The Magnetic Optical Activity of the $n \rightarrow \pi^*$ Carbonyl Transition

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THE theoretical expressions for the magnetic optical rotation (m.o.r.) and magnetic circular dichroism (m.c.d.) of an electronic transition each contain three terms, labelled *A*, *B*, and *C*, whose dispersion forms are shown in Ref. 1. The *A* and *C* terms originate in the first-order Zeeman splitting and are only present for degenerate transitions. The *B* terms arise from perturbation of the wave-functions by the magnetic field and exist for all transitions.

We present here the results of an investigation of the m.c.d. of the $n \rightarrow \pi^*$ transition in ketones. These are of current interest for two reasons. First, since the o.r.d. and c.d. of naturally optically-active ketones have provided so much valuable stereochemical information[2] it is worthwhile to investigate the possibility of parallel behaviour in m.o.r. and m.c.d. Second, Briat *et al.*[3] and Shashoua[4] have recently reported m.o.r. data for

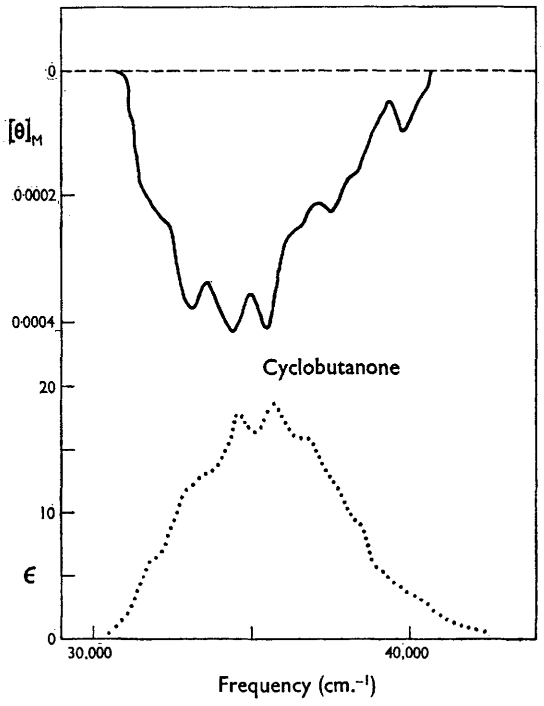

FIGURE 1. *Cyclobutanone.* $[\theta]_M$ *is the molar ellipticity per unit magnetic field;* ϵ *is the molar extinction coefficient.*

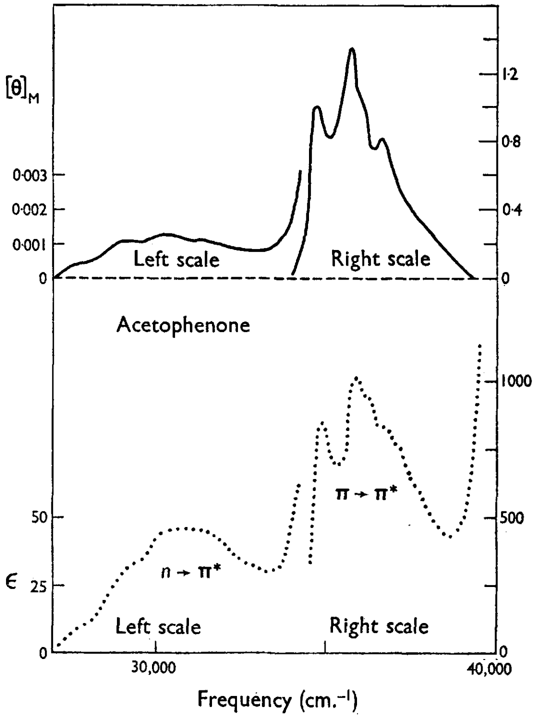

FIGURE 2. *Acetophenone.* $[\theta]_M$ *is the molar ellipticity per unit magnetic field;* ϵ *is the molar extinction coefficient.*

acetone, ethyl methyl ketone, methyl propyl ketone, isobutyl methyl ketone, and acetophenone, which appear to show *A* terms, particularly in the pure liquids. Only *B* terms are expected theoretically and attempts to explain the results have failed,[5] suggesting the possibility of error in the data.

