Special Effects in Nuclear Magnetic Resonance Spectra of Nitronate Anions

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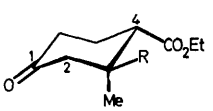
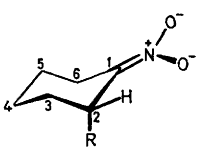
Summary ^{13}C N.m.r. spectra of nitronate anions show a marked solvent-dependent shift which correlates with electronic distribution in these anions; a deshielding effect of the nitronate grouping observed with ^1H n.m.r. spectra shows the axial conformer of 2-substituted cyclohexanenitronate anions to be preferred.

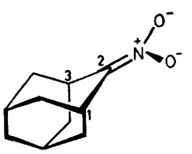
We have found that ^{13}C n.m.r. spectra of the nitronate anion (**2**) [derived from compound (**1**)] and anions from 1-nitropropane, 2-nitropropane, and 2-nitrocamphane,† respectively, show an appreciable solvent effect [$(CD_3)_2SO$ *vs.* CD_3OD] specific to the carbon atom of the nitronate grouping. In each case the resonance from this carbon atom appears at *ca.* 10 p.p.m. to lower field in methanol compared with Me_2SO.‡ It has been suggested[1] that the solvent-dependent (especially protic *vs.* aprotic solvents) u.v. spectra of certain nitronate anions are a consequence of differing charge distributions in the nitronate grouping, with greater electron density on oxygen atoms when the solvent is protic owing to hydrogen bonding between these atoms and the solvent. Our results strongly support this interpretation, since the shift to low field in methanol for nitronate carbon signifies depletion of charge density at this carbon for the reason given.



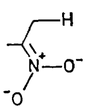
(1) R = $CHMeNO_2$
(2) R = $C(Me){=}NO_2^-$



(3) R = H
(4) R = Me
(5) R = Ph



(6)



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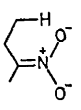

(8)

We have also found that ^1H n.m.r. spectra of nitronate anions (**2**)—(**6**)† reveal downfield shifts for specific protons, which give information about preferred conformation in mobile systems. In general, whenever the conformation of a nitronate anion requires a proton to lie in or near the plane defined by the atoms of the nitronate anion [as in (**7**) or (**8**) for the cases investigated], then this proton experiences a downfield shift of *ca.* 1·5 p.p.m. relative to its standard unperturbed position (the deshielding effect of the nitro-group in nitro-alkanes[2] and -arenes[3] has been recognised, but is difficult to quantify because of uncertainty of rotamer populations about the C–NO_2 bond). On conversion of compound (**1**) into its anion (**2**) in CD_3OD, spectral simplification occurs owing to ^2H-exchange at C-2 and C-6 and loss of the proton α to the nitro-group, but of particular note is the movement of the signal due to 4-H from δ 2·88 for (**1**) to 4·46 for (**2**). The latter observation can be explained if the ethoxycarbonyl and nitronate substituent are equatorial[4] on a chair ring [as depicted in (**2**)]. Then, if the conformation denoted by projection (**9**) is appreciably

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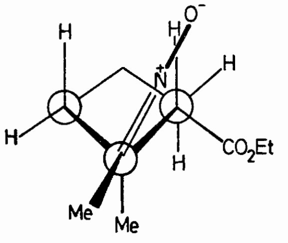
† For {^1H} ^{13}C n.m.r. spectra, 0·5 M-solutions of nitronate anions were prepared either [(**2**) and anion from 2-nitrocamphane] by deprotonation *in situ* using NaH (1·1 equiv.) for solutions in $(CD_3)_2SO$ or $NaOCD_3$ (1·1 equiv.) in CD_3OD, or by dissolving salts ($Et\bar{C}HNO_2Li^+$, $Me_2\bar{C}NO_2Li^+$) in the appropriate solvent. For ^1H n.m.r. spectra, anions were prepared as 0·2—0·4M-solutions by deprotonation *in situ* using either $NaOCD_3$ (2 equiv.) for solutions in CD_3OD [anions (**2**)—(**6**)] or a slight excess of NaH in $(CD_3)_2SO$ for anion (**2**). All solutions were prepared and maintained under inert atmosphere.

