The Structures of Nitronate Salts in Solution as Determined by ^{13}C and ^{1}H N.m.r. Spectroscopy

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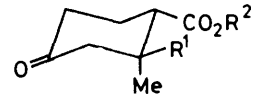
The ^{13}C and ^{1}H n.m.r. spectra of a series of nitroalkanes and their nitronate anions in the solvents dimethyl sulphoxide and methanol are recorded and assigned. In methanol, the resonance of the α-carbon atom of nitronates appears at *ca.* 10 p.p.m. to lower field than in dimethyl sulphoxide. This observation is explained by postulating a solvent-dependence of charge distribution in nitronate anions, such that in methanol, hydrogen-bonding causes a higher electron density to reside on the oxygen atoms of the anions. This supports a similar suggestion previously made using other spectroscopic techniques. The influence of temperature and the nature of the metallic counterion on the ^{13}C n.m.r. spectra of the nitronates is described. A deshielding effect of the nitronate grouping on neighbouring protons is used to deduce the preferred conformation of nitronate anions. The axial conformation is favoured for 2-methyl- and 2-phenyl-cyclohexane nitronate anion.

RECENT attention to the chemistry of nitronate anions has been centred on their applications in synthesis[1] and the subtleties of their interconversion with the corresponding nitro-compounds.[2] These areas might profit from a knowledge of the factors which influence the structure of nitronate anions in solution. Furthermore, nitronate anions are excellent subjects for studying the effect of solvents and cations on the structures of ambident nucleophiles. In this respect they are superior to enolate anions,[3] because nitronates, in contrast to enolates, can be readily formed quantitatively in protic as well as aprotic solvents.

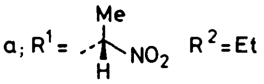
Following the discovery of a long-range deshielding effect in ^{1}H n.m.r. spectroscopy of several nitronate anions, which permits the preferred conformation(s) of flexible systems to be inferred (see below and ref. 4), we examined the ^{13}C n.m.r. spectra of a representative group of these anions. Previously, the solvent dependence of the electronic spectra,[5-7] i.r.,[6] and ^{1}H n.m.r. spectra of nitronate anions [5,7] had been studied. Our work complements and extends those investigations.

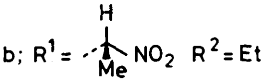
^{13}C *N.m.r. Spectra of Nitronate Anions and their Parent Nitro-compounds.*—^{13}C N.m.r. data for seven nitronate anions and the parent nitroalkanes in the solvents methanol (CD_3OD) and dimethyl sulphoxide [DMSO, $(CD_3)_2SO$] are given in Table 1. The very low solubility of the available primary sodium alkanenitronates in DMSO prevented their examination in this solvent. Also, with these salts, the hydrogen atom attached to the nitronate carbon quickly exchanges with deuterium in CD_3OD (confirmed by ^{1}H n.m.r.) and it was impossible to observe the ^{13}C signal for the nitronate carbon owing to a diminished nuclear Overhauser effect (n.O.e.), and signal broadening caused by C–D coupling. The use of CH_3OH containing a small proportion of CD_3OD resolved this problem (some deuteriated solvent was required for the lock signal). It was impossible to measure the chemical shift of the nitronate α-carbon in sodium adamantane-2-nitronate owing to the very low solubility of this salt in DMSO, as well as the apparent long relaxation time of this carbon atom compounded by a weak n.O.e.

Assignments given in Table 1 are supported where possible by off-resonance decoupling experiments. In general we observe that large downfield shifts of 30—45 p.p.m. occur for the α-carbon on anion formation, agreeing with other results reported for alkanenitronates.[8]

