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THE OPTICAL ROTATORY DISPERSION OF SOME DIALKYL ETHERS CONTAINING A SECONDARY BUTYL GROUP.

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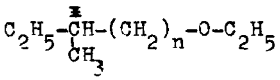
Although optically active aliphatic ethers containing a sec.butyl group are known since 1896 (1), no attempts have been made to relate the value of their specific rotation at different wavelengths, to their optical purity.

The O.R.D. of aliphatic ethers, systematically investigated in the case of a series of ethers of γ-nonanol (2) between 678 and 436 m/u, appears to be complex, the complexity being attributed to the presence in the ethers of two chromophoric systems (3).

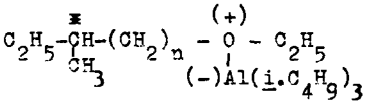
We have prepared the series of aliphatic ethers (I) and (II), having known optical purity (4), and we have investigated their optical rotatory dispersion.



$C_2H_5-\underset{CH_3}{\overset{*}{C}}H-(CH_2)_n-O-C_2H_5$

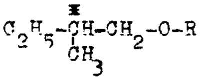
(I)

n=0,1,2



$C_2H_5-\underset{CH_3}{\overset{*}{C}}H-(CH_2)_n-\underset{(-)Al(\underline{i}.C_4H_9)_3}{\overset{(+)}{O}}-C_2H_5$

(III)



$C_2H_5-\underset{CH_3}{\overset{*}{C}}H-CH_2-O-R$

(II)

R= $-CH_3$, $-C_2H_5$, $-CH(CH_3)_2$, $-\underline{n}.C_4H_9$; $-CH_2-CH(CH_3)_2$, $-C(CH_3)_3$

The molar rotation, the relationship between absolute structure and sign of rotation at 589 $m\mu$ in the absence of solvents and the optical purity of the samples of ethers used are reported in Table 1.

TABLE 1

Molar rotation (at 589 $m\mu$) and optical purity of some optically active alkyl ethers.

Compound	$[M]_D^{25}$ (homog.)	Optical purity, %
(+)(S)-[*sec*.butyl]-ethyl-ether	+28.91°	80.0
(+)(S)-[2-methylbutyl]-methyl-ether	+ 0.65°	98.1
(+)(S)-[2-methylbutyl]-ethyl-ether	+ 1.16°	98.1
(+)(S)-[2-methylbutyl]-*i*.propyl-ether	+ 1.61°	98.1
(+)(S)-[2-methylbutyl]-*n*.butyl-ether	+ 1.76°	98.1
(+)(S)-[2-methylbutyl]-*i*.butyl-ether	+ 2.26°	97.9
(+)(S)-[2-methylbutyl]-*t*.butyl-ether	+ 0.23°	97.7
(+)(S)-[3-methylpentyl]-ethyl-ether	+10.57°	95.8

The data clearly show that the well known very low $[M]_D$ values of the [2-methylbutyl]-alkyl ethers (II) are not due to low optical purity of the samples (4b). Furthermore at 589 $m\mu$ the relationship between the sign of rotation, in the absence of solvents, and the absolute structure of the asymmetric carbon atom is the same as in the paraffins (5).

However the value of the optical rotation at 589 mμ for the ethers of series (I) is much higher than that of the corresponding paraffin when n=0, becomes lower for n=1 and reaches a value not very different from that of the corresponding paraff for n=2.

The O.R.D. curves of the ethers of the series (II), reported in Fig.1, show a maximum which is not due to a Cotton effect (6); according to earlier literature suggestions (3), these curves might be interpreted by assuming that in the compounds investigated are present two chromophoric systems giving opposite contributions to the rotatory power.

This interpretation seems to be confirmed by the remarkable difference between the O.R.D. curves of the series (I) ethers and the O.R.D. curves of the corresponding complexes (III) of these ethers with $Al(\underline{i}.C_4H_9)_3$, in which the electronic system of the ethereal oxygen is drastically changed by the presence of the $\overset{(+)}{>O} - \overset{(-)}{Al}<$ bond.

In fact the O.R.D. curves of type (III) complexes (Fig.2) follow very closely a one term Drude equation with the value of the constant λ. in the range of that one found for the paraffins. Therefore a strong decrease or a suppression of the contribution by the ethereal chromophoric system to the optical rotation due to the complexation, can reasonably be postulated.

