Optical Rotary Dispersion and Circular Dichroism of *S*-4-Methylhexan-3-one

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WHILE the optically active absorption band associated with the $n \rightarrow \pi^*$ transition of the carbonyl chromophore has been extensively investigated in many compounds, little is known about the other electronic transitions of the carbonyl group.

We report results of u.v., o.r.d., and c.d. investigations† on *S*-4-methylhexan-3-one (I)‡ between 400 and 185 mμ. According to previous reports on aliphatic ketones,[1] the u.v. spectrum of (I), in n-heptane solutions, shows an absorption in the range 260—310 mμ (λ_{max} 285 mμ, ϵ_{max} 25·5) and a second absorption below 200 mμ (λ_{max} *ca.* 189 mμ, ϵ_{max} *ca.* 250). In the vapour phase, the latter absorption appears as a system of at least two bands with a maximum at *ca.* 193 mμ and a shoulder at *ca.* 196 mμ.

The o.r.d. of (I) shows a positive Cotton effect at 283 mμ in methanol solution, a multiple Cotton effect in the 300 mμ region in n-heptane solution (Figure 1), and a negative Cotton effect at 285 mμ in the vapour phase (Figure 2). Below 200 mμ, a second Cotton effect appears which is positive both in n-heptane solution and in the vapour phase (Figures 1, 2).

The c.d. of (I) correspondingly shows a positive band in methanol solution (λ_{max} 284 mμ, $\Delta\epsilon_{max}$ + 0·123), a weaker positive band with a well-resolved vibrational fine structure in n-heptane solution (λ_{max} 299 mμ, $\Delta\epsilon_{max}$ + 0·016) and a

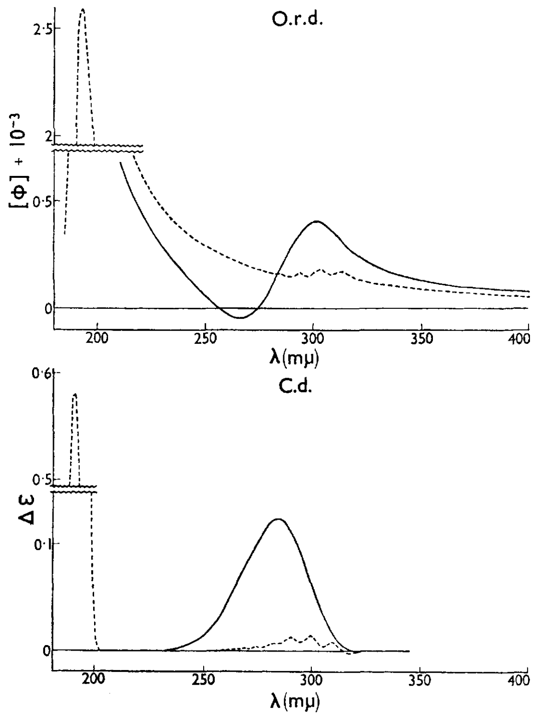

FIGURE 1. *O.r.d. and c.d. curves of S-4-methylhexan-3-one at room temperature in methanol (—) and in n-heptane solution (----).*

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† The u.v., o.r.d., and c.d. measurements were carried out using a Cary 14 spectrophotometer, a Cary 60 spectropolarimeter, and a Roussel-Jouan Dicrograph II, respectively.

‡ A sample of (I) (optical purity 81%) was prepared by the procedure of P. D. Bartlett and C. H. Stauffer (*J. Amer Chem. Soc.*, 1935, **57**, 2580).

negative band at 290 mμ in the vapour phase. Below 200 mμ, the c.d. curve shows a positive band in n-heptane (λ_{max} 190 mμ, $\Delta\epsilon_{max}$ + 0·60), while in the vapour phase it shows at least two bands at 193 and 197 mμ (see Figures 1 and 2).

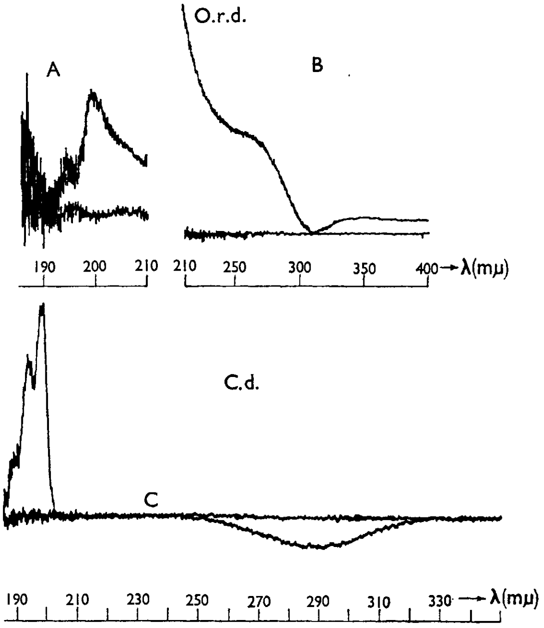

FIGURE 2. *O.r.d. and c.d. curves of* S-4-*methylhexan*-3-*one in the vapour phase at room temperature.*

(A) path length 5 cm., range 0·1°, in the absence of liquid phase;
(B) path length 10 cm., range 0·1°, in the presence of liquid phase;
(C) path length 5 cm., sensibility 1·10^{-5}, in the presence of liquid phase.

The c.d. of (I) at various temperatures, in hydrocarbon solution was investigated and shows that the sign of the band at about 290 mμ is inverted on lowering the temperature; at −180° the c.d. band has λ_{max} 288 mμ, $\Delta\epsilon_{max}$ −1·0.

The band system at about 190 mμ should have at least two optically active electronic transitions with rotational strength greater than that of the transition around 290 mμ. The position of this band system agrees well with that reported for the penultimate band in the u.v. spectrum of some ketones.[2]

The change of sign of the Cotton effect at *ca.* 290 mμ on going from the vapour phase to n-heptane solution at the same temperature (27°) shows that the rotational strength of the $n \rightarrow \pi^*$ transition is strongly dependent on intermolecular interactions. Therefore the change of magnitude and sign of the c.d. band at *ca.* 290 mμ, on change of temperature of the hydrocarbon solution of the ketone, cannot only be attributed to different positions of conformational equilibria at different temperatures.[3]

On changing from a hydrocarbon solution to the vapour phase at 27°, the sign of the c.d. band at *ca.* 290 mμ is inverted while the positive sign of the 190 mμ band is maintained. This shows that the two electronic transitions of the carbonyl chromophore investigated are affected, in different ways, by the asymmetric field variations, which are due to the difference of conformational equilibria and intermolecular interactions in n-heptane solution and in the vapour phase.

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[1] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules", Methuen, London, 1963, pp. 58, 158.

[2] J. S. Lake and A. J. Harrison, *J. Chem. Phys.*, 1959, **30**, 361; A. B. F. Duncan, *J. Chem. Phys.*, 1940, **8**, 444; H. Mohler, *Helv. Chim. Acta*, 1937, **20**, 285.

[3] A. Moscowitz in "Optical Rotatory Dispersion and Circular Dicroism in Organic Chemistry, ed. G. Snatzke, Heyden and Son, London, 1967, p. 329.