Magnetic Circular Dichroism Studies. Part 55.[1] The Aliphatic Nitro Chromophore

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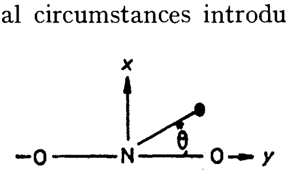
The magnetic circular dichroism (m.c.d.) of twelve nitroalkanes is reported. For several of these compounds two distinct m.c.d. bands are observed in the 240—350 nm region. The presence of these bands is interpreted in terms of two electronic transitions, *viz.* a $\sigma\rightarrow\pi^*$ transition at *ca.* 320 nm and an $n\rightarrow\pi^*$ transition at *ca.* 270—280 nm. The magneto-optical B values for the $\sigma\rightarrow\pi^*$ transition appear to be small in magnitude throughout the series of compounds; the B values for the $n\rightarrow\pi^*$ transition are generally much larger in magnitude and are sensitive to alkyl substitution and to solvent effects. A qualitative interpretation of the spectra is given in terms of the effects of static and structural–vibrational perturbations on the m.c.d. associated with symmetry-forbidden transitions. Solvent effects observed in the m.c.d. spectra of the nitroalkanes are also discussed.

SOME time ago we reported the magnetic circular dichroism (m.c.d.) spectra of a number of aliphatic ketones,[2,3] and we noted then that for saturated ketones there appeared to be a variation with geometrical structure of the sign and magnitude of the magneto-optical B term associated with the $n\rightarrow\pi^*$ transition. Later,[4-6] group theoretical arguments were employed to develop a set of sector rules useful for analysing the magneto-optical activity associated with a locally symmetry-forbidden transition when that transition gains intensity through static perturbations. This analytical protocol was subsequently extended to include vibrational-structural (vibructional) effects,[7-9] and it has proven quite useful for correlating the aforementioned m.c.d. data on saturated ketones with their structures.[8-11] It is of interest now to extend the investigations to include other chromophores which exhibit forbidden electronic transitions of $n\rightarrow\pi^*$ character.

Nitroalkanes show a weak absorption band at *ca.* 270—280 nm, which has been assigned by several workers [12] to an $n\rightarrow\pi^*$ transition, and we report here the m.c.d. spectrum associated with this transition for a number of such compounds. A detailed interpretation of the observed magneto-optical activity of the nitroalkanes along the lines of that presented for ketones is not possible at this time. Amongst other reasons, this is due to special circumstances introduced by internal rotation about the C_α–N bond. However, an interpretation based upon vibructional and gross structural effects provides a qualitative understanding of the data.



EXPERIMENTAL

The m.c.d. spectra were obtained with JASCO model J-5 and J-40 circular dichrometers equipped with 49.5 kG superconducting and 15.0 kG electromagnets, respectively.[13] The u.v. absorption spectra were recorded on a Cary 14M spectrophotometer. The magneto-optical B values and the dipole strengths were obtained by planimetric integration of the normalized spectra using the relationships (1) and (2) [14] where the molar magnetic ellipticity $[\theta]_M$ is

$$B(\text{debye}^2\ \text{bohr magnetons/cm}^{-1}) \approx -(33.56\lambda_{\text{max.}})^{-1}\int_{\text{band}}[\theta]_M d\lambda \qquad (1)$$

$$D(\text{debye}^2) \approx (108.9\lambda_{\text{max.}})^{-1}\int_{\text{band}}\varepsilon(\lambda)d\lambda \qquad (2)$$

expressed in units of deg cm^2 dmol^{-1} gauss^{-1} and the extinction coefficient ε has units of 1 000 cm^2 mol^{-1}. In those instances where amplitudes of both positive and negative sign were observed in the m.c.d. spectrum, the integration was carried out over both bands and the reported B values are those appropriate to the entire band. For an absorption band which is partially overlapped on the short wavelength side by another band of greater intensity, it was assumed that the band shape is symmetrical with respect to the absorption maximum.

