The Magnetic Circular Dichroism of Carbonyl Compounds[1]

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Summary The magnetic circular dichroism (m.c.d.) of a number of carbonyl compounds has been measured.

SINCE the carbonyl chromophore has played such an important role in the development of organic chemical applications[2] of optical rotatory dispersion and optical circular dichroism, several attempts have been made to measure the magnetic rotatory dispersion and magnetic circular dichroism (m.c.d.) of optically inactive ketones.[3] However because of the low intensity of the effect and instrumental

difficulties[4] until now only three ketones (cyclobutanone, 2-bromocyclobutanone and acetophenone) were reported to show a measurable m.c.d. Cotton effect whereas other aliphatic and alicyclic ketones gave effects too small to be distinguished from the noise level.

Improvement of the sensitivity of a Durrum-JASCO spectropolarimeter equipped with a 49·5 kG superconducting magnet made it possible for the first time to obtain reliable m.c.d. curves for every carbonyl compound examined by us. Some typical examples are listed in Table 1 and depicted in Figure 1. The common features of the observed m.c.d. curves can be summarized as follows:

(1) The m.c.d. Cotton effect corresponding to the n–π^* transition of the carbonyl group is of very low intensity ($[\theta]_M$ = 4—60 × 10^{-5} deg.mol^{-1}cm.^{2} gauss^{-1}). (2) The wavelength position of the m.c.d. maximum usually does not coincide with the maximum of the u.v. absorption band (see Table 1) and is frequently shifted by 2—16 nm to lower wavelength. (3) In several cases (see 2, 3, 7, 8, and 9 in the Table) two Cotton effects of opposite sign were observed in the carbonyl region. This, and the almost ideal *S*-shape of the m.c.d. curve of cyclohexanone (Figure) might be attributed to an m.c.d. A-term.[5] However the dissymmetric intensity distributions in several compounds (*e.g.* 2, 3, and 9 in the Table) are better accommodated by describing them as two B-terms, which correspond to the theoretical prediction.[6] O.r.d. and c.d. spectra are often very sensitive to solvational equilibria, whose existence is indicated by the appearance of two bands of opposite sign undergoing drastic intensity variations with changes in solvent polarity.[7] This explanation cannot be applied to the reported m.c.d. abnormality, since the m.c.d. spectra are rather insensitive (Table) to solvent changes (and even to concentration effects as shown for No. 7 in Table 1). (4) Most significantly, the strength, sign and, when two bands have been observed, their relative intensities are highly dependent on the structure of the compound.

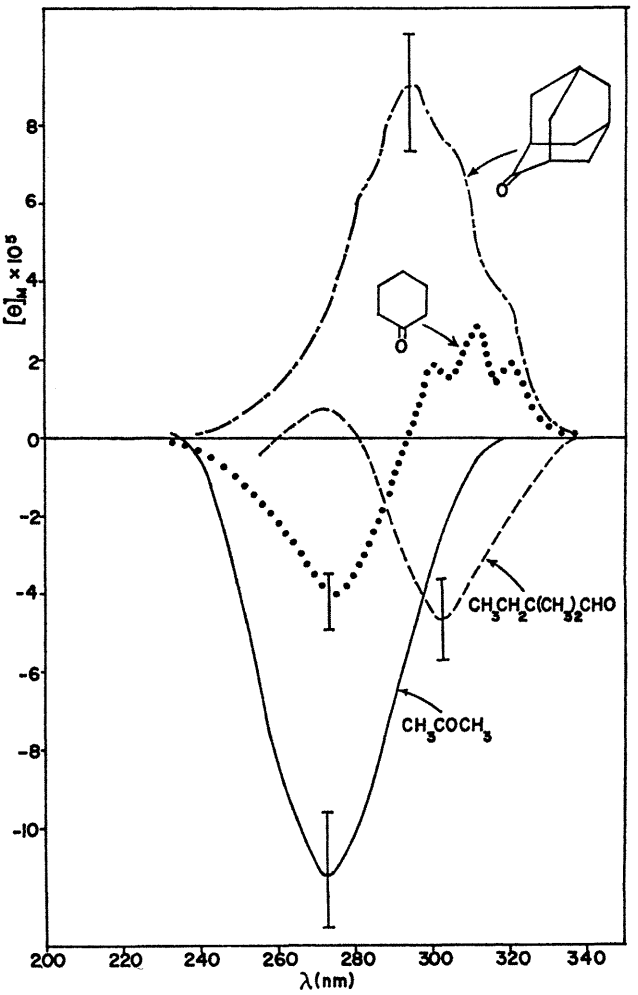

FIGURE. Magnetic circular dichroism curves of acetone (———), cyclohexanone (• • • •), adamantanone (— — — —) and 2,2-, dimethylbutyraldehyde (– – – –) in cyclohexane. The vertical bar indicates the signal-to-noise ratio.

Magnetic circular dichroism data[a] (20°) *of various carbonyl compounds*

	Compound	Solvent[a]	Absorption λ, nm (ε)	M.c.d., λ, nm ($[\theta]_M \times 10^5$)[b]		
1.	Butan-2-one	Cyclohexane	279 (16)		275 (−12)	
		Methanol	272 (17)		263 (−9)	
2.	3-Methyl-butan-2-one	Cyclohexane	284 (20)	263 (−4)		300 (+2)
3.	3,3-Dimethylbutan-2-one	Cyclohexane	287 (21)	259 (−2)		297 (+9)
		Methanol	282 (24)	250 (−5)		292 (+10)
4.	Cyclopentanone	Cyclohexane	300 (15·5)		289 (−19)	
		Methanol	286 (18)		285 (−16)	
5.	2-Chlorocyclopentanone	Cyclohexane	305 (36)		305 (−56)	
		Methanol	302 (31)		300 (−62)	
6	Norbornanone	Cyclohexane	294 (23)		278 (−4)	
7	Cyclohexanone	Neat	288 (16)	277 (−4)		309 (+2)
		Methanol	281 (15)	270 (−6)		309 (+2)
		Cyclohexane (2 molar)	289 (15)	275 (−4)		312 (+3)
		Cyclohexane (0·2 molar)	289 (15)	274 (−3)		309 (+3)
8.	2-Methylcyclohexanone	Cyclohexane	288 (18)	275 (−3)		314 (+3)
		Methanol	284 (19)	273 (−5)		305 (+3)
9.	4-t-Butyl-cyclohexanone	Cyclohexane	290 (18)	270 (−1)		304 (+4)
10.	2-Chlorocyclohexanone	Cyclohexane	304 (35)		310 (−41)	
11.	Cyclononanone	Cyclohexane	293 (14)		289 (−5)	
		Methanol	285 (17)		275 (−4)	
12.	2-Methylbutyraldehyde	Cyclohexane	295 (24)		302 (−22)	
13.	2-Cyclohexenone	Cyclohexane	334 (27)	298 (−48)		358 (+39)
		Methanol	317 (34)	295 (−51)		338 (+40)

[a] 0·5–2 M solutions; [b] M.c.d. $[\theta]_M$ values are expressed in deg.mol.$^{-1}$cm.^{2} gauss^{-1}.

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