Far-u.v. Circular Dichroism Spectra of (*S*)-(+)-1,2,2-Trimethylpropyl Ethyl Ether: Solvent Effects

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Summary Circular dichroism spectra recorded far into the vacuum u.v. region for solutions of a simple ether demonstrate that the positions of the bands depend on the extent of hydrogen bonding with the solvent.

Recently two communications have appeared in the literature concerning the vacuum u.v. circular dichroism (c.d.) spectra of simple ethers in the vapour phase.[1,2] In the present paper we report solution phase c.d. spectra due to a single ether chromophore, measured far into the vacuum u.v. region. Fluorinated solvents[3] that are especially transparent were used to record the c.d. properties of the open-chain aliphatic ether (*S*)-1,2,2-trimethylpropyl ethyl ether (**1**) from 200 to 145 nm. The results demonstrate that the positions of the c.d. bands observed for carbohydrates in aqueous solution will vary with the extent of hydrogen bonding of the sugar chromophores with the solvent.[4]

$Bu^tCH(Me){-}OR$
(**1**) $R = Et$
(**2**) $R = {-}CH{=}CH_2$

Compound (**1**) was prepared from (*S*)-3,3-dimethylbutan-2-ol.[5] A sample of the alcohol with $[\alpha]_D^{25}$ + 7·82° (neat) and optical purity 96·5%, was converted into the (*S*)-1,2,2-trimethylpropyl vinyl ether (**2**) (40% yield) by a transvinylation reaction catalysed by mercury(II) acetate using 2-ethylhexyl vinyl ether as the vinylating agent.[6] A chemically pure sample of (**2**), obtained by preparative g.l.c., showed the following physical constants: b.p. 114 °C; n_D^{25} 1·4086; d_4^{25} 0·7788; $[\alpha]_D^{25}$ − 9·90° (neat). Catalytic hydrogenation of (**2**), at room temperature in the presence of the catalyst Adams Pt, gave (**1**) in quantitative yield with b.p. 115 °C, n_D^{25} 1·3911, d_4^{25} 0·7523, and $[\alpha]_D^{25}$ + 44·8°. Owing to the complete stereospecificity of the sequence adopted,[7] the optical purity of the ether (**1**) was assumed to be the same as that of the starting alcohol.

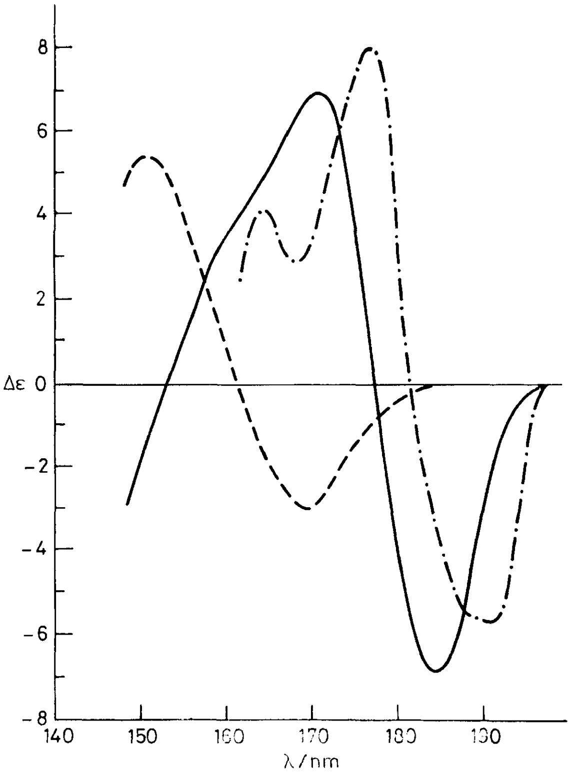

Figure. C.d. spectra of (*S*)-1,2,2-trimethylpropyl ethyl ether at 20 °C in the vapour phase (– · – · –), perfluorohexane solution (———), and in 1,1,1,3,3,3-hexafluoropropan-2-ol solution (– – –).