The compounds used in this study were obtained from the following sources: nitromethane, spectroquality from MC/B (Norwood); nitroethane and 2-nitropropane from Aldrich; 1-nitrobutane, 2-nitro-2,4,4-trimethylpentane, nitrocyclohexane, and nitrocyclopentane were samples used in previous mass spectrometric work [15] and were provided by Professor H. Feuer (Purdue University); 2-nitro-2-methylpropane was prepared from the corresponding amine by the procedure of Kornblum *et al.*; [16a] 1-nitropropane and 1-nitropentane from the corresponding bromides by the Victor–Meyer reaction; [16b] 1-nitroadamantane by nitration of adamantane; [17] and 2-nitroadamantane by oxidation of the amine (Aldrich Chemical Co.) with perbenzoic acid in benzene solution. The purities of all samples were checked by g.l.c. The solvents used were methanol (Photrex reagent from Baker Chemical Co.), iso-octane (Spectroquality, from MC/B), and 1,1,1,3,3,3-hexafluoropropan-2-ol (Sequanalgrade, from Pierce Chemical Co.).

RESULTS

The m.c.d. and absorption data are compiled in Table 1 and the spectra, in iso-octane, of a few representative nitroalkanes which differ in the degree of methyl substitution at the α-carbon are reproduced in Figure 1. There nitro-

TABLE 1

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

Compound	Solvent [a]	Absorption [b] $\lambda_{max.}$/nm (ε)	M.c.d./nm [c] $\lambda_{max.}$($10^4 \times [\theta]_M$)	10^7B [d]	10^2D [e]
Nitromethane (1)	Neat	271 (15.1)	275 (−4.7)	19	3.1
	IO	278 (17.9)	278 (−5.8)	22.9	2.7
	M	273 (15.3)	277 (−5.4)	22.8	2.7
	HFIP	265 (15.7)	268 (−4.2)	15	2.7
Nitroethane (2)	Neat	275 (19.0)	278 (−4.5)	17.0	3.7
	IO	278 (20.6)	278 (−5.1)	21.7	3.3
	M	274 (18.2)	278 (−4.4)	17.7	3.2
1-Nitropropane (3)	Neat	277 (22.9)	277 (−3.2)	12.6	4.3
	IO	279 (23.6)	280 (−4.0)	16.8	4.1
	M	275 (22.3)	278 (−3.1)	12.4	4.0
	HFIP	269 (30.0)	280 (0.5)	−2.4	5.5
1-Nitrobutane (4)	Neat	277 (24.7)	277 (−2.5)	10.0	5.0
	IO	278 (24.2)	280 (−3.5)	14.2	3.0
	M	273 (25.0)	275 (−3.3)	13.5	4.1
	HFIP	267 (37.8)	310 (0.5)	−2	6.2
1-Nitropentane (5)	Neat	277 (27.5)	277 (−3.1)	13.0	5.1
	IO	278 (25.3)	279 (−3.3)	14.1	4.2
	M	274 (24.8)	277 (−2.6)	9.4	4.5
	HFIP	269 (38.0)	280 (1.2)	−5.6	6.7
2-Nitropropane (6)	IO	279 (22.0)	275 (−0.7), 310 (0.4)	0.5	3.4
	M	278 (21.1)	300 (0.8)	−4.6	3.4
	HFIP	270 (28.1)	270 (2.0)	−10	4.4
Nitrocyclohexane (7)	Neat	278 (33.3)	270 (−1.7), 310 (0.6)	3.3	5.9
	IO	280 (28.6)	270 (−1.6), 320 (0.5)	5.4	4.4
	M	277 (30.0)	265 (−1.1), 305 (1.0)	−0.6	4.9
	HFIP	270 (58.0)	274 (5.9)	−25	9.0
Nitrocyclopentane (8)	Neat	278 (25.9)	279 (−1.8),	6.8	4.6
	IO	280 (24.1)	280 (−2.9)	11	3.8
	M	277 (22.5)	275 (−1.0), 320 (0.4)	2.4	3.8
	HFIP	269 (31.0)	272 (2.9)	−12	5.1
2-Nitroadamantane (9)	IO	282 (38.4)	282 (−7.9)	36	6.3
	M	279 (32.2)	280 (−6.3)	25	5.6
2-Methyl-2-nitropropane (10)	IO	280 (24.0)	280 (1.3)	−9.7	3.5
	M	279 (22.2)	285 (3.8)	−20.3	3.4
	HFIP	271 (31.3)	273 (6.5)	−25	4.9
1-Nitroadamantane (11)	IO	281 (30.5)	282 (−1.3), 320 (0.6)	3.1	5.9
	M	280 (38.6)	285 (6.2)	−20.6	5.9
	HFIP	270 S (69.7)	278 (13.4)	−50	
2-Nitro-2,4,4-trimethylpentane (12)	IO	280 (24.5)	285 (6.9)	−32	3.7
	M	280 (25.6)	285 (8.1)	−35	3.7
	HFIP	271 (42.3)	272 (13.3)	−55	6.9

