The Structure of Nitro-anion-radicals. An Investigation employing Electron Spin Resonance Spectroscopy and INDO (Intermediate Neglect of Differential Overlap) Molecular Orbital Calculations

By **Bruce C. Gilbert** * and **Michael Trenwith,** Department of Chemistry, University of York, Heslington York YO1 5DD

INDO Molecular orbital calculations support e.s.r. evidence which suggests that aliphatic nitro-anion-radicals are pyramidal about the nitrogen atom. In contrast, aromatic nitro-anion-radicals appear to be planar about nitrogen except in cases where *ortho*-substitution causes twisting and bending of the nitro-group.

MANY organic compounds which contain the nitro-function readily undergo one-electron reduction to form anion-radicals which are sufficiently long-lived for investigation by e.s.r. spectroscopy. Earlier applications of this technique to the elucidation of conformational aspects of some aliphatic and aromatic nitro-anion-radicals are summarised in the review by Geske.[1]

Our continuing interest [2,3] in the information about the geometry of a radical obtainable from its e.s.r. spectrum has prompted us to investigate some representative nitro-anion-radicals in greater detail, with particular reference to the shape of the nitro-function. Previously it has been proposed on the basis of ^{14}N anisotropic hyperfine splittings obtained from solid state spectra of various aromatic [4a] mono- and di-nitro-anions and

---

[1] D. H. Geske, *Progr. Phys. Org. Chem.*, 1967, **4**, 125.

[2] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc.* (*A*), 1971, 124.

[3] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 786.

[4] (*a*) W. M. Fox, J. M. Gross, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1966, 448; (*b*) M. C. R. Symons and J. H. Sharp, *Nature*, 1969, **224**, 1297.

aliphatic anions,[4b] that there is a tendency for the nitro-group to become pyramidal (particularly for the aliphatic species). We have also argued[2] that, since a(N) for aliphatic nitro-anion-radicals ($RNO_2^{-\cdot}$, *ca.* 2·5 mT) is considerably greater than that for the analogous nitroxides ($R_2NO\cdot$, *ca.* 1·5 mT), despite the similar unpaired electron density on nitrogen in the two cases, there arises the possibility of a greater degree of bending at nitrogen in the former series. This might be as expected for the more highly oxygenated radical [for example, the 1,3-dioxolan-2-yl radical ($\cdot\overline{CHOCH_2CH_2O}$) is more bent at the radical centre than is tetrahydrofuran-2-yl ($\cdot\overline{CHOCH_2CH_2CH_2}$)]. Recently-obtained ^{13}C data for some aliphatic species have also been tentatively rationalised[5] on the basis of non-planarity.

We have made a detailed study of the splitting constants (including those from ^{13}C) in the e.s.r. spectra of some aliphatic anion-radicals and have performed INDO MO calculations[6] for the anion-radicals of nitromethane, nitroethane, and nitrobenzene. It was hoped that the calculations would provide corroborative evidence to support semi-quantitative conclusions, based on e.s.r., concerning possible skeletal deformations (including bending and twisting) in these radicals.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E3 spectrometer equipped with 100 kHz modulation and an X band klystron. Hyperfine splittings were measured to within ±0·005 mT by comparison with the spectra from an aqueous solution of Fremy's salt [a(N) = 1·3091 ± 0·0004 mT[7]] and from a solution of *p*-benzosemiquinone in aqueous ethanol [a(H) = 0·2368 ± 0·0001 mT[8]]. Machine operating conditions under which the observation of ^{13}C satellites is facilitated have been noted.[2]