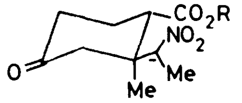


(1)


a; $R^1 = \overset{Me}{\underset{H}{C}}NO_2$ $R^2 = Et$


b; $R^1 = \overset{H}{\underset{Me}{C}}NO_2$ $R^2 = Et$

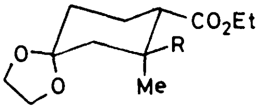
c; $R^1 = CHMeNO_2$ $R^2 = Bu^t$



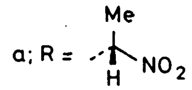
(2)

a; R = Et

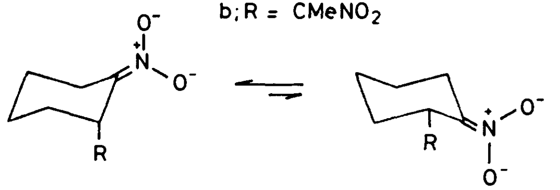
b; R = Bu^t



(3)


a; $R = \overset{Me}{\underset{H}{C}}NO_2$

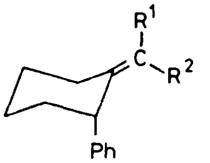
b; $R = \bar{C}MeNO_2$



(4a) R = Ph (4b) R = Ph

(4c) R = H (4d) R = H

(4e) R = Me (4f) R = Me



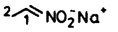
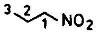
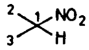
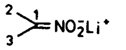
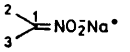
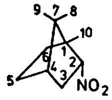
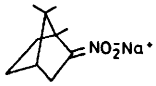
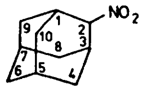
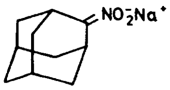
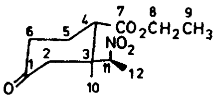
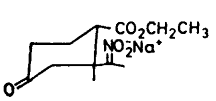
(5)

a; $R^1 = Ph$ $R^2 = OAc$

b; $R^1 = OAc$ $R^2 = Ph$

Table 1

^{13}C Shieldings for nitroalkanes and nitronate anions, in p.p.m. downfield from Me_4Si

Compound	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	$C(NO_2^-)$ $C(NO_2)$	$C[NO_2^-; CD_3OD]$ $-C[NO_2^-; (CD_3)_2SO]$
CH_3NO_2	CH_3OH–CD_3OD	63.0													
$CH_2NO_2^-Na^+$	,,	109.8												46.8	
	,,	71.4	12.5												
	,,	112.3	13.1												
	CD_3OD	78.1	22.0	11.1											
	$(CD_3)_2SO$	77.0	20.3	10.4											
	CD_3OD	119.1	21.6	11.2										41.0	9.8
	$(CD_3)_2SO$	109.3	20.1	11.6										32.3	
	CD_3OD	79.9	21.1	21.1											
	$(CD_3)_2SO$	78.5	20.3	20.3											
	CD_3OD	121.5	19.0	19.0										41.6	9.9
	$(CD_3)_2SO$	111.6	18.2	18.2										33.1	
	CD_3OD	120.9	19.0	19.0										41.0	13.9
	$(CD_3)_2SO$	107.0	18.7	18.7										28.5	
	CD_3OD*	*a*	93.9	33.4	45.8	28.0	29.7	53.2	20.0	19.2	14.4				
	$(CD_3)_2SO$*	49.7	92.3	32.0	43.9	26.9	28.2	51.9	19.4	18.6	13.8				
	CD_3OD*	*a*	135.1	38.4	45.3	28.4	33.5	52.9	20.6	19.3	13.5			41.2	13.4
	$(CD_3)_2SO$*	48.6	131.7	37.7	43.7	27.6	33.2	49.9	20.1	18.9	13.5			29.4	
	CD_3OD		89.4	other signals at 28.2, 32.5, 33.1, 37.8, 38.0										44.7	
	$(CD_3)_2SO$		87.6	other signals at 26.1, 30,6, 31.7, 36.0, 36.3											
	CD_3OD	33.3	134.1	33.3	38.3	29.1	37.6	29.1	38.3	38.3	38.3				
	$(CD_3)_2SO$	30.8	*b*	30.8	37.2	27.7	36.8	27.7	37.2	37.2	37.2				
	$CDCl_3$	207.9	39.8	42.5	45.9	25.4	46.9	172.4	61.0	13.9	13.9	88.2	17.6		
	CD_3OD	210.5	40.3	43.6	47.2	26.3	48.2	174.2	62.0	14.4	14.4	90.1	18.0		
	$(CD_3)_2SO$	208.5	38.4	42.7	45.5	25.4	47.5	173.0	60.9	14.2 or 14.4	14.2 or 14.4	89.1	17.7		
	CD_3OD														
	1Eq base	216.6	43.6	44.6		24.9		175.6	61.4	14.6	16.2	125.4	22.2	34.3	
	2Eq base	216.8	43.9	44.5	48.1	24.8	50.0	175.6	61.5	14.6	16.1	124.9	22.4		9.9
	$(CD_3)_2SO$	210.1	38.6	43.0	41.5	23.8	48.8	173.9	59.4	14.0	15.6	115.5	21.2	26.4	