[a] IO = iso-octane, M = methanol, HFIP = 1,1,1,3,3,3-hexafluoropropan-2-ol. [b] Molar extinction coefficient in 1 000 $cm^2 mol^{-1}$ S = shoulder. [c] Molar magnetic ellipticity in deg $cm^2 dmol^{-1} G^{-1}$. [d] B Value in units of debye^2 bohr magnetons/cm^{-1}. [e] Dipole strength in debye^2

methane (1) exhibits the largest negative m.c.d. amplitude, with a B value of 22.9×10^{-7}, whereas the spectrum of 2-methyl-2-nitropropane (10) shows a positive m.c.d. amplitude with a B value of -9.7×10^{-7}. The m.c.d. spectrum of 1-nitrobutane (4) has a single band of negative sign which is of lower intensity (B 14.2×10^{-7}) than that of nitromethane. The m.c.d. spectrum of 2-nitropropane (6) shows bands of opposite sign at 275 (negative) and 310 nm (positive). Bisignate curves are also observed in the m.c.d. spectra of other compounds in which the nitro group is attached to a secondary carbon atom, *e.g.*, nitrocyclohexane (7) and nitrocyclopentane (8). This situation also obtains for 1-nitroadamantane (11), which has a tertiary α-carbon atom.

The experimental data therefore suggest that the m.c.d. spectra of the nitroalkanes in the wavelength region under consideration are composed of two overlapping bands. It appears that the longer wavelength band is of low intensity throughout the series of compounds investigated, whereas the sign and amplitude of the shorter wavelength band are highly dependent upon the degree of methyl substitution at the α-carbon. The latter band is negative for nitromethane, negative but less intense for the secondary nitroalkanes, and is positive for the tertiary nitro compounds. The changes in the m.c.d. sign pattern are therefore very similar to those observed in the series of aliphatic ketones [3] wherein the sign of the m.c.d. band associated with the carbonyl $n \rightarrow \pi^*$ transition changes progressively from negative to positive with an increase in the number of α-methyl substituents. It can also be seen from a comparison of the B values given in Table 1 that in addition to the influence of α-alkyl substituents, there is a further effect associated with non-α-substitution. For example, the B values for the series of secondary nitroalkanes (6)—(9) vary from 0.5×10^{-7} to 36×10^{-7}.

Spectral changes associated with changes in solvent polarity or hydrogen-bonding ability have been widely used to assign the $n \rightarrow \pi^*$ character of an absorption band. In fact, the assignment of the weak absorption band at *ca.* 270—280 nm in nitro compounds rests mainly upon the small blue shift which this band undergoes in polar solvents.[18] We have therefore obtained the m.c.d. spectra of the nitroalkanes in three different solvents, *viz.*, iso-octane, methanol, and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). The latter solvent is known to undergo particularly strong hydrogen bonding due to the electron-withdrawing effect of the fluorine atoms.[19] The spectral data are listed in Table 1, and Figure 2 shows the m.c.d. and absorption spectra of nitrocyclohexane (7) in these three solvents as an example of the changes observed. In going from iso-octane to methanol as the solvent the bisignate nature of the m.c.d. spectrum of (7) is preserved, but there is a considerable blue shift in the crossover point; the absorption spectrum is nearly constant. Dramatic increases in both the m.c.d. and absorption intensities are observed in HFIP solution. Here the m.c.d. is all positive and the absorption maximum is shifted to the blue by *ca.* 10 nm relative to the maximum in iso-octane solution. As can be readily seen from the data in Table 1, the solvent-induced changes in B values are consistent throughout the entire series; a relatively small decrease in B is observed upon going from iso-octane to methanol, and a considerably larger decrease is observed upon going to HFIP solution. Furthermore, the B values of the neat liquids, which can be regarded as solutions of the nitroalkanes in weakly polar solvents (themselves), are consistently less positive than the B values obtained in iso-octane solution.