Aliphatic nitro-anion-radicals were generated in aqueous solution principally by one-electron reduction of nitro-compounds in a rapid-mixing flow system[9] at pH 8—9. The radical $\cdot CMe_2OH$ [from titanium(III), hydrogen peroxide, and isopropyl alcohol] was found to be a most effective reductant[10] and $\cdot CO_2^-$ (from formate ion) was also employed,[11] although less effectively. A two-entry, single-stage mixing-chamber coupled to an aqueous sample cell was employed. One reactant stream contained 12·5% (w/v) titanium(III) chloride solution (10 ml l^{-1}), disodium ethylenediaminetetra-acetate (6 g l^{-1}), isopropyl alcohol (or sodium formate), and ammonia (*d* 0·880) to give an effluent pH 8—9. The second stream contained 100-volume hydrogen peroxide (3 ml l^{-1}), isopropyl alcohol (or sodium formate), and the appropriate nitro-compound. Each stream was deoxygenated with a nitrogen purge; flow rates and the concentrations of nitro-compound and donor substrate were adjusted to obtain maximum signal levels. In addition, spin-trapping of the methyl radical (from reaction of hydroxyl with dimethyl sulphoxide[12]) with suitable nitro-*aci*-anions[5,13] was found to be a particularly effective method for preparing the radicals $MeCH_2NO_2^{-\cdot}$, $Me_2CHNO_2^{-\cdot}$, and $Me_3CNO_2^{-\cdot}$. All materials were commercial samples which were used without further purification except for 2-methyl-2-nitropropane which was prepared from t-butylamine by the method of Kornblum and Clutter.[14]

INDO Calculations[6,15,16] were carried out with versions of the INDO programme kindly supplied by the Quantum Chemistry Programme Exchange; the sub-routine to perform annihilation of the quartet spin state[17] was incorporated by Dr. M. F. Chiu and utilised the appropriate parameters.[16] Calculations were executed both on the Elliot 4130 computer at the University of York and on the 1906A at the S.R.C. Atlas Computer Laboratory, Chilton.

RESULTS AND DISCUSSION

(*a*) *Aliphatic Radicals.*—Simple aliphatic nitro-anion-radicals have been prepared in aqueous solution by electrolytic[18,19] and chemical[10] reduction, and by radical addition to nitro-*aci*-anions[13] and nitrite ion.[20] The available ^{13}C data are as follows: $^-O_3SCH_2NO_2^{-\cdot}$ a(C) = 0·237 mT;[5] $^-O_2CNO_2^{-\cdot}$ a(C) = 0·374 mT;[20] $^-SCH_2NO_2^{-\cdot}$ a(C) < 0·14 mT (undetectable);[5] $^-O_2CCH_2NO_2^{-\cdot}$ a(β–C) < 0·14 mT, a(γ–C) = 1·075 mT;[5] $MeCOCH_2NO_2^{-\cdot}$ a(β–C) undetectable, a(γ–C) = 1·105 mT.[21]

We have investigated the anion-radicals of $MeNO_2$, $EtNO_2$, Pr^iNO_2, and Bu^tNO_2 and the related tertiary alkyl-substituted radicals $HOCH_2CMe_2NO_2^{-\cdot}$ and $[HOCH_2]_3CNO_2^{-\cdot}$; splittings for ^{14}N and ^1H are close to those previously reported[10,13,18,19] for the first three species (see Table 1 for details of the first two). For $Bu^tNO_2^{-\cdot}$ a(N) = 2·659 and a(9H) = 0·020 mT; for $HOCH_2CMe_2NO_2^{-\cdot}$ a(N) = 2·643 and a(8H) = 0·020 mT; for $[HOCH_2]_3CNO_2^{-\cdot}$ a(N) = 2·531 mT. Results for ^{13}C satellites are as follows. For $MeNO_2^{-\cdot}$ no splitting could be detected and we place an upper limit on $a(^{13}C)$ of *ca.* 0·2 mT. The β–C splitting for $EtNO_2^{-\cdot}$ also defied detection (we estimate it as <0·25 mT) and the observed splitting of 0·605 mT is attributed to the γ-carbon

---

[5] G. P. Laroff and R. W. Fessenden, *J. Magnetic Resonance*, 1973, **9**, 434.

[6] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026.

[7] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.

[8] M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **42**, 1350.

[9] R. O. C. Norman and B. C. Gilbert, *Adv. Phys. Org. Chem.*, 1967, **5**, 53.

[10] M. McMillan and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1968, 590.

[11] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 400.

[12] W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625.

[13] B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S Perkin II*, 1972, 1272.

[14] N. Kornblum and R. J. Clutter, *J. Amer. Chem. Soc.*, 1954, **76**, 4494.