[a] Under solvent peak. [b] Too weak to be observed.

* Some assignments tentative.

The chemical shift differences for β- and γ-carbons in nitroalkanes and their anions are much smaller (*ca.* 4 p.p.m.). Long-range deshielding of carbon atoms by the nitronate group, analogous to the dramatic effects seen in ^{1}H n.m.r. spectra (see below and ref. 4), are not observed.

A significant observation made during our study of nitronate anions was a solvent-dependent variation in the chemical shift of the α-carbon atom of the nitronate group. In general, this carbon atom resonates at about 10 p.p.m. to lower field in methanol, compared to DMSO (*cf.* Table 1, last column). In contrast, the chemical shift of the α-carbon atom in the parent nitroalkanes is almost solvent independent (*cf.* Table 1).

The quantity of base used (1 or 2 equiv.) to generate nitronate anions in methanol did not significantly affect the chemical shifts of their carbon resonances. The effect of changing the concentration of a nitronate anion on the chemical shifts in its spectrum was examined using lithium propane-2-nitronate. Over the concentration range 0.25—1.0 M (the upper limit in DMSO, for solubility reasons) the chemical shifts of its carbon resonances did not change by more than 0.1 p.p.m. (CD_3OD) or 0.3 p.p.m. [$(CD_3)_2SO$].

On varying the temperature at a fixed concentration (0.5 M), small changes were observed in the shielding of the nitronate carbon atom of lithium propane-2-nitronate. As temperature increased from 253 to 323 K in CD_3OD

the chemical shift of the α-carbon moved upfield (δ 122.7 to 121.2 p.p.m.; 4 measurements), whilst the methyl resonance remained unchanged (δ 19.0 p.p.m.). As the temperature was increased in DMSO from 298 to 323 K the α-carbon resonance moved slightly downfield from 111.5 to 112.0 p.p.m. (3 measurements) whilst the methyl resonance was unchanged (δ 18.2 p.p.m.).

On the basis of i.r. spectral evidence (position of C=N stretch), it was concluded [6] that lithium alkanenitronate salts are more covalent than the corresponding sodium and potassium salts, since shifts to longer wavelengths were observed as the charge density on the cation decreased. ^{13}C N.m.r. evidence supports this idea. In methanol, where the salts are predicted to be dissociated, the chemical shifts of the spectra of lithium and sodium propane-2-nitronate are very similar (lithium salt: δ CH_3 19.0; CNO_2^- 121.5; sodium salt: δ CH_3 19.0; CNO_2^- 121.0 p.p.m.). However, in DMSO CNO_2^- appears at δ 111.6 for lithium propane-2-nitronate but at δ 107.0 p.p.m. for sodium propane-2-nitronate. In this solvent the lithium salt has covalent character diminishing the negative charge density on the α-carbon of the nitronate anion, which therefore resonates at lower field compared to the sodium salt.

The Origin of ^{13}C Solvent Effects in Nitronate Anions and Comparison with Theories proposed on the Basis of Electronic Spectral Evidence.—From an investigation into the effects of solvents on anion structure, Kerber and Porter observed [5] that the ^{1}H n.m.r. and electonic spectra of salts of 1-nitroindene and 9-nitrofluorene showed significant changes between protic and aprotic solvents. It was concluded that in protic solvents hydrogen bonding to the oxygen atoms of the nitronate tends to localise the negative charge on oxygen. Analogous effects had already been observed in phenoxide salts.[9]