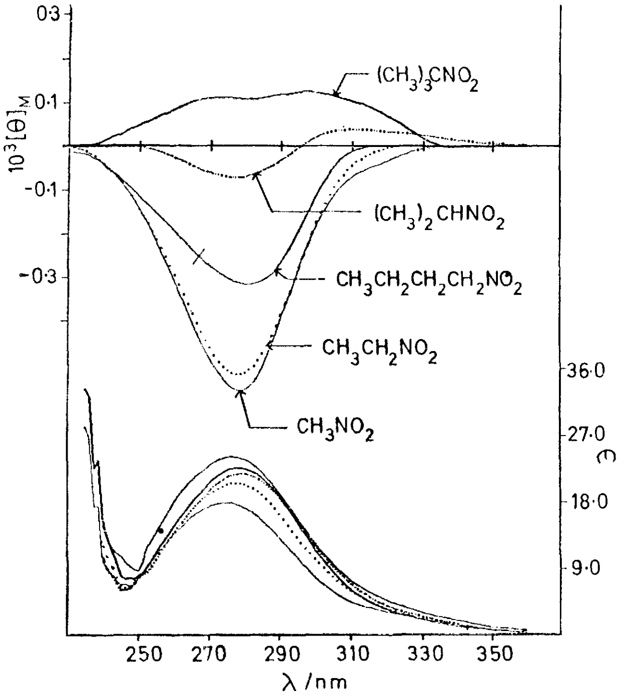


FIGURE 1 M.c.d. (upper curves) and absorption (lower curves) spectra (in iso-octane) of a series of α-substituted nitroalkanes in the near u.v. spectral region

TABLE 2

Nitromethane electronic states [a]

State	Energy (eV)
N (ground)	0.0
$\sigma_1 \rightarrow \pi^*$	3.4
$n_0 \rightarrow \pi^*$	3.9
$\pi_0 \rightarrow \pi^*$	6.4
$\pi_0 \rightarrow \sigma^*$	9.6

[a] Data from ref. 21.

TABLE 3

Calculated and experimental dipole strengths for nitromethane [a]

Chromophoric vibrations	Dipole strength × 10^2 (debye^2)	
	$n \rightarrow \pi^*$	$\sigma \rightarrow \pi^*$
Out-of-plane bend (b_1)	1.02	0.48
In-plane bend (b_2)	0.02	0.06
Antisymmetric stretch (b_2)	0.06	0.12
Equilibrium (no vibration)	0.002	0.06
Experimental [b]	2.7	

[a] All excitations from the highest n or σ orbitals to virtual orbitals and all excitations from bonding orbitals to the lowest π^* orbitals were included in the CI basis set. [b] Solvent: iso-octane.

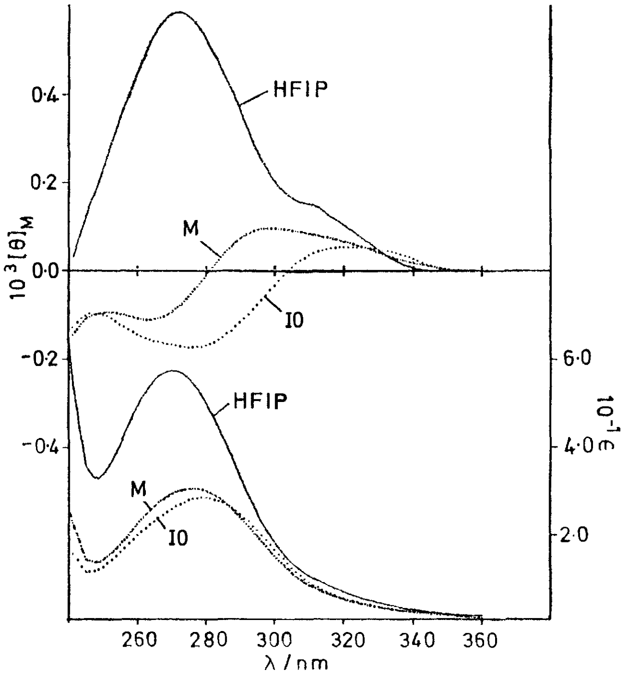


FIGURE 2 M.c.d. (upper curves) and absorption (lower curves) spectra of nitrocyclohexane in iso-octane (IO), methanol (M), and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP)