[15] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 1968, **90**, 4201.

[16] D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.*, 1968, **48**, 5532.

[17] T. Amos and L. C. Snyder, *J. Chem. Phys.*, 1964, **41**, 1773.

[18] L. H. Piette, P. Ludwig, and R. N. Adams, *J. Amer. Chem. Soc.*, 1962, **84**, 4212.

[19] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1962, **37**, 1326; 1963, **38**, 1254.

[20] H. Zeldes and R. Livingston, *J. Amer. Chem. Soc.*, 1968, **90**, 4540.

[21] R. Livingston, J. K. Dohrmann, and H. Zeldes, *J. Chem. Phys.*, 1970, **53**, 2448.

For $\text{Pr}^i\text{NO}_2^{\overline{\cdot}}$ a(β–C) < 0·3 mT and a(γ–C) = 0·511 mT. The satellites for $\text{Bu}^t\text{NO}_2^{\overline{\cdot}}$ and $\text{HOCH}_2\text{CMe}_2\text{NO}_2^{\overline{\cdot}}$ both have $a(^{13}\text{C})$ *ca.* 0·37 mT; from the relative intensities of these compared with the main signals it is clear that they derive definitely from the γ-carbons (and possibly also from fortuitously equivalent β-carbons). For the anion of tris(hydroxymethyl)nitromethane, a(β–C) = 0·395, a(γ–C) = 0·550 mT.

Now the simple dialkyl nitroxides referred to earlier are regarded as being essentially planar about nitrogen,[22] and our INDO calculations [23] for $\text{Me}_2\text{NO}\cdot$ corroborate this. Thus the origin of the observed β-^{13}C splittings for these radicals [*e.g.* 0·61 ± 0·01 mT for [24] $^{13}\text{CH}_3\overset{+\cdot}{\text{N}}\text{-}(\text{CMe}_2\text{CH}_2\text{CMe}_3)\text{O}^-$] is understandable in terms of spin polarisation involving the unpaired electron on nitrogen and the σ electrons in the N–C bond [an n.m.r. study [25] of some stable nitroxides has confirmed that a(β–C) is negative]. The increase in a(N) and evident decrease in a(β–C) for nitro-anion-radicals compared with nitroxides suggests that the former prefer a non-planar structure (*i.e.* with bending about nitrogen); the orbital of the unpaired electron then acquires some *s* character [raising a(N)] whereas the transfer of positive spin to the β-carbon through the σ system opposes the negative spin density induced at the carbon by spin polarisation. The consequent reduction in $a(^{13}\text{C})$ is analogous to that for a(α–H) when oxygen substitution (and hence bending) is introduced in an alkyl radical.[2,3]

Further evidence for bending derives from the analysis [4b] of the solid-state spectra of some aliphatic nitro-anions;[26] the anisotropy in the nitrogen splitting leads to a calculated 2*p* : 2*s* ratio for the unpaired electron on nitrogen of 11·4. Anisotropic splittings for ^{14}N have also been determined for the closely-related neutral radicals $\text{R}^1\text{N}(\text{OR}^2)\text{O}\cdot$ from solid-state spectra,[27] and we can use these to derive the 2*p* : 2*s* ratio for the electron on nitrogen as 11·6. These results clearly correspond to a non-planar radical centre for both $\text{RNO}_2^{\overline{\cdot}}$ and $\text{R}^1\text{N}(\text{OR}^2)\text{O}\cdot$, these being less pyramidal than NO_3^{2-} (for which the ratio [4b] is 7·8) but considerably more bent than $\text{ArNO}_2^{\overline{\cdot}}$.[4a,b]