In a study [6] of the electronic spectra of substituted 1-phenylethane-1-nitronates, it was claimed that polar solvents of diminished hydrogen bonding ability cause absorption at longer wavelengths. For the examples cited (sodium propane-2-nitronate and sodium ethanenitronate) the absorption maxima in methanol reported can be accurately reproduced. We have been unable to reproduce the results given for alkanenitronates in acetonitrile or propylene carbonate, the aprotic solvents examined, because the nitronate salts quoted are of too low solubility in these solvents for accurate absorption measurements to be taken. However, in accord with ref. 6, the long-wavelength u.v. absorption maximum for the sodium nitronate of *trans*-4-ethoxycarbonyl-3-methyl-3-(1-nitroethyl)cyclohexanone shows significant changes in the solvents methanol, acetonitrile, and propylene carbonate: 235 (ε 6500), 248 (4900), and 259 (4400) nm respectively. U.v. absorption data for ethanenitronate and propane-2-nitronate anions in methanol, DMSO, and DMF (dimethylformamide) have been reported [10] and demonstrate a similar marked solvent dependence.

In methanol, we find $\lambda_{max.}$ for sodium ethanenitronate, sodium and lithium propane-2-nitronate, lithium propane-1-nitronate, sodium and lithium cyclohexanenitronate, and sodium bornane-2-nitronate to be in the range 227—237 nm ($\lambda_{max.}$ 227 nm, ε 17 700 for lithium propane-2-nitronate). In acetonitrile only lithium propane-2-nitronate was sufficiently soluble for accurate measurements to be made ($\lambda_{max.}$ 221 nm, ε 11 200). This value is not in accord with ref. 6. In propylene carbonate, sodium ethanenitronate and propanenitronate were insoluble; sodium bornane-2-nitronate gave $\lambda_{max.}$ 247 nm (*cf.* $\lambda_{max.}$ 232 nm in methanol).

Evidently the limited solubility of the majority of nitronates examined precludes the use of u.v. spectroscopy as a satisfactory technique for studying the structure of the nitronate group in various solvents. DMSO was unsuitable as a solvent owing to its cut-off at *ca.* 260 nm.

The ^{13}C n.m.r. measurements described above uphold the suggestions [5] of Kerber, because the chemical shift differences observed for the nitronate carbon atom can be ascribed to a solvent-dependent redistribution of electron density in the nitronate anion. In methanol, hydrogen bonding to oxygen atoms of the nitronate will diminish negative charge on the carbon atom of the nitronate anion. ^{17}O N.m.r. measurements [8] also indicate that in protic solvents such as methanol and water, the negative charge of aliphatic nitronate anions resides principally on the oxygen atoms. This behaviour was also seen in anions derived from 2-nitropyrroles.[11]

^{1}H N.m.r. Spectra of Nitronate Anions.—*Introduction.* In a synthetic project we studied base-catalysed addition of nitroethane to 4-ethoxycarbonyl-3-methylcyclohex-2-en-1-one (' Hagemann's ester '), obtaining a mixture of adducts (1a) and (1b). To prove these adducts are epimeric, they were treated with NaH in $(CD_3)_2SO$, giving in each case an identical ^{1}H n.m.r. spectrum for the nitronate anion (2a). This spectrum revealed for two protons of (2a) large chemical shift differences compared with the spectrum of the parent nitro-compounds (*cf.* Table 2). In (2a), H-4 resonates 1.76 p.p.m. downfield from its position in (1a). A similar effect was observed with (2a) in CD_3OD. There is also a doublet (*J* 13 Hz) in the spectrum of (2a) in $(CD_3)_2SO$, which is assigned to H-2_{ax} (see below), *ca.* 1.7 p.p.m. downfield from its position in the spectrum of (1a). The resonance from H-2_{eq} in (2a) appears in a multiplet (5H) between δ 1.9 and 2.5. Signals from H-2_{ax} and H-2_{eq} were not observed in CD_3OD owing to base-catalysed exchange. Similar deshielding effects were observed in spectra of the anions (2b) and (3b) derived from the t-butyl ester (1c) and acetal (3a), respectively. As a rule, whenever a proton lies in the plane of a nitronate grouping and near to one of its oxygen atoms, then a downfield shift relative to the position in the corresponding nitro compound is observed. Analogous effects have been described with the neutral nitro-group,[12] the oximido-group,[13] an alkoxy-anion,[14] and the carboxylate group.[15] We present a comprehensive study of the ^{1}H n.m.r. spectra of a range of nitronate anions which enables this effect to be qualitatively described (*cf.* Table 2). A long-standing controversy

