Correlation between the Signs of Magnetic Circular Dichroism Bands and Structure in Carbonyl Compounds

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Summary Empirical rules for rationalization of the signs of m.c.d. bands of carbonyl compounds are presented.

THE magnetic circular dichroism spectra of a number of aliphatic ketones have recently been shown to be sensitive to the structural environment around the carbonyl group.[1] At a wavelength characteristic of the lowest energy isotropic transition ketones exhibited a single positive or negative m.c.d. band or an S-shaped curve with the positive component at longer wavelength,† and, whilst the effect of the molecular environment was discussed, no comprehensive rationale was proposed.[1]

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† With the exception of 1,1,1-trichloropropan-2-one.

We have now derived an empirical correlation between the sign(s) of the m.c.d. band(s) and the molecular structure in terms of the effect of substituents on the α and α' 'axial' σ-bonds, based on data now available. (Our conclusions are based on results in cyclohexane solution in order to avoid complications from solvent effects.)

The carbonyl group will have, at any one time, four bonds (C–H, C–Cl or C–C) in conformations (A), (B), or (C), such that these bonds overlap with the π-orbital of the carbonyl group. We take it as axiomatic that the sign of the m.c.d. band will be governed by the ground-state conformation of least energy. We conclude that the sign of the m.c.d. band is specifically determined by the substituents on these four bonds in this conformation.

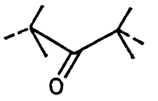
If, in the conformation of least energy, all four of the 'axial' bonds are C–H bonds, a single negative m.c.d. band is observed [*e.g.* ketones (**1**)—(**5**), (**19**), and (**20**) (Table, numbering of ketones follows ref. 1)]. If one of these bonds is a C–Me bond, however, a second, positive m.c.d. band is observed at longer wavelength in addition to the negative band [*e.g.* ketones (**6**), (**8**), (**11**), and (**12**)]. Further substitution by methyl groups on the α-carbon atoms leads to an increase in the strength of the positive band, and, with three or four 'axial' bonds bearing a methyl group, to the disappearance of the negative band, *e.g.* ketones (**14**) and (**15**). Substitution of the β-carbon of an 'axial' group decreases the positive contribution of the C_α bond in question. Thus, whilst C_α–CH_2–C and C_α–CH–C_2 bonds give rise to weak positive m.c.d. bands [*e.g.* ketone (**21**)], a C_α–C–C_3 bond contributes to the negative m.c.d. band. Hence 3,3,5,5-tetramethylcyclohexanone (**45**) exhibits only a negative m.c.d. band. In the Table are given the predicted sign(s) of the m.c.d. band(s), based on our conclusions, for the first twenty ketones from reference 1 (although our conclusions apply equally to the rest of the data), together with the observed sign(s). There are a few apparent exceptions, namely ketones (**9**), (**10**), (**34**) (3-methylcyclohexanone) and (**37**) (2-t-butylcyclohexanone) which we would expect to exhibit a weak positive component on the long wavelength side which has not yet been observed. No ketones exhibit two m.c.d. bands when one is expected from our conclusions.

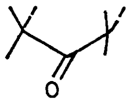
TABLE

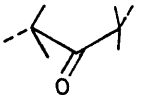
Predicted and observed sign(*s*) *of m.c.d. band*(*s*) *of ketones*

Ketone[a]		Sign(s)[b] of m.c.d. band(s) Predicted	Observed
(**1**)	Me_2CO	–	–
(**2**)	Me·CO·Et	–	–
(**3**)	Me·CO·Pr^n	–	–
(**4**)	Et·CO·Bu^n	–	–
(**5**)	$Pr^n{}_2CO$	–	–
(**6**)	Me·CO·Pr^i	– +	– +
(**7**)	Me·CO·Pr^c	– +	– +
(**8**)	Pr^i·CO·Et	– +	– +
(**9**)	Me·CO·Bu^s	– +	–
(**10**)	Me·CO·CH(Me)Pr^n	– +	–
(**11**)	Me·CO·Bu^t	– +	– +
(**12**)	$Pr^i{}_2CO$	– +	– +
(**13**)	$Pr^c{}_2CO$	– +	– +
(**14**)	Bu^t·CO·Pr^i	+	+
(**15**)	$Bu^t{}_2CO$	+	+
(**19**)	Cyclobutanone	–	–
(**20**)	Cyclopentanone	–	–
(**21**)	Cyclohexanone	– +	– +
(**22**)	Cycloheptanone	–(+)	– +
(**23**)	Cyclo-octanone	–	–

[a] Pr^c = cyclopropyl. [b] Signs refer only to the convention previously adopted.[10]


(A)


(B)


(C)

Thus, we conclude that the various C_α 'axial' bonds, in conformations (A), (B), and (C) may be graded according to their contribution to the m.c.d. curve. C_α-H, C_α–C–C_3 (and C_α–Cl) bonds contribute to the negative m.c.d. band, whereas C_α–Me, and, to a lesser extent, C_α–CH–C and C_α-CH–C_2 bonds contribute to the positive m.c.d. band (C_α bonds in the plane of the carbonyl group do not contribute). This behaviour may be rationalized on the basis of Kosower's discussion[2] of vibrational coupling.[3] All four 'axial' σ-bonds contribute to the vibrational levels of the excited state but not equally to all vibrational levels. Those bands that contribute most to the lowest energy levels will be those with lowest lying σ^*-orbitals whilst higher vibrational levels will have larger contributions from bonds with higher lying σ^*-orbitals. Thus the different bond contributions may lead to separate m.c.d. bands of opposite sign.[2] More simply S shaped curves may result from the red shift in the n–π^* transition produced by all C_α–C bonds.[1]

Our analysis shows that the optical properties of the ketones depend on σ- and σ^*-levels of the α 'axial' bonds[4] (also the n-orbitals in the case of chlorine), *i.e.* on the relative electron-accepting or -donating properties of the σ-bonds.[5] A similar treatment has been applied to the rationalization of the natural c.d. of α,β-unsaturated ketones,[6,7] dienes,[8] and olefins.[9]

These conclusions constitute the first attempt to rationally correlate the m.c.d. of ketones with molecular environment, and are of necessity based on data already published. They are valid, with a few minor exceptions, for all the ketones for which data are available and form a basis for further theoretical and experimental work.

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