TABLE. C.d. characteristics of (*S*)-1,2,2-trimethylpropyl ethyl ether.[a]

	First band		Second band		Third band	
Solvent	λ_{max}/nm	$\Delta\epsilon_{max}$	λ_{max}/nm	$\Delta\epsilon_{max}$	λ_{max}/nm	$\Delta\epsilon_{max}$
Vapour phase	191 ~188 (sh)	−5·6 −5·6	177	+8·0	164	+4·1
n-Heptane	185	−7·4				
Perfluorohexane	185	−6·6	171	+6·7	~160 (sh)	+3·4
Trifluoroethanol	174	−2·8				
HFIP	170	−3·1	150	+5·4		

[a] Optical purity of the sample 96·5%; all the measurements were carried out at 20 °C. In all cases the total optical density of the cell, solvent, and sample was kept below 1·0 optical density units.

The c.d. spectrum of (**1**) in perfluorohexane solution (Figure) shows at least three bands with maxima at 185 and 171 nm, and a shoulder at 160 nm. A blue shift of the c.d. bands is observed for the protic solvent 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) so that only two bands at 170 and 150 nm are detectable. In contrast, all the c.d. bands of (**1**) are shifted to lower energies for the vapour phase. Here three well resolved bands are observed at 190, 177, and 164 nm.

The assignment of the two lower energy transitions of the simple ether chromophore[1,8] to Rydberg-type transitions from the highest energy nonbonding orbital on oxygen is consistent with the shifts in the c.d. spectra. Conclusive experimental evidence for the Rydberg character of the transition associated with the 190 nm c.d. band comes from the c.d. spectra of (**1**) in hydrocarbon solution at different temperatures. As expected,[9] a large blue shift was observed on lowering the temperature (+ 20 °C, λ_{max} 184 nm, $\Delta\epsilon_{max}$ − 7·4; − 40 °C, λ_{max} 181 nm, $\Delta\epsilon_{max}$ − 8·7; − 80 °C, $\lambda_{max} < 180$ nm, $\Delta\epsilon_{max}$ n.d.).

Furthermore, the intensities of the c.d. bands vary on changing the solvent, and the difference is larger on changing from aprotic solvents to the protic ones (Table). We can conclude that the nature of the solvent markedly affects the intensities and positions of the c.d. bands in question. This is reflected not only in the c.d., but also in the optical rotation of (**1**) at 589 nm: $[\alpha]_D^{20}$ + 42·8° (*c* 3·1, n-heptane) (1 dm cell) and $[\alpha]_D^{20}$ + 19·6° (*c* 2·9 g/dl, HFIP) (1 dm cell). No rationalization is possible at present since the contribution from other c.d. bands at the shorter wavelengths must be taken into consideration in order to understand the relationship between the c.d. bands and optical rotation in different solvents. However, it is clear that the differences in optical rotation with solvent observed for ethers,[10] polyethers,[11] and carbohydrates[4] are due to solvent interaction with the ether chromophores rather than conformational or structural changes.

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[1] E. H. Sharman, O. Schnepp, P. Salvadori, C. Bertucci, and L. Lardicci, *J. Chem. Soc., Chem. Commun.*, 1979, 1000.

[2] M. Levi, R. Arad-Yellin, B. S. Green, and A. Gedanken, *J. Chem. Soc., Chem. Commun.*, 1980, 847.

[3] M. Goodman and I. Rosen, *Biopolymers*, 1964, **2**, 537; H. R. Dickinson and W. C. Johnson, Jr., *Appl. Opt.*, 1971, **10**, 681.

[4] R. C. Nelson and W. C. Johnson, Jr., *J. Am. Chem. Soc.*, 1976, **98**, 4290 and 4296.

[5] P. Newman, P. Rutkin, and K. Mislow, *J. Am. Chem. Soc.*, 1958, **80**, 465.

[6] W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, 1957, **79**, 2828.

[7] P. Salvadori and L. Lardicci, *Gazz. Chim. Ital.*, 1964, **94**, 1205; E. Chiellini, *ibid.*, 1972, **102**, 830.

[8] M. B. Robin, 'Higher Excited States of Polyatomic Molecules,' Academic Press, New York, 1974, vol. 1, p. 265.

[9] A. F. Drake and S. F. Mason, *Tetrahedron*, 1977, **33**, 937.

[10] G. B. Consiglio, Tesi di laurea, Pisa, 1965.

[11] T. Harano, A. Sato, T. Tsuruta, and W. C. Johnson, Jr., *J. Polym. Sci., Polym. Phys. Ed.*, 1979, **17**, 1601.