Spectral Assignments.—The two detailed molecular orbital calculations which have been carried out for nitromethane [20,21] are in essential agreement with respect to the assignment of the lower energy transitions. The assignments obtained by Harris [21] are given in Table 2. Two electronic transitions are predicted to lie in the region of the spectrum which concerns us here. These are the locally symmetry forbidden $n \rightarrow \pi^*$ transition and a transition of $\sigma \rightarrow \pi^*$ character at lower energy. Although it is formally electric dipole allowed, the CNDO/S-CI calculations of Harris [21] yield a dipole strength of zero for the latter transition. Some CNDO/2-CI calculations which we performed (Table 3) support Harris's results. We therefore conclude that the $\sigma \rightarrow \pi^*$ band should lie to the red of the $n \rightarrow \pi^*$ band, and that both bands gain the major part of their intensities through vibrational coupling with higher-lying states. When such vibrational perturbations are included in the CNDO/2-CI calculations,[6] the $n \rightarrow \pi^*$ band is predicted to be the more intense of the two. The above theoretical predictions are supported by the solvent effect work [18] previously mentioned and by studies of the natural optical activity of a number of nitrosteroids [22,23] which exhibit, in addition to the 280 nm band, a Cotton effect at *ca.* 330 nm.

As was pointed out previously, the m.c.d. spectra of several of the nitroalkanes exhibit two bands of opposite sign, a situation which is superficially similar to that observed in the m.c.d. spectra of some saturated ketones.[2,3,5,8–11] In the case of the ketones, the oppositely signed bands were shown [5,6] to arise from different vibrational modes through which the carbonyl $n\rightarrow\pi^*$ transition gains intensity. In principle, this interpretation of the m.c.d. spectra could also be applied to the nitroalkanes. However, in view of the evidence outlined in the preceding paragraph, we favour the assignment of the positive m.c.d. amplitude at longer wavelength to the $\sigma\rightarrow\pi^*$ transition, with this band being at least partially overlapped by the stronger $n\rightarrow\pi^*$ transition which appears at 270—280 nm in the absorption spectrum. In further support of this assignment it is worthwhile to note that the u.v. spectra of virtually all of the nitroalkanes investigated in this study are decidedly unsymmetrical about the 270—280 nm absorption maximum and show a long tail which extends to the red of 350 nm (see, for example, Figure 1).

It further appears from the data that the magnitude of the B term associated with the $\sigma\rightarrow\pi^*$ transition is small for all the compounds. Hence the differences in the B values reported in Table 1, which values were obtained by integration over both bands, will be interpreted as reflecting predominantly the changes in the contributions which the $n\rightarrow\pi^*$ transition makes to the total observed spectrum.

Before concluding this section it is necessary to point out that deMaine *et al.*[24,25] have obtained some evidence from u.v. spectra that nitromethane is capable of forming dimers in nonpolar solvents. It might therefore appear possible to attribute the two observed m.c.d. bands to different (monomeric and dimeric) species. We have been unable to reproduce the results of deMaine and his co-workers, but in order to further eliminate this possibility we investigated the concentration dependence of the m.c.d. spectrum of nitrocyclopentane (8), a molecule in which the two oppositely signed B terms are of approximately the same magnitude. The normalized intensities of the two m.c.d. bands remained unchanged, within experimental error, over a concentration range of from 8 (neat liquid) to 0.06M, a result which is at variance with the hypothesis that the oppositely signed B terms reflect the presence of a monomer–dimer equilibrium.

DISCUSSION

A locally symmetry-forbidden transition gains intensity through static (structural) and vibrational perturbations of the chromophoric eigenstates. A recent theoretical treatment [8] has shown that the B value of such a transition can be written as the sum (3) of three

$$B(A\rightarrow J) = B^{\mathrm{V}}(A\rightarrow J) + B^{\mathrm{S}}(A\rightarrow J) + B^{\mathrm{VS}}(A\rightarrow J) \qquad (3)$$

partial B values. Here $B^{\mathrm{S}}(A\rightarrow J)$ represents the contribution of the static perturbation, $B^{\mathrm{V}}(A\rightarrow J)$ that of the vibrational ones, and the term $B^{\mathrm{VS}}(A\rightarrow J)$ arises from the interaction of the vibrational perturbations with the totally symmetric part of the static one. The partial B values may be further decomposed: equations (4) where $B_{\Gamma}{}^{\mathrm{S}}(A\rightarrow J)$ arises from that part

$$B^{\mathrm{S}}(A\rightarrow J) = \sum_{\Gamma} B_{\Gamma}{}^{\mathrm{S}}(A\rightarrow J), \qquad (4)$$

of the static perturbation which forms a basis for the Γth irreducible representation of the chromophoric point group, and (5) and (6) where the summations are over

$$B^{\mathrm{V}}(A\rightarrow J) = \sum_{r} B_{r}{}^{\mathrm{V}}(A\rightarrow J) \qquad (5)$$

$$B^{\mathrm{VS}}(A\rightarrow J) = \sum_{r} B_{r}{}^{\mathrm{VS}}(A\rightarrow J) \qquad (6)$$

the normal vibrational modes. Thus, $B_{r}{}^{\mathrm{V}}(A\rightarrow J)$ is the purely vibrational contribution of the rth normal mode to the total B value, and $B_{r}{}^{\mathrm{VS}}(A\rightarrow J)$ results from the interaction of the rth normal mode with the totally symmetric part of the static perturbation.

