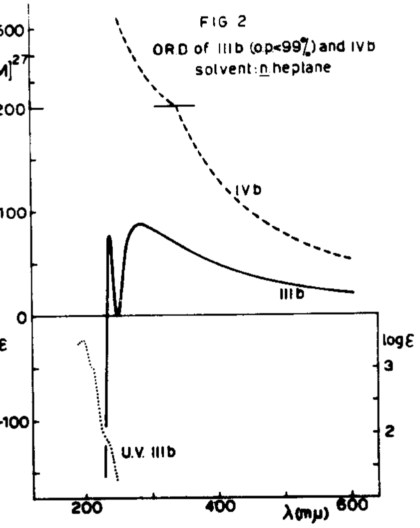


FIG 2

ORD of IIIb (o.p<99%) and IVb solvent: n.heptane

are higher than that of the sulfides.

TABLE I

$[M]_{589}$ of some ethers, sulfides and of their complexes with $Al(\underline{i}.C_4H_9)_3$

n=0	Ia, $+30.0^{(i)}$	IIa, $+25.2^{(i)}$	IIIa, $+19.7^{(ii)}$	IVa, $+26.0^{(ii)}$
n=1	Ib, $+0.8^{(i)}$	IIb, $+23.5^{(i)}$	IIIb, $+21.8^{(ii)}$	IVb, $+55.4^{(ii)}$
n=2	Ic, $+10.6^{(i)}$	IIc, $+18.4^{(i)}$		

(i) in isoctane; (ii) in n.heptane; optical purity of Ia, Ib and Ic respectively 80%, 98% and 96%; optical purity of IIIa and IIIb respectively $<$ 48% and $\leqslant$ 99%.

According to the above as well as to our previous results the behavior of the complex of Ia appeared anomalous; therefore we have reinvestigated the O.R.D. of Ia and, for sake of comparison, Ib and Ic extending the measurements down to 200 mμ (2) (Fig.3).

No further anomaly was noted in O.R.D. of Ib which shows only the already reported maximum at about 390 mμ; O.R.D. curve of Ic reaches a maximum at 226 mμ and then rapidly decreases as forseen in our previous paper. O.R.D. curve of Ia, contrarily to our pre vious hypothesis, shows a maximum at 237 mμ and the optical rotation becomes negative below 210 mμ hence showing a path similar to the O.R.D. curves of Ib, Ic, IIIa and IIIb (11).

The O.R.D. curve of IIa is simple down to 240 mμ following closely the one term Drude equation and crossing the O.R.D. curve of Ia at about 250 mμ (Fig.4).

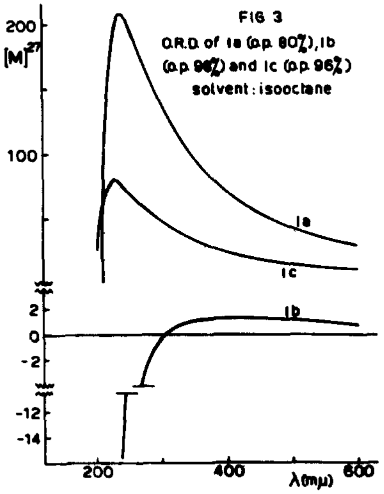


FIG 3

O.R.D. of Ia (o.p. 80%), Ib (o.p. 96%) and Ic (o.p. 96%)

solvent: isooctane

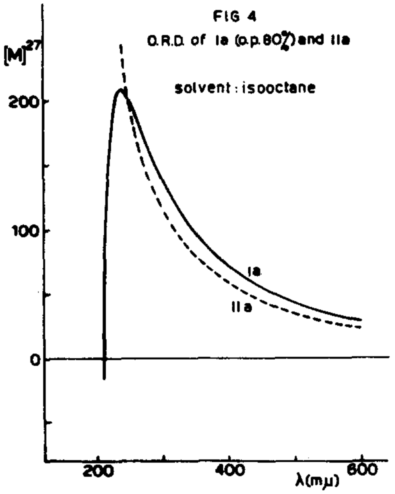


FIG 4

O.R.D. of Ia (o.p. 80%) and IIa

solvent: isooctane

According to the present results the following conclusions can be drawn:

1) - In the compounds I and III we have examined, the contribution to the rotation by the chromophoric systems at the longest wavelength, connected with the presence of the heteroatom, has negative sign when the asymmetric atom has (S) absolute configuration.

2) - Despite of the fact that the nature of the electronic transitions connected with the presence of the heteroatom in I and III is probably differnt (12), the contribution to the rotation above 230 mμ arising from the above transitions similarly disappears or at least strongly decreases by complexing the ethers and the sulfides with $Al(\underline{i}.C_4H_9)_3$.

3) - Contrarily to what has been hypothesized in a proceding paper (1), for what it concerns the already discussed contribution to the rotation by the different chromophoric systems, Ia has a behavior similar to that one of the other members of the series as well as IIIa.

4) - The differences between the rotatory power of ethers or thioethers and their complexes with Al(i.C_4H_9)$_3$, outside of the spectral range of the Cotton effects, cannot be used in all cases to establish the Cotton effect sign.

The lower optical activity of IIa with respect to that one of Ia in the range between 250 mμ and 600 mμ (Fig.4) can be possibly interpreted admitting that, in the complexation of sec.butylethyl-ether with Al(i.C_4H_9)$_3$, a very large change in optical rotation occurs due to changes in conformational equilibrium of the ether skeleton,which not only cancels the expected increase in optical rotation owing to changes in chromophoric systems due to complexation, but also makes the rotatory power of the complex lower than that one of the ether.

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9. For IIIa and IIIb, the existence of a Cotton effect was proved by C.D. measurements (Due respectively to the courtesy of Société Jouan, Paris and Japan Spectroscopic Co., Nippon Bunko); in fact the C.D. curves show a maximum at 237 mμ for IIIa and at 242 mμ for IIIb.

10. IVa and IVb had been distilled at 5 x 10^{-5} mm Hg, heating the distillation vessel respectively at 30° and 40°.

Analysis: IVa, Found: Al 8.48. $C_{18}H_{41}SAl$ requires, Al 8.52 %.
IVb, Found: Al 8.53. $C_{18}H_{41}SAl$ requires, Al 8.52 %.

11. O.R.D. curve of Ia (vapor phase) shows a negative Cotton effect between 185-190 mμ, practically corresponding to the maximum at the longest wavelength of the U.V. absorption of the ethers.

12. For the electronic transition responsible of the absorption at about 235 mμ in aliphatic sulfides see for instance: J.Sicé, *J.Phys.Chem.*, **64**, 1573 (1960); A.Balasubramanian, *Indian J.Chem.*, **1**, 415 (1963) [*C.A.*, **60**, 3622 (1964)]; L.B.Clark and W.T.Simpson, *J.Chem.Phys.*, **43**, 3666 (1965).
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