The considerably larger β-^{13}C splittings for $^-\text{O}_2\text{CNO}_2^{\overline{\cdot}}$ and $[\text{HOCH}_2]_3\text{CNO}_2^{\overline{\cdot}}$ than for the simple alkyl-substituted anion-radicals may reflect a more nearly planar radical centre for these examples. This could result from increased conjugation ($^-\text{O}_2\text{CNO}_2^{\overline{\cdot}}$) and steric compression ($[\text{HOCH}_2]_3\text{CNO}_2^{\overline{\cdot}}$) both of which might encourage flattening; indeed, for $^-\text{O}_2\text{CNO}_2^{\overline{\cdot}}$ the low nitrogen splitting (1·438 mT) confirms this [20] and it is also interesting that a(N) for $[\text{HOCH}_2]_3\text{CNO}_2^{\overline{\cdot}}$ (2·531) is smaller than those for the other tertiary alkyl-substituted anions. Little can be added concerning the γ-carbon splittings, but we can employ a value of *ca.* 0·4 mT (for $\text{Bu}^t\text{NO}_2^{\overline{\cdot}}$) as characteristic of a γ-carbon whose averaged value of $\cos^2\theta$ is $\frac{1}{2}$ (θ is the dihedral angle between the $\text{C}_\beta\text{–C}_\gamma$ bond and the unpaired electron's orbital on nitrogen). If the γ-carbon interacts with the unpaired electron by hyperconjugation (with a $\cos^2\theta$ relationship), the large values of $a(\gamma\text{-}^{13}\text{C})$ in $^-\text{O}_2\text{CCH}_2\text{NO}_2^{\overline{\cdot}}$ and $\text{CH}_3\text{COCH}_2\text{NO}_2^{\overline{\cdot}}$ suggest that the favoured conformation has the $\text{C}_\beta\text{–C}_\gamma$ bond eclipsing the half-filled orbital. These would then provide further instances of conformational preference dominated by an interaction involving an inductive effect (β–γ bond) and a lone-pair of electrons at the formal radical centre (*cf.* $\cdot\text{CHOHCH}_2\text{OH}$ [3]). Such an interaction would also have a tendency to flatten the radical centre and may account for the reduction in a(N), compared to the nitromethane anion-radical, for $^-\text{O}_3\text{SCH}_2\text{NO}_2^{\overline{\cdot}}$ and $^-\text{SCH}_2\text{NO}_2^{\overline{\cdot}}$ as well as for $^-\text{O}_2\text{CCH}_2\text{NO}_2^{\overline{\cdot}}$ and $\text{CH}_3\text{COCH}_2\text{NO}_2^{\overline{\cdot}}$.

We have also performed INDO MO calculations, which have enjoyed considerable success in calculations of radical geometries (see, *e.g.*, refs. 2, 3, 6, 15, and 16) for $\text{MeNO}_2^{\overline{\cdot}}$ and $\text{EtNO}_2^{\overline{\cdot}}$. The following bond-lengths, typical of aliphatic nitro-compounds,[28,29] were employed: *R*(N–O) 1·21, *R*(C–N) 1·475, *R*(C–H) 1·101, and *R*(C–C) 1·54 Å. Starting geometries are depicted in Figures 1(a) and (b), respectively, with $\widehat{\text{ONO}}$ 127°, while Figure 1(c) defines the parameters which were varied.

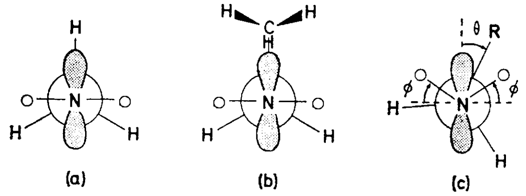

FIGURE 1 Starting geometries for INDO calculations on (a) $\text{MeNO}_2^{\overline{\cdot}}$ and (b) $\text{EtNO}_2^{\overline{\cdot}}$; (c) the variable parameters defining bending (ϕ) and rotation (θ), for $\text{MeNO}_2^{\overline{\cdot}}$ (R = H), and $\text{EtNO}_2^{\overline{\cdot}}$ (R = Me). The angle ϕ is that made by the projection of the N–O bond on the plane passing through nitrogen parallel to the plane of the paper