TABLE 2

^{1}H N.m.r. data for nitro-compounds and nitronate anions

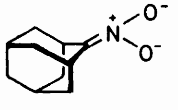
Nitro compound/ nitronate anion	Solvent [a]	Chemical shifts (multiplicity, coupling constants in Hz, assignment)	ΔH [b]
(1a)	A (Very similar spectrum in B)	1.16 (s, Me–C), 1.20 (t, CH_3CH$_2$), 1.52 (d, CH_3CH), 1.9—2.95 (m, CH_2COCH_2CH_2), 2.88 (q, H-4), 4.20 (q, CH_2Me), and 4.98 (q, CHNO$_2$)	
(2a)	B	1.07 (s, Me–C), 1.20 (t, CH_3CH$_2$), 1.9—2.5 (m, CH_{eq}COCH_2CH_2), 1.89 (s, MeC=N), 4.19 (q, CH_2Me), 4.20 (d, J 13, H-2$_{ax}$), and 4.63 (q, H-4)	1.76 (H-4) 1.7 (H-2$_{ax}$)
	A	*inter alia* 4.46 (q, J 5, 11, H-4)	1.58 (H-4)
(2b)	B	*inter alia* 3.98 (d, J 13, H-2$_{ax}$), 4.38 (q, H-4), and H-2$_{eq}$ <2.5	1.47 (H-4) 1.5 (H-2$_{ax}$)
(3b)	A	*inter alia* 3.25 (d, J 12, H-2$_{ax}$), 4.58 (m, H-4), and H-2$_{eq}$ <2.0	2.18 (H-4) 1.5 (H-2)
(4a)/(4b)	A	1.2—2.3 (m, H-6$_{ax}$, H-3, H-4, H-5), 3.2 (d, H-6$_{eq}$), 4.62 (m, $w_{\frac{1}{2}}$ 10, H-2), and 7.22 (narrow m, 5 × ArH) For H-2 $w_{\frac{1}{2}}$ at other temp.: 9 (273, 248, 243 K), 8 (223, 213 K), and 7.5 (198 K)	1.49 (H-2)
(4c)/(4d)	A	1.60 (m, H-3, H-4, H-5) and 2.57 (m, H-2, H-6)	0.37 (H-2, H-6)
(4e)/(4f)	A	1.10 (d, Me), 1.2—2.3 (m, H-6$_{ax}$, H-3, H-4, H-5), 3.12 (d of m, J 17, $w_{\frac{1}{2}}$ 8, H-6$_{eq}$) and 3.55 (m, H-2)	1.17 (H-2)
(6)	A	1.9br (s, 10 H) and 3.40br (s, H-2)	0.70 (H-2)
(7a)	A	0.95—1.98 (m, 14 H), 1.98—2.37 (m, H-2$_{eq}$, H-9$_{eq}$), and 4.28 (d of t, J 13, 4, H-1$_{ax}$)	
(7b)	A	0.75—1.94 (m, 14 H), 2.17 (m, H-9$_{ax}$), 2.56 (d of m, J 12, H-9$_{eq}$), and 2.89 (d of t, J 14, 5, H-2$_{eq}$)	*ca.* 0.7 (H-2$_{eq}$)
(11)	A	1.2—1.8 (m, H-5, H-6, H-7), 2.01 (d of m, J 17, H-3$_{endo}$), 2.38 (d of m, J 17, H-3$_{exo}$), 2.44 (narrow m, H-4), and 3.22 (narrow m, $w_{\frac{1}{2}}$ 5.5, H-1)	0.4 (H-1)
(12)	A	0.88 (s, 7,7-Me$_2$), 1.32 [s, C(1)–Me], 0.9—1.3 (m, 1 H), 1.5—1.9 (m, 4 H), 2.05 (d, J 17, H-3$_{endo}$), and 2.66 (d of m, J 17, $w_{\frac{1}{2}}$ 9, H-3$_{exo}$)	0.24 (Cl-Me)

[a] A = CD_3OD; B = $(CD_3)_2SO$. [b] ΔH is the difference in chemical shift between the proton shifted downfield in nitronate and the corresponding proton in the parent nitro-compound.