In our earlier work on saturated ketones,[9] we found ' vibructional ' effects, associated with the $B^{\mathrm{V}} + B^{\mathrm{VS}}$ terms of equation (3), to be a principal factor governing the observed variations in the m.c.d. intensity. Hence, we began our analysis of the nitroalkane spectra by focusing upon these same terms.

The electronic states of the nitro chromophore form bases for the irreducible representations of the C_{2v} point group and, to the order of approximation implied by equations (3)—(6), these states are mixed among themselves by vibrational perturbations and by a static perturbation U which is associated with the substituent atoms. If one neglects interactions among them, the perturbing atoms contribute additively to U [equation (7) where U_i depends only upon the nature of the ith

$$U = \sum_{i}^{\text{substituents}} U_i \qquad (7)$$

perturber and its geometric disposition *vis-à-vis* the nitro chromophore].

If we consider only the static perturbation and use first-order perturbation theory, we may write the electronic states of a nitroalkane as equation (8) where

$$|A\rangle = |A^0\rangle + \sum_{i}\sum_{K^0\neq A^0}(E_A{}^0 - E_K{}^0)^{-1}\langle K^0|U_i|A^0\rangle|K^0\rangle \qquad (8)$$

$|A^0\rangle$ and $|K^0\rangle$ are unperturbed chromophoric states with energies $E_A{}^0$ and $E_K{}^0$, respectively.

It is shown in ref. 8 [equation (19) *et seq.*] that $B_{r}{}^{\mathrm{VS}}(A\rightarrow J)$ depends additively upon first-order changes wrought by the totally symmetric component of U in symmetry-allowed matrix elements. We wish therefore to consider quantities such as those in equation (9)

$$\langle A|\hat{O}|J\rangle - \langle A^0|\hat{O}|J^0\rangle = \sum_{i}\left\{\sum_{K^0\neq A^0}(E_A{}^0 - E_K{}^0)^{-1}\langle A^0|U_i(A_1)|K^0\rangle\langle K^0|\hat{O}|J^0\rangle + \sum_{K^0\neq J^0}(E_J{}^0 - E_K{}^0)^{-1}\langle K^0|U_i(A_1)|J^0\rangle\langle A^0|\hat{O}|K^0\rangle\right\} \qquad (9)$$

where $U(A_1)$ is the totally symmetric part of U_i, $\hat{O}$ is an arbitrary operator which forms a basis for one of the irreducible representations of C_{2v}, and where the matrix element $\langle A^0|\hat{O}|J^0\rangle$ is symmetry-allowed. Specifically, equation (9) represents a change in the magnitude, but not the polarization, of an electric or magnetic dipole transition moment from which m.c.d. intensity is vibrationally borrowed, or a change in the magnitude of a vibrational coupling term which effects the intensity borrowing.

If we assume free rotation about the C_α–N bond (see Appendix), we may average equation (9) over the rotation angle to obtain an expression of the form (10)

$$\overline{\langle A|\hat{O}|J\rangle - \langle A^0|\hat{O}|J^0\rangle} = \sum_{i}^{\text{substituents}} f_i \qquad (10)$$

where f_i depends only upon the nature of the ith extrachomophoric atom, its distance from the origin (which lies on the C_α–N axis), its perpendicular distance from the C_α–N axis, and the form of the operator $\hat{O}$. $B_r^{\mathrm{VS}}(A\rightarrow J)$ is a weighted sum of such changes in symmetry-allowed matrix elements, and so we may write equation (11) where g_{ri} is a function of the same properties of substituent i as is f_i.

$$B_r^{\mathrm{VS}}(A\rightarrow J) = \sum_{i}^{\text{substituents}} g_{ri} \qquad (11)$$

