Vapour-phase Vacuum-ultraviolet Circular-dichroism Spectrum of (+)-3-Methylcyclopentanone

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WE report the first observations of circular dichroism in the vacuum u.v. (below *ca.* 50×10^3 cm.$^{-1}$). These measurements have been made on the vapour of (+)-3-methylcyclopentanone (purified by g.l.c.; its optical purity was acceptable by comparison with the results of Djerassi *et al.*,[1] using an instrument of special design which will be described later). Circularly polarized beams are received at separate photomultipliers, the outputs of which are compared using a d.c. bridge circuit. The c.d. and absorption spectra from 30×10^3 to 45×10^3 cm.$^{-1}$ were measured with a Durrum–Jasco ORD/CD/UV-5 instrument; absorption in the 45—60×10^3 cm.$^{-1}$ region was measured with a McPherson Model 225 spectrometer. A path length of 1 mm. was employed at 25° in all measurements; at this temperature the vapour pressure of (+)-3-methylcyclopentanone is 6·24 mm.

There are four distinguishable bands (or groups

of bands) in the absorption and c.d. spectra (Figure). The first, centred at about 33×10^3 cm.$^{-1}$, is the familiar n–π^* transition, weak in absorption but fairly strong in ellipticity. The second, near 52×10^3 cm.$^{-1}$, has been assigned to n–σ^* by McMurray[2] and to n'–π^* by Barnes and Simpson[3] in open-chain ketones. Earlier work on formaldehyde[4] and acetaldehyde[5] suggested that the second bands of these molecules were $n \rightarrow 3s$ Rydberg transitions; however, such excitations are normally absent in condensed phase spectra, whereas we have clearly observed this band in both c.d. and absorption spectra of (+)-3-methylcyclopentanone in cyclohexane solution. The third (56—58×10^3 cm.$^{-1}$) may be n–σ^*.[3] The fourth band (near 60×10^3 cm.$^{-1}$) may be the first vibronic component of the π–π^* band. The third and fourth bands show strong ellipticity of opposite sign.

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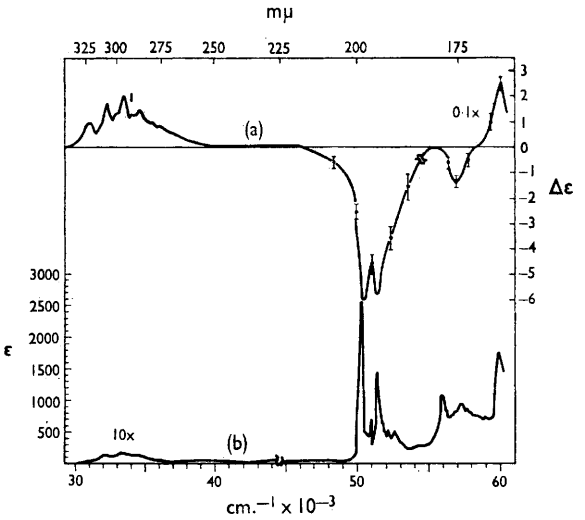

FIGURE. *Vapour absorption* (b) *and circular dichroism* (a) *spectra of* (+)-3-*methylcyclopentanone.*

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