Circular Dichroism Spectra of Aliphatic Ethers

By Edward H. Sharman and Otto Schnepp
(*Department of Chemistry, University of Southern California, Los Angeles, California* 90007)
and Piero Salvadori, Carlo Bertucci, and Luciano Lardicci
(*Centro di Studio del C.N.R. per le Macromolecole Stereoordinate ed Otticamente Attive, Istituto di Chimica Organica, Facoltà di Scienze M.F.N., Università di Pisa, Italy*)

Summary The c.d. spectra of three chiral open-chain saturated ethers are described in the spectral region 140—200 nm.

We present here absorption and circular dichroism spectra of the three open chain saturated ethers (**1**)—(**3**)

$$(S)\text{—Et}\overset{*}{\text{C}}\text{HMe}[\text{CH}_2]_n\text{OEt}$$

(**1**), $n = 0$
(**2**), $n = 1$
(**3**), $n = 2$

in the vacuum u.v. region between 200 and 140 nm. The ethers (**1**)—(**3**) were obtained by catalytic hydrogenation (Raney Ni) of the corresponding vinyl ethers prepared as reported elsewhere.[1] The specific rotations and optical purities of the samples are listed in Table 1. The spectra in the vapour phase were studied with a vacuum u.v.–c.d. instrument which has been described previously,[2] and those in solution with a Jobin Yvon mark III dichrograph and with a Cary 14 spectrophotometer. The gas phase spectra were recorded at room temperature using sample cells of lengths 1 and 10 cm, and the pressures were in the range of 0·2—10 Torr. The solution spectra were studied using 1·0 and 0·1 mm sample cells with concentrations of *ca.* 5 g l^{-1} in n-heptane. The temperature range over which the solution spectra were studied was −80 °C to room temperature. The spectra are summarized in Table 2 where the peak frequencies and intensities are listed. In the Figure the absorption and c.d. spectra of (**1**) are shown in the gas and solution phases.

Table 1. Properties of ethers studied.

Compound	$[\alpha]_D^{25}$ (neat)/°	Optical purity	B.p./°C
(+)-(*S*)-(**1**)	+28·29	83%	80–81
(+)-(*S*)-(**2**)	+1·00	98%	109
(+)-(*S*)-(**3**)	+8·12	96%	137

TABLE 2. Summary of the absorption and c.d. spectra of the ethers studied in the vapour phase.

Ether	Absorption maxima cm^{-1}	ϵ_{max} l mol^{-1} cm^{-1}	C.d. maxima cm^{-1}	$\Delta\epsilon_{max}$ l mol^{-1} cm^{-1}	R[a] 10^{-40} e.s.u.	g[b] 10^{-3}
(**1**)	52,820	840	53,100	−6·1		
	53,570	860	53,730	−6·2	−8·0	−7·3
	58,240	2450	57,060	+5·6	+6·4	+1·3
			63,050	+2·3	+3·4	+0·9
(**2**)	53,100	1270	52,970	−0·16		
	54,060	1283	54,220	−0·16	−0·19	−0·11
	59,100	2040	58,700	−0·47	−0·36	−0·10
			63,300	+0·53	+0·69	+0·24
(**3**)	53,100	760				
	53,810	770	53,300	−1·3	−1·7	−1·6
	58,900	1630	57,900	−2·8		
			59,370	−2·8	−3·3	−1·2
			62,730	+2·3	+1·4	+1·5

[a] R = rotational strength (L. Velluz, M. Legrand, and M. Grosjean, 'Optical Circular Dichroism,' Academic Press, New York, 1965).
[b] $g = \Delta\epsilon/\epsilon$.

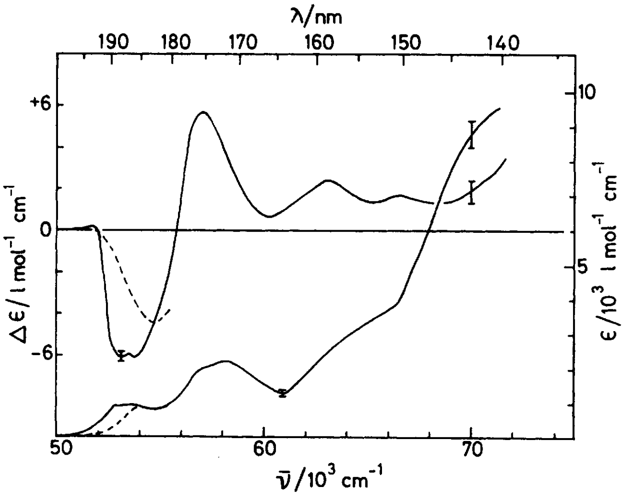

FIGURE. Hydrocarbon (n-heptane) solution (- - - - - - -) and vapour phase (———) absorption and c.d. spectra of (*S*)-*s*-butyl ethyl ether (**1**) at room temperature. C.d. resolution is 200—300 cm^{-1}.

The absorption spectra contain clear evidence of the first two transitions corresponding to the lowest energy c.d. bands but at higher frequency the absorption increases steeply and little structure is observed. The transitions in dimethyl ether corresponding to those observed here have been assigned,[3] in order of increasing energy, as $n_0 \rightarrow 3s$, $n_0 \rightarrow 3p$, and $n_0 \rightarrow 4s$ with the order of the last two remaining uncertain. Here, n_0 represents the non-bonding π orbital on the oxygen which is assumed to be the highest occupied orbital. However, Tsubomura and his co-workers have assigned[4] the lowest frequency transition of ethers as $n_0 \rightarrow \sigma^*_{CO}$.

The behaviour of both the c.d. and absorption spectra of (**1**) between 200 and 180 nm on either going from the vapour phase to a hydrocarbon solution (Figure) or decreasing the temperature, is consistent with Robin's assignment; in both cases a marked blue shift of the longest wavelength band is observed as expected for a Rydberg-type transition.[3]

This work was supported by a grant from the National Institutes of Health (at University of Southern California).

(*Received*, 1*st May* 1979; *Com.* 461.)

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