If we now restrict ourselves to carbon or hydrogen substituents bonded directly to the α-carbon, and assume that all α-substituents of a given type have the same C_α-substituent bond length and are equidistant from the C_α–N axis, equation (11) becomes (12) where n_{H} and n_{C}

$$\begin{aligned} B_r^{\mathrm{VS}}(A\rightarrow J) &= \sum_{\mathrm{H}} g_{r\mathrm{H}} + \sum_{\mathrm{C}} g_{r\mathrm{C}} \\ &= n_{\mathrm{H}}g_{r\mathrm{H}} + n_{\mathrm{C}}g_{r\mathrm{C}} \qquad (12) \end{aligned}$$

are the number of hydrogen and carbon substituents, respectively. We now further assume that the differences in normal modes among structurally similar nitroalkanes are unimportant for purposes of estimating the B_r^{VS} terms. The vibructional contributions to $B(n\pi^*)$, denoted by $\bar{B}(n\pi^*)$, for such nitroalkanes may then be written as (13) where B_0 represents the purely vibrational

$$\begin{aligned} \bar{B}(n\pi^*) &= B^{\mathrm{V}}(n\pi^*) + B^{\mathrm{VS}}(n\pi^*) \\ &= B_0 + n_{\mathrm{H}}g_{\mathrm{H}} + n_{\mathrm{C}}g_{\mathrm{C}} \quad (13) \end{aligned}$$

contribution, which is assumed to be constant, and g_{H} and g_{C} depend only upon the type of substituent atom. Since $n_{\mathrm{H}} + n_{\mathrm{C}} = 3$ for the nitroalkanes, we may simply write (14) where β_0 and β_1 are constants and the B_0 term

$$\bar{B}(n\pi^*) = \beta_0 + n_{\mathrm{C}}\beta_1 \qquad (14)$$

in equation (13) has been absorbed into β_0.

Equation (14) predicts that, subject to the assumptions stated above, the vibructional contribution to the B value associated with the $n\rightarrow\pi^*$ transition of a nitroalkane should be a linear function of the number of β-carbons in the molecule. If these vibructional contributions are important factors in determining the total B values, one would thus expect to observe a general correlation between the degree of α-substitution in a nitroalkane and the total B value associated with its $n\rightarrow\pi^*$ transition. When the data are arranged so that the compounds are divided into classes on the basis of their degree of α-substitution (Figure 3), it is evident that such a correlation exists. For example, the B values (in iso-octane) of nitromethane (1), nitroethane (2), 2-nitropropane (6), and 2-methyl-2-nitropropane (10) are 22.9, 21.7, 9.5, and −9.7, all × 10^{-7}, respectively. This trend towards more negative values of $B(n\pi^*)$ with increasing substitution at the α-carbon appears to be quite general; the only apparent exceptions are the nitroadamantanes (9) and (11). In these instances the rigidity of the adamantane skeleton probably renders invalid the assumption of constant vibrational contributions to $\bar{B}(n\pi^*)$.

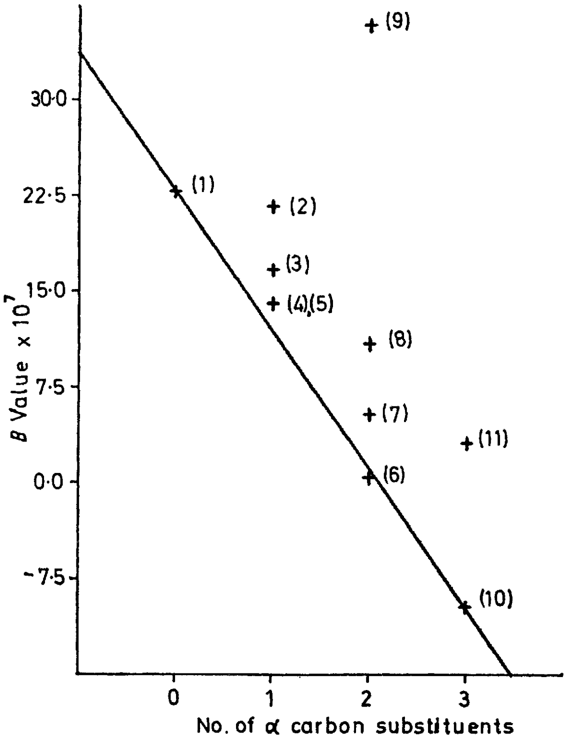


FIGURE 3 B Values of a series of nitroalkanes plotted as a function of the degree of α-substitution. The solid line gives the $\bar{B}$ values predicted by equation (14) when the values for (1) and (10) are used in evaluating the constants β_0 and β_1

