Magnetic Circular Dichroism of Nitroalkanes[1]

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Summary The magnetic circular dichroism of several nitroalkanes has been measured and the results interpreted on the basis of a σ–π^* transition at 310 nm and an n–π^* transition at about 275 nm.

WE have investigated the magnetic circular dichroism (m.c.d.) of a large number of saturated ketones and have found that the sign and magnitude of the m.c.d. bands associated with the n–π^* transition of the carbonyl chromophore are related to the structure and stereochemistry of the molecule.[2] As the theory[2d] developed for ketones[2c] is applicable to the m.c.d. associated with symmetry-forbidden transitions in general we have extended our investigations to nitroalkanes.

The m.c.d. and absorption spectral data for the investigated nitroalkanes are in the Table. Examination of the data reveals that: (i) the wavelengths of the maxima in both m.c.d. and absorption closely correspond. (ii) The intensity and sign of the principal m.c.d. effect is directly related to the degree of α-alkyl substitution of the nitroalkane, *e.g.*, nitromethane shows the strongest negative m.c.d. band around 270 nm. The intensity of this band becomes less negative on going from 1-nitrobutane to 2-nitropropane and finally assumes a positive value with 2-nitro-2-methylpropane. In the series of secondary nitroalkanes (Table) the m.c.d. is also sensitive to the nature of the alkane group. (iii) For some compounds, in particular for the secondary nitroalkanes, two m.c.d.

TABLE. M.c.d. and absorption data for aliphatic and alicyclic nitro compounds

Compound	Solvent[a]	Absorption λ_{max}/nm (ϵ/mol^{-1} cm^{-1})	M.c.d. λ_{max}/nm ($[\theta]_M \times 10^4$/deg cm^2 dmol^{-1} G^{-1})
Nitromethane	IO	275 (16·0)	275 (−6·0)
	M	267 (15·6)	273 (−6·2)
	HFIP	265 (15·7)	268 (−4·2)
Nitroethane	IO	277 (19·9)	277 (−5·4)
	M	275 (18·1)	274 (−5·0)
	HFIP	266 (20·7)	270 (−1·6)
Nitrobutane	IO	279 (23·4)	275 (−4·1)
	M	275 (25·2)	275 (−4·1)
	HFIP	267 (37·8)	210 (0·5)
2-Nitropropane	IO	280 (21·6)	320 (0·3) 276 (−2·0)
	M	277 (21·1)	320 (0·5) 276 (−1·4)
	HFIP	270 (28·1)	270 (2·0)
Nitrocyclohexane	IO	280 (27·3)	320 (0·5) 270 (−1·9)
	M	278 (30·5)	303 (0·9) 276 (−1·4)
	HFIP	270 (58·0)	274 (5·9)
cis-1-Nitro-4-t-butylcyclohexane	IO	271 (26·3)	280 (−5·8)
	M	279 (23·9)	280 (−4·2)
	HFIP	265 (33·7)s[a]	290 (0·9)
Nitrocyclopentane	IO	280 (22·9)	277 (−3·3)
	M	278 (22·8)	320 (0·5 275 (−1·5)
	HFIP	269 (31·0)	272 (2·9)
2-Nitro-2-methylpropane	IO	280 (24·0)	300 (0·5)
	M	279 (22·6)	280 (3·5)
	HFIP	271 (31·3)	273 (6·5)
2-Nitro-2,4,4-trimethylpentane	IO	280 (24·0)	281 (5·8)
	M	279 (24·8)	281 (9·1)
	HFIP	271 (42·3)	272 (13·3)
1-Nitro-adamantane	IO	282 (39·0)	280 (2·0)
	M	280 (40·7)	323 (0·7) 283 (−1·3)
	HFIP	270 (69·7)s	278 (13·4)

[a] IO = iso-octane, M = methanol, HFIP = 1,1,1,3,3,3-hexafluoroisopropyl alcohol, s = shoulder.

bands of opposite sign are observed. The second band around 320 nm, is uniformly positive when observed and its intensity appears to be little affected by the extent of substitution at the α-carbon. In absorption a band of low intensity is evidently responsible for the long wavelength tail. (iv) The m.c.d. and absorption intensities and positions are strongly perturbed by a solvent of strong hydrogen bonding capability such as hexafluoroisopropyl alcohol (Table). (v) The magnetic ellipticities of the nitroalkanes are 5—10 times those observed for ketones.

The CNDO/S-CI calculation of Harris[3] for nitromethane predicts that the lowest energy excitation of the nitro chromophore is of σ–π^* nature and that it is of zero intensity although symmetry allowed. The next higher energy transition is the symmetry forbidden n–π^* transition. The only previous experimental evidence for the presence of the σ–π^* transition has come from o.r.d.–c.d. studies of nitrosteroids.[4] We believe that our m.c.d. measurements provide additional support for this assignment. Thus, although the m.c.d. of nitroalkanes and ketones are similar in that two m.c.d. bands of opposite sign are often observed, these must be related to different vibronic modes within the n–π^* transition of the carbonyl chromophore, whereas in the case of nitro compounds these effects must be attributed to two separate electronic transitions.

An interpretation of the m.c.d. of nitroalkanes is complicated by the low barrier of the nitro group to internal rotation.[5] We believe that an approach which averages structural perturbations over the internal rotation angle coupled with the hyperconjugation mechanism invoked by Totty and Hudec[6] for ketones will provide a tractable approach to the problem.

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[1] For preceding paper on magnetic circular dichroism studies, see L. Seamans, A. Moscowitz, R. E. Linder, E. Bunnenberg, G. Barth, and C. Djerassi, *J. Mol. Spectroscopy*, 1975, **56**, 441.

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