Keeping θ = 0°, the total energy becomes more negative as bending is introduced; ϕ was increased in 1° steps and an energy minimum was found to occur for both $\text{MeNO}_2^{\overline{\cdot}}$ and $\text{EtNO}_2^{\overline{\cdot}}$ at 6°. Calculated splittings and energies for both planar and pyramidal radicals are given in Table 1. It is encouraging to find that the calculated splittings (especially after spin annihilation) for the minimum energy conformation of $\text{MeNO}_2^{\overline{\cdot}}$ are in good agreement with experiment, being much better than those for the planar geometry. Even closer agreement is achieved setting ϕ = 7°, the total energy being not greatly higher in this case. In particular, the direction of change of both a(N) and $a(^{13}\text{C})$ with bending is as anticipated. For $\text{MeNO}_2^{\overline{\cdot}}$, with ϕ = 7°, the 2*p* : 2*s* ratio (after annihilation) for the unpaired electron on nitrogen is 21·1. The theoretical values of a(β–H),

---

[22] E. G. Janzen, *Topics Stereochem.*, 1971, **6**, 177.

[23] B. C. Gilbert and M. Trenwith, unpublished results.

[24] R. Brière, G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Mol. Phys.*, 1971, **20**, 211.

[25] G. F. Hatch and R. W. Kreilick, *J. Chem. Phys.*, 1972, **57**, 3696.

[26] C. Chachaty, *Compt. rend., Ser. C.*, 1966, **262**, 680.

[27] C. Chachaty and C. Rosilio, *J. Chim. phys.*, 1967, **64**, 777.

[28] 'Tables of Interatomic Distances,' Chem. Soc. Special Publ. No. 11, London, 1958.

[29] 'Handbook of Chemistry and Physics,' Chemical Rubber Co., Cleveland, 46th edn., 1965—1966.

a(γ-C), and a(γ-H) for $\mathrm{EtNO_2}^{\overline{\cdot}}$ are not strictly comparable with experiment since the calculations in Table 1 refer specifically to the conformation with the methyl group eclipsing the half-filled orbital. However, INDO predicts the expected low β-hydrogen splitting for this conformation compared to a freely-rotating CH_3 group, and the calculated γ-C splitting is of the appropriate order of magnitude.

TABLE 1

Calculated hyperfine splittings (mT) and total energies (a.u.) for $\mathrm{MeNO_2}^{\overline{\cdot}}$ and $\mathrm{EtNO_2}^{\overline{\cdot}}$ [a]

			$a(\gamma\text{-H})$ [b]	$a(\gamma\text{-C})$	$a(\beta\text{-H})$ [c]	$a(\beta\text{-C})$	$a(^{14}N)$	$a(^{17}O)$	Total energy
$\mathrm{MeNO_2}^{\overline{\cdot}}$	ϕ [d] = 0°	ba [e]			1·262	−0·737	1·115	0·511	−55·4583084
		aa [f]			1·140	−0·247	1·118	0·504	
	ϕ = 6°	ba			1·203	−0·433	1·423	0·487	−55·4585189
		aa			1·098	−0·032	2·276	0·492	
	ϕ = 7°	ba			1·183	−0·336	1·521	0·480	−55·4584882
		aa			1·083	0·037	2·643	0·488	
	Experimental [g]				1·203	<0·2	2·582		
$\mathrm{EtNO_2}^{\overline{\cdot}}$	ϕ = 0°	ba	−0·058	0·615	0·738	−0·606	1·163	0·516	−63·8976761
		aa	0·069	0·498	0·642	−0·188	1·167	0·510	
	ϕ = 6°	ba	0·156	0·643	0·499	−0·460	1·477	0·492	−63·8978973
		aa	0·224	0·523	0·454	−0·107	2·360	0·497	
	ϕ = 7°	ba	0·192	0·640	0·458	−0·382	1·581	0·483	−63·8978946
		aa	0·249	0·522	0·422	−0·055	2·755	0·492	
	Experimental [g]		0·045	0·605	0·963	<0·25	2·597		

[a] Conformation with the methyl group eclipsing the unpaired electron (see text). [b] Arithmetic average of three values for $\mathrm{EtNO_2}^{\overline{\cdot}}$. [c] For $\mathrm{MeNO_2}^{\overline{\cdot}}$ average of three values. [d] See Figure 1(c). [e] Before annihilation of the quartet spin state. [f] After annihilation. [g] See text.