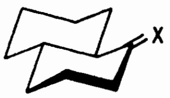
concerning the preferred conformation of 2-substituted cyclohexanenitronates is thereby resolved.

Cyclohexanenitronates. The preferred conformation of 2-substituted cyclohexanenitronates has been discussed [16] in the context of the kinetic protonation of these anions. Using the concept of $A^{1,3}$ strain, Johnson and Malhotra [17] proposed that the axial conformer [*e.g.* (4a)] would be preferred over the equatorial conformer [*e.g.* (4b)]. This conclusion was disputed on the basis of evidence from n.m.r. [18] and u.v. spectroscopy.[19] However, comparing the chemical shift of H-2 in the 2-phenylcyclohexanenitronate anion with values for model compounds, in which the orientation of the corresponding hydrogen atom is known, allowed these suggestions to be refuted.[20] Furthermore, crystal structure analysis of (5a) and (5b) proved that the axial conformers shown were preferred, at least in the crystal.[21] Studies of several oximes,[22] iminoxyl radicals,[23] and *o*-methoxyphenylhydrazones [24] of 2-substituted cyclohexanones also strongly suggest that their axial chair conformers are favoured. 2-Substituted *N*-acylpiperidines prefer the chair conformation with the 2-substituent axial.[25]

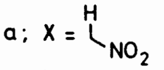
The ^{1}H n.m.r. spectrum of cyclohexanenitronate anion shows a signal for H-2$_{ax}$ (H-6$_{ax}$) and H-2$_{eq}$ (H-6$_{eq}$) averaged at δ 2.57, owing to fast exchange between conformers (4c) and (4d) presumed to occur at ambient probe temperature (298 K). To specify the true chemical shifts of H$_{ax}$ and H$_{eq}$ adjacent to the nitronate grouping it is necessary to examine nitronates incapable of ring inversion and for this purpose adamantane-2-nitronate (6) and *trans*-decalin-1-nitronate (7b) were studied. The spectrum of (6) shows a signal at δ 3.40 due to H-1 and H-3. In the spectrum of (7b) only the signal from one proton is significantly deshielded and is assigned to H-2$_{eq}$ (δ 2.9, dt, J 14 and 5 Hz). The difference between the values for (6) and (7b) reflects the usual difference



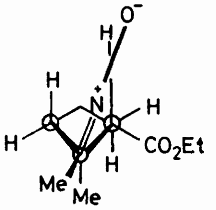
(6)



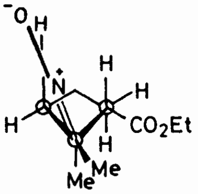
(7)



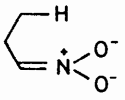
b; X = NO_2^-



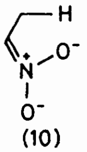
(8a)



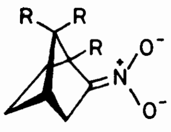
(8b)



(9)



(10)



(11) R = H
(12) R = Me

between the chemical shifts of C-C*H*$_2$X and C-C*H*X-C.[26] Comparing the value for (7b) with that for the cyclohexanenitronate anion shows that an equatorial proton appears *ca.* 0.7 p.p.m. below its axial counterpart adjacent to a nitronate group.

The ^{1}H n.m.r. spectrum of 2-methylcyclohexanenitronate anion [(4e) $\rightleftarrows$ (4f)] shows two downfield signals at δ 3.12 (1H, d of m, J 17 Hz, $w_{\frac{1}{2}}$ 8 Hz) and 3.55 (1H, m) assigned to H-6$_{eq}$ and H-2$_{eq}$ in preferred conformer (4e), respectively, by comparison with the corresponding values for model compounds (6) and (7b). 2-Phenylcyclohexanenitronate [(4a) $\rightleftarrows$ (4b)] shows downfield signals at 3.20 (1H, d of m) and 4.62 (1H, m, $w_{\frac{1}{2}}$ 10 Hz), assigned to H-6$_{eq}$ and H-2$_{eq}$, respectively. The phenyl subsituent at C-2 will cause a *ca.* 1.5 p.p.m. downfield shift on H-2 compared with H-6. Hence, the preferred conformation of 2-phenylcyclohexanenitronate is (4a).