Once the classification of the nitroalkanes on the basis of their degree of α-substitution has been accomplished, our model assumes that the variance in B values within a class is accounted for by non-α-vibructional effects and by the purely static terms in equation (3). In the analysis of the m.c.d. of saturated ketones,[5,6,9] we could further refine the model by using information obtained from the spectrum of formaldehyde about the purely vibrational contributions to $B(n\pi^*)$. Unfortunately, the prototypical nitroalkane, HNO_2, is unobtainable, and so no such analysis is possible here. A further complication appears when we attempt to quantify the effects of static (structural) perturbations. A protocol for doing this was developed for saturated ketones,[5] but again such an analysis is not possible for the nitroalkanes. This difficulty arises from the fact that, due to the assumed free internal rotation about the C$_\alpha$–N bond, no structural perturbations of a pure symmetry type can be isolated. All the nitroalkanes thus exhibit static perturbations (whether electrostatic or mesomeric in nature) belonging to all three nontotally symmetric representations of the chromophoric point group. Furthermore, any non-α-vibructional effects, which are associated with the totally symmetric parts of the static perturbations, are for the same reason inseparable from the purely structural effects. About all that can be said then is that, all other things being equal, there should be a general correlation of m.c.d. intensity within a class with the total number of extrachromophoric atoms, and that the contribution of an extrachromophoric atomic perturber should decrease with increasing distance of the atom from the nitro chromophore. An example of this type of trend can be seen in the data for the primary nitroalkanes in iso-octane solution: the B values for nitroethane (2), 1-nitropropane (3), 1-nitrobutane (4), and 1-nitropentane (5) are 21.7, 16.8, 14.2, and 14.1, all $\times 10^{-7}$, respectively.

When we consider the secondary and tertiary nitroalkanes, the assumption of constancy of B^V within a class becomes considerably more tenuous. This has already been alluded to above with regard to the nitroadamantanes relative to the other compounds. Moreover, there may be a significant degree of conformational mobility in (7) and (8),* and there is some evidence for steric hinderance of free internal rotation of the nitro chromophore in (12) (see Appendix). In view of these considerations, further attempts at analysis of the m.c.d. spectra of the secondary and tertiary nitroalkanes are unwarranted outside of a considerably more detailed framework than is used in this work.

Conclusions.—The near u.v. m.c.d. spectra of nitroalkanes are most likely due to two electronic transitions. These give rise to a $\sigma\rightarrow\pi^*$ band at *ca.* 320 nm and an $n\rightarrow\pi^*$ band at *ca.* 270—280 nm. The B values of the $\sigma\rightarrow\pi^*$ band are small; those of the $n\rightarrow\pi^*$ band are usually larger in magnitude and vary with molecular structure in a manner that is at least qualitatively explicable. In particular, the observed trend toward more negative B values with increasing degree of substitution at the α-carbon can be attributed to vibructional effects, in which static (structural) perturbations interact with vibrational perturbations so as to alter the efficacy of the vibronic coupling through which the $n\rightarrow\pi^*$ transition gains m.c.d. intensity.

APPENDIX

Internal Rotational Barriers in Nitroalkanes.—The internal rotational barriers in nitromethane and nitroethane have been measured by microwave spectroscopy and are *ca.* 0.01 kcal mol^{-1}.[27,28] These molecules can therefore be considered to exhibit free rotation about the C–N bond at room temperature. Similarly low barriers of from 0.07 to 0.10 kcal mol^{-1} have been calculated for trifluoro-,[29,30] tribromo-,[29] and trichloro-nitromethane,[29] and it seems reasonable to conclude that an analogous situation exists for those nitroalkanes in which the nitro group is bonded to a tertiary carbon atom, *e.g.* compounds (10)—(12). Compound (12) could well be an exception however, since the Dreiding model shows that the t-butyl group in the 2-position interferes sterically with the rotation of the nitro group. No experimental data are available on the internal rotational barriers in compounds in which the nitro chromophore is attached to a secondary carbon atom but, in view of the data on nitroethane,[28] which indicate that no increase in the barrier results from the replacement of one hydrogen atom of nitromethane by a methyl group, we assume that the secondary nitro compounds can also be considered to exhibit essentially free rotation about the C–N bond.

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* The population ratio of axial to equatorial conformers in (7) is 20 : 80;[26] the populations for (8) are not known

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