‡ *E.g.* for $Me_2\bar{C}NO_2$ in $(CD_3)_2SO$ (downfield from Me_4Si) 18·2 (CH_3) and 111·6 (CNO_2); in CD_3OD δ 19·0 and 121·5 p.p.m.

populated, 4-H lies in the plane of the nitronate grouping [*Cf.* (**8**)] and should be deshielded.[5] This effect is relatively insensitive to changing from protic to aprotic solvent as shown by the appearance of the 4-H resonance of (**2**) in $(CD_3)_2SO$ at δ 4·63. In this solvent, the signals from protons at C-2 are also observed and one of them is markedly deshielded (at δ 4·20, all other signals have $\delta \leqslant 2{\cdot}5$). This low field signal probably arises from 2-H_{ax} owing to significant population of conformer (**10**) as well as (**9**).



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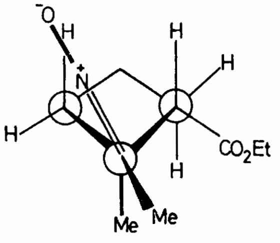

(10)

One nitronate oxygen and the C=O group have been omitted for clarity.

When the nitronate grouping is exocyclic to a cyclohexanoid ring [as in compounds (**3**)—(**6**)] it causes equatorial but not axial protons at C-2 and C-6 to experience an appreciable downfield shift. This is shown by comparing data for the cyclohexylnitronate anion (**3**) in which signals for 2-H_{ax} (6-H_{ax}) and 2-H_{eq} (6-H_{eq}) average at δ 2·57, with data for the adamantylnitronate ion (**6**) [signal for pseudo-equatorial 1-H (3-H) at δ 3·40]. These results imply that the difference in chemical shift between axial and equatorial protons α to a nitronate grouping in a cyclohexanoid system is *ca.* 1·5 p.p.m., the equatorial proton resonating at lower field.

In the ^{1}H n.m.r. spectrum of 2-methylcyclohexylnitronate anion (**4**) the signal for 2-H appears at δ 3·55 and by comparison with the spectrum of anion (**6**) is assigned to a proton residing principally at an equatorial position [the equatorial proton at C-6 resonates at δ 3·12, also well removed from the remaining 7-proton envelope (δ 1·2—2·3)]. Similarly, the spectrum of 2-phenylcyclohexanenitronate anion (**5**) shows 6-H_{eq} at δ 3·2 and 2-H at δ 4·62 (*cf.* δ 3·13 for 2-H in *cis*-2-phenyl-1-nitrocyclohexane). These results indicate a preference for the conformations depicted for anions (**4**) and (**5**). Our findings support the proposal[6] that 'allylic^{1,3} strain' in the equatorial conformer of 2-substituted cyclohexanenitronate anions will cause the axial conformer to be preferred. They contradict the suggestion[7] based on examination of u.v. spectra of 2-arylcyclohexanenitronate anions and molecular models of these compounds that their equatorial conformers are more stable.

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[3] D. Meuche and E. Heilbronner, *Helv. Chim. Acta*, 1962, **45**, 1965; P. R. Wells and P. G. E. Alcorn, *Austral. J. Chem.*, 1963, **16**, 1108; I. Yamaguchi, *Mol. Phys.*, 1963, **6**, 105; Yu. V. Baskov, T. Urbanski, M. Witanowski, and L. Stefaniak, *Tetrahedron*, 1964, **20**, 1519; see also reference 1(a).

[4] The relative stereochemistry of these substituents is *trans*, A. L. Begbie, unpublished results.

[5] By analogy with the effect observed with the neutral nitro-group (refs. 2 and 3), the oximido-group (A. C. Huitric, D. B. Roll, and J. R. De Boer, *J. Org. Chem.*, 1967, **32**, 1661 and references therein), an alkoxy-anion (S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 1965, **87**, 5247), and the carboxylate anion (L. Pogliani and M. Ellenberger, *J. Amer. Chem. Soc.*, 1974, **96**, 1621).

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