Nitronates (2a), (2b), *and* (3b) *and bicyclo*[2.2.1]-*heptanenitronates*. To explain specific deshielding of H-4 and one H-2 proton in the ^{1}H n.m.r. spectra of (2a), (2b), and (3b) we propose that these anions are an equilibrium mixture (*ca.* 1 : 1) of two conformers [(8a) and (8b) for (2a), and corresponding species for (2b) and (3b)] in fast exchange. Significant population of conformers placing a nitronate oxygen atom near the C-3 methyl group can be ruled out because its chemical shift hardly varies between the nitronate anions and their precursors [*e.g.* (2a) and (1a)]. Population of a conformer expected to cause deshielding of H-2$_{eq}$ would bring about an unfavourable steric interaction between the C-4 ester grouping and the nitronate methyl group. Therefore, we prefer assigning the signal at δ 4.20 to H-2$_{ax}$ deshielded in conformer (8b). Note that the effect of the nitronate grouping in (2a), (2b), and (3b) on H-2$_{ax}$ and H-4 is through six centres in a plane (9), whereas in the 2-substituted cyclohexanenitronates discussed in the previous section the nitronate group deshields *via* five centres in a plane (10).

Conversion of 2-nitronorbornane into its anion (11) causes H-1 to shift from δ 2.82 to 3.22, whereas H-4 shifts from δ 2.34 to 2.44. The chemical shift difference between H-3$_{exo}$ and H-3$_{endo}$ is 0.36 (*exo* proton at lower field) compared to 0.31 p.p.m.[27] in bicyclo[2.2.1]heptane. Examination of a Dreiding model of (11) with the 6-membered ring in a boat conformation shows that the nitronate group bisects the angle H-3$_{ax}$/C-3/H-3$_{endo}$ and the dihedral angle between H-1 and C=N is *ca.* 20°. The observed chemical shifts of H-1, H-3$_{exo}$, and H-3$_{endo}$ in the spectrum of (11) indicate that this Dreiding model is a good representation of the actual conformation.

Converting 2-nitrobornane into its anion (12) causes a downfield shift (0.24 p.p.m.) on the C-1 methyl group and an upfield shift (0.08 p.p.m.) on the bridgehead methyl groups. H-3$_{exo}$ shifts from δ 2.20 to 2.66 (d of m) whereas H-3$_{endo}$ moves upfield from 2.20 to 2.05 [d, 17 Hz; note absence of long-range coupling to H-7 seen in (11)]. It has been suggested [28] that bicyclo[2.2.1]-heptanes may undergo deformation modes called *contra* and *synchro* twisting to alleviate interactions between substituents. The observed shifts for (12) suggest a distortion which moves the nitronate grouping away from the C-1 methyl group and nearer to H-3$_{exo}$.

EXPERIMENTAL

Materials.—4-Ethoxycarbonyl-3-methyl-3-(1-nitroethyl)-cyclohexanone [mixture of epimers (1a) and (1b)] was prepared by Michael addition of nitroethane to Hagemann's ester catalysed by ethanolic benzyltrimethylammonium ethoxide.[29] The t-butyl ester (1c) was prepared similarly from 4-t-butoxycarbonyl-3-methylcyclohex-2-en-1-one. The acetal (3a) was prepared from (1a) by a standard procedure. 2-Nitroadamantane, nitrocyclohexane, *cis*-1-nitro-2-phenylcyclohexane, 1-nitro-*trans*-decalin, *endo*-2-nitronorbornane, and *endo*-2-nitrobornane were prepared from the corresponding oximes using the Iffland procedure.[30] They were purified by either recrystallising, distilling, or subliming *in vacuo* as appropriate. 2-Nitroadamantane was best purified by chromatography on silica gel, eluting with dichloromethane–light petroleum (b.p. 40—60 °C) (9 : 1) followed by sublimation *in vacuo* (70 °C at 15 mm Hg) to give analytically pure material: m.p. 179—180 °C, $\nu_{max.}$ (CH_2Cl_2) 2992s, 2860s, 1550—1535vs, and 1454s cm^{-1} (Found: C, 66.2; H, 8.0; N, 7.75. $C_{10}H_{15}NO_2$ requires C, 66.25; H, 8.35, N 7.75%).