On this basis we propose the following interpretation of the experimental facts we have observed:

1) - in the series (II) ethers, having absolute structure (S), the chromophoric system connected with the ethereal group gives a negative contribution to the rotatory power while the second chromophoric system, similar to that one of the paraffins, gives a positive contribution. As both the contributions are of the same order of magnitude at least between 600 mμ and 300 mμ, the molar rotatory power of the ethers are very small while the molar rotatory power of the complexes with $Al(\underline{i}.C_4H_9)_3$, in which the contribution by the oxygen atom is decreased, is much higher than that of the ethers.

2) - Admitting that the chromophoric system connected with the ethereal oxygen gives similar negative contributions in all the ethers of the series (II), the displacement of the O.R.D. curves maxima, by changing the structure of the not asymmetric alkyl group (Fig.1), might be due to the variation of the positive contribution to the rotatory power by the chromophoric system connected with the (S) alkyl group. Such a contribution can be evaluated from the rotation of the corresponding paraffins having a $>CH_2$ group in the place of the -O- group of the ethers(7).

3) - In [1-methylpropyl]-ethyl-ether (I, n=0) the two chromophoric systems give contributions of the same sign to the optical rotation. The molar rotatory power of the ether is therefore higher than that of the corresponding

paraffin (3-methyl-hexane [(8)]) but smaller than that one of the complex with $Al(\underline{i}.C_4H_9)_3$ (Fig.2).

4) - In the (S)[3-methylpentyl]-ethyl-ether (I, n=2) the contribution of the chromophoric system connected with the oxygen atom is negative but much smaller than that observed in the series (II) ethers according to the larger distance between the oxygen atom and the asymmetric carbon atom. Therefore the molar rotatory power of the ether is slightly lower than both those of the corresponding paraffin (3-methyl-octane [(8)]) and of the complex with $Al(\underline{i}.C_4H_9)_3$.

According to our hypothesis the large differences in molar rotations we observed in the ethers and in their complexes should be related much more to electronic factors than to different conformational equilibria.

Experiments are in progress to investigate if O.R.D. curves of ethers and of their complexes with Lewis acids can be used to determine the position of the asymmetric carbon atom with respect to the oxygen atom, not only in simple aliphatic ethers containing a sec.butyl group as shown by our data, but also in compounds of other series containing ether groups.

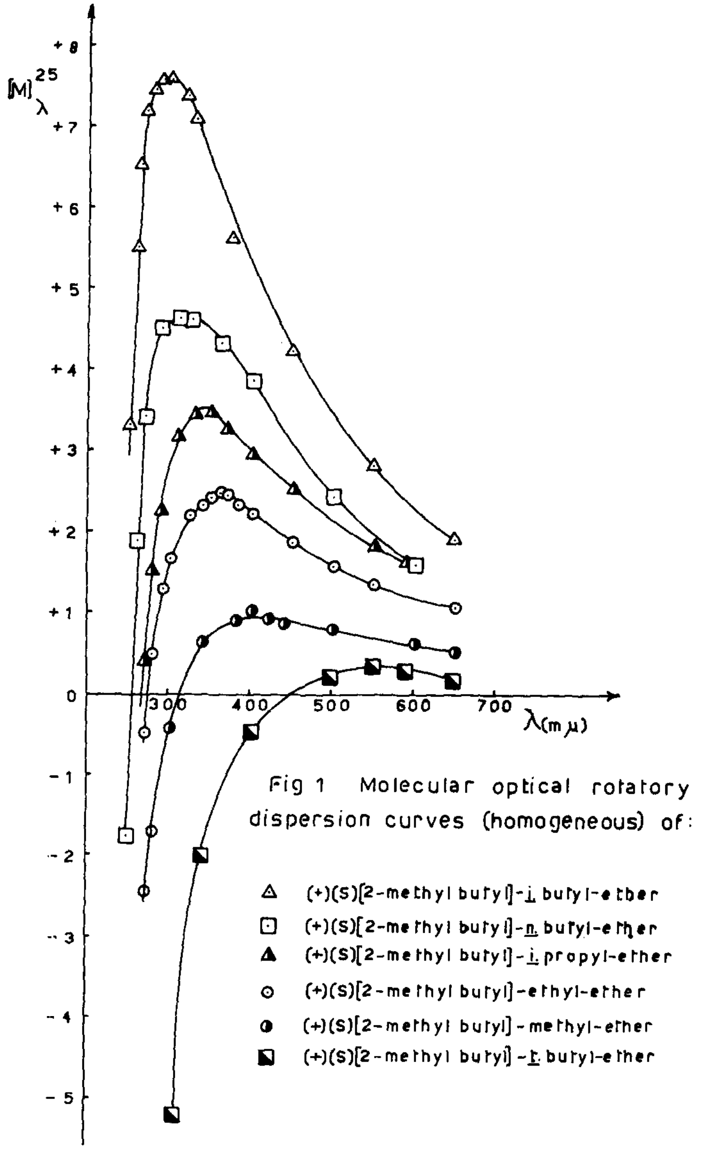


Fig 1 Molecular optical rotatory dispersion curves (homogeneous) of:

△ (+)(S)[2-methyl butyl]-i. butyl-ether
⊡ (+)(S)[2-methyl butyl]-n. butyl-ether
▲ (+)(S)[2-methyl butyl]-i. propyl-ether
⊙ (+)(S)[2-methyl butyl]-ethyl-ether
◐ (+)(S)[2-methyl butyl]-methyl-ether
◩ (+)(S)[2-methyl butyl]-t. butyl-ether

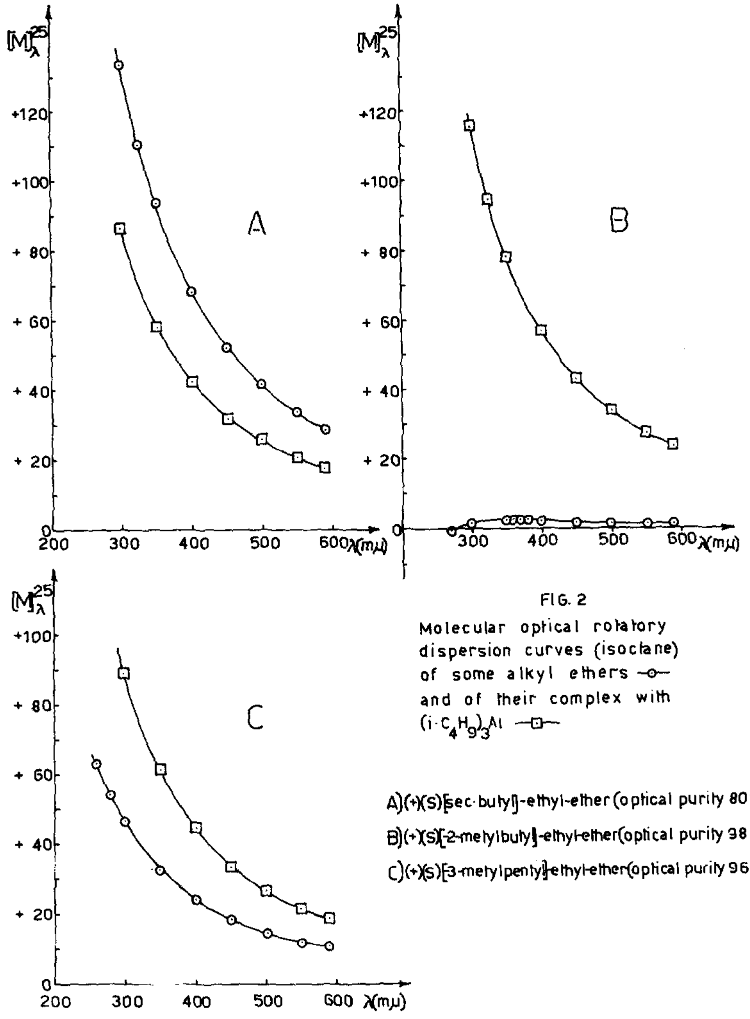


FIG. 2

Molecular optical rotatory dispersion curves (isoctane) of some alkyl ethers —○— and of their complex with $(i\text{-}C_4H_9)_3Al$ —□—

A)(+)(S)[sec-butyl]-ethyl-ether (optical purity 80%)

B)(+)(S)[2-metylbutyl]-ethyl-ether (optical purity 98%)

C)(+)(S)[3-metylpentyl]-ethyl-ether (optical purity 96%)

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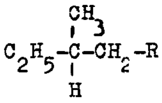
6. The circular dichroism curves between 220 mμ and 600 mμ show no maximum and no point of inflexion. We are grateful to the Société Jouan (Paris) for the Circular dichroism measurements.

7. It is interesting to note that in the series of (S) paraffins (IV), having the same structure of the series (I) and (II) ethers, the oxygen atom being substituted by a $-CH_2-$ group, the optical activity increases in the same order as in the ethers.



$C_2H_5-\overset{CH_3}{\underset{H}{C}}-CH_2-R$

R=	$[M]_D$
$-CH_2-CH_3$	+ 9.9°(a)
$-CH_2-CH_2-CH_3$	+ 11.4° (a)
$-CH_2-CH(CH_3)_2$	+ 11.9°(b)
$-CH_2(CH_2)_3-CH_3$	+ 13.7° + 14.0°(c)
$-CH_2-CH_2-CH(CH_3)_2$	+ 14.4°(d)

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