We have examined the following compounds (all in n-heptane): acetone, ethyl methyl ketone, isopropyl methyl ketone, isobutyl methyl ketone, cyclobutanone, 2-bromocyclobutanone, cyclopentanone, cyclohexanone, 2- and 4-methylcyclohexanones, cyclododecanone, tetramethylcyclobutane-1,3-dione, isophorone, dicyclopropyl ketone, dicyclobutyl ketone, *cis*-2-decalone, norcamphor, acetophenone, *p*-methyl-, *p*-methoxy-, *p*-chloro-, and *p*-bromo-acetophenone, benzophenone, and the thioketone, thiobenzophenone. Only cyclobutanone, (Fig. 1), 2-bromocyclobutanone, and acetophenone (Fig. 2) show clearly measurable effects in a field of 44,000 gauss in the $n \rightarrow \pi^*$ region in the apparatus described elsewhere.[6] These m.c.d. effects are close to the limit of sensitivity of our apparatus and hence we estimate experimental uncertainties of about ± 25%. Similar effects were observed in several other compounds (2—3 times smaller than in cyclobutanone) but were too small to be reliably measured.

It is very difficult to draw conclusions concerning the variations of m.c.d. with stereochemistry, since the effects are so small. It is interesting that the cyclobutanones gave clearly measurable results, while other cyclic ketones did not. This might be related in some way to the planar conformation of the former.[7] However, it is clear that considerable improvements in experimental techniques will be necessary before substantial application of the m.c.d. of ketones to structural problems can be envisaged. It is also worth stressing that natural and magnetic optical activity are quite independent phenomena, and one cannot necessarily expect any great sensitivity of m.c.d. to stereochemical environment.

In no case is evidence found of a change of sign in $[\theta]_M$ in the absorption region, as would be expected from Briat *et al.* and Shashoua's results. Further, by assuming explicit expressions for m.o.r. and m.c.d. band shapes[8] the maximum variation of $[\theta]_M$ expected on the basis of the earlier work can be estimated. The results are shown in Table 1,

TABLE 1

Substance	Maximum variation of $[\theta]_M$ over $n \rightarrow \pi^*$ region		
	Present Work	Estimated† from Ref. 3	Estimated† from Ref. 4
Aliphatic ketones	$<2 \times 10^{-4}$	$1—2 \times 10^{-2}$	8×10^{-3}
Acetophenone	1×10^{-3}	2×10^{-2}	1×10^{-2}

† M.c.d. is estimated from measured m.o.r. assuming a damped oscillator band shape (ref. 8).

TABLE 2. *Faraday and absorption parameters*

Compound	B^a	D^b	$\frac{B}{D}$
Cyclobutanone	$1{\cdot}88 \times 10^{-6}$	$2{\cdot}75 \times 10^{-2}$	$6{\cdot}8 \times 10^{-5}$
2-Bromocyclobutanone	$1{\cdot}62 \times 10^{-5}$	$18{\cdot}3 \times 10^{-2}$	$8{\cdot}9 \times 10^{-5}$
Acetophenone	$-5{\cdot}06 \times 10^{-6}$	$6{\cdot}79 \times 10^{-2}$	$-7{\cdot}5 \times 10^{-5}$

[a] Approximate values determined from $\int \frac{[\theta]_M}{\nu} d\nu$ by numerical integration of experimental data—see Ref. 8. B is in units debye^2 Bohr magneton/cm.$^{-1}$ $[\theta]_M$ is the molar ellipticity per unit magnetic field defined as for natural optical activity (using the sign convention of natural optical activity).

[b] Determined from $\int \epsilon \, d\nu$ by numerical integration of experimental data. D is the dipole strength in debye^2.

together with our experimental findings. We are led to conclude that the data of Briat *et al.* and Shashoua are in error and that no discrepancy with theory exists. The only alternative is that background contributions from higher-energy transitions are interfering in the m.o.r., but these would be expected to be monotonic.

In Table 2, the Faraday parameter B (measuring the magnitude of the m.c.d.) and the dipole strength D (both defined in ref. 8) for the cyclobutanones and acetophenone are tabulated. It is interesting that the ratio B/D for the cyclobutanones is about the same, even though B and D individually vary considerably. The other noteworthy result is the change in sign of the m.c.d. (and B) caused by an adjacent benzene ring. This is probably due to contributions from low-lying $\pi \rightarrow \pi^*$ excited states. It is curious, however, that no observable effect was obtained in benzophenone.

We have also studied the m.c.d. of the $\pi \rightarrow \pi^*$ transitions in the substituted acetophenones, substantial B terms being observed in all cases.

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