1-Nitro-*trans*-decalin was isolated as a mixture of epimers which was distilled *in vacuo* (b.p. 82 °C at 0.75 mmHg) to give a colourless oil: $\nu_{max.}$ (film) 2920s, 2850s, 1550s, and 1450s cm^{-1} (Found: C, 65.35; H, 9.05; N, 7.6. $C_{10}H_{17}NO_2$ requires C, 65.55; H, 9.35; N, 7.65%). Pure *trans*, *trans*-1-nitrodecalin was obtained by stirring the mixture of epimers in ethanol with a catalytic amount (5 mol %) of NaOEt for 20 h at room temperature. Ethanol was removed and dichloromethane was added. Filtration and evaporation gave pure *trans,trans*-1-nitrodecalin as a colourless oil.

1-Methyl-2-nitrocyclohexane (80% *cis* isomer) was prepared by oxidising 2-methylcyclohexanone oxime with trifluoroperoxyacetic acid.[33]

Nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane were commercial products distilled before use. Pure solvent-free nitronate salts were prepared using the general method described.[31] Solvents were purified and dried according to standard methods.[32]

N.m.r. Measurements.—^{13}C N.m.r. spectra were recorded at 22.63 MHz for *ca.* 0.5 M solutions (except where noted otherwise for experiments examining concentration dependence) in CD_3OD or $(CD_3)_2SO$ in 10 mm diameter sample tubes by the pulse Fourier transform technique. A Bruker WH90 spectrometer was used with 4 or 8 K of data storage for accumulation of the free induction decays. The noise-modulated proton decoupling was sufficient to decouple the complete range of proton–carbon coupling, and pulses of approximately 25—36° (7—10 μs) were used. To confirm certain assignments, where possible the single frequency off-resonance decoupling technique was used.

The spectra for nitronate anions were recorded by either addition of 1.1 equivalents of base ($NaOCD_3$ or NaH) to the nitro compound in the appropriate solvent, or by dissolving pure pre-prepared nitronate salts, all manipulations being carried out under an inert atmosphere. For primary alkanenitronates, a 4 : 1 mixture of CH_3OH–CD_3OD was used, with the deuteriated solvent serving as the deuterium locking signal. Chemical shifts were measured downfield from Me_4Si (δ 0.00).

^{1}H N.m.r. spectra (internal reference Me_4Si) of 0.2—0.4 M solutions at 60 MHz [(1) and (2)], 90 MHz [(7a) and (7b)], and 100 MHz were recorded for all other compounds and their anions.

U.v. Spectroscopic Measurements.—The wavelengths of maximum absorption in the u.v. spectra of nitronate anions were determined by dissolving pure nitronate salts in the appropriate solvent. Measurements were made using a Pye Unicam SP 800 spectrophotometer, calibrated with a holmium filter, and are believed to be accurate to better than $\pm$ 1 nm. Where extinction coefficients varied, the highest value obtained was recorded.

Methanol was spectroscopic grade which was further purified by refluxing with sodium hydride and distilling under inert atmosphere. (*N.b.* Commercial spectroscopic grade methanol contained impurities which reacted with the nitronates; the above treatment was a satisfactory method for their removal.) Acetonitrile was spectroscopic grade, stirred with calcium hydride for 24 h, decanted, then distilled under an inert atmosphere. Propylene carbonate was stirred with molecular sieves (3A) for 24 h, then fractionally distilled *in vacuo*. All solvents were stored under argon in bottles fitted with a rubber septum. Prior to use, solvents were deoxygenated with argon. U.v. spectral measurements were made immediately after making up the nitronate solutions.

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