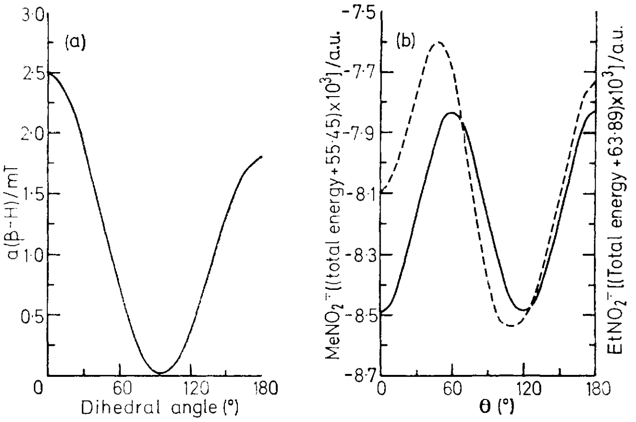

FIGURE 2 (a) Variation with dihedral angle of calculated β-hydrogen splitting (after annihilation) for $\mathrm{MeNO_2}^{\overline{\cdot}}$. (b) Total energy for $\mathrm{MeNO_2}^{\overline{\cdot}}$ and $\mathrm{EtNO_2}^{\overline{\cdot}}$ as a function of θ: $\mathrm{MeNO_2}^{\overline{\cdot}}$ ——; $\mathrm{EtNO_2}^{\overline{\cdot}}$ · · · ·

For both $\mathrm{MeNO_2}^{\overline{\cdot}}$ and $\mathrm{EtNO_2}^{\overline{\cdot}}$ we have also investigated rotation about the N–C bond with a fixed degree of bending at nitrogen ($\phi = 7°$). The variation with dihedral angle of a(β–H) for $\mathrm{MeNO_2}^{\overline{\cdot}}$, after annihilation, is shown in Figure 2(a); for $\mathrm{EtNO_2}^{\overline{\cdot}}$ the curve is almost identical. For both radicals the angular dependence of the β-hydrogen splitting was found to follow an empirical relationship of the form $a(\beta\text{–H}) = B_0 + B \cos\theta + B' \cos^2\theta$ (rather than a simple $\cos^2\theta$ dependence) with, for $\mathrm{MeNO_2}^{\overline{\cdot}}$, B_0, B, and B' equal to 0·023, 0·359, and 2·114 mT, respectively (for $\mathrm{EtNO_2}^{\overline{\cdot}}$, 0·025, 0·360, and 2·150, respectively). The last term in each case ($B' \cos^2\theta$) still clearly dominates as expected for hyperconjugative interaction; however, caution should evidently be exercised in making precise conformational predictions for γ-alkyl substituents based on the magnitude of a(β–H) in non-planar radicals of this type.

The calculated energies [Figure 2(b)] indicate that for $\mathrm{MeNO_2}^{\overline{\cdot}}$ the eclipsing conformation [Figure 1(a)] is the one of lowest energy, with the three-fold barrier to rotation about the N–C bond being $|E(\theta = 0°) - E(\theta = 60°)| = 1·72$ kJ mol^{-1}. This figure may be compared with a theoretical estimate of the barrier to rotation in the nitromethane molecule of 0·04 kJ mol^{-1}.[30] It is impossible to say at this stage whether or not the difference is significant. The corresponding curve for $\mathrm{EtNO_2}^{\overline{\cdot}}$ is similar except that minima of different energy are obtained. Although one of these has the methyl group eclipsing the orbital of the unpaired electron [Figure 1(b)], which is as expected[1,18,19] from consideration of the lower a(β–H) value than for $\mathrm{MeNO_2}^{\overline{\cdot}}$, it is surprising that the overall minimum energy occurs at θ = 110°. In this conformation the calculated (averaged) value of a(β–H) after annihilation is 1·547 mT which is not in accord with the experimental observation since appreciable contributions from such a conformation would lead to a *larger* value of a(β–H) than for $\mathrm{MeNO_2}^{\overline{\cdot}}$. At present we are unaware of the reason for the discrepancy and prefer not to draw further conclusions concerning the calculated conformational preference, except to note that INDO predicts a barrier to rotation of $|E(\theta = 110°) - E(\theta = 50°)| = 2·47$ kJ mol^{-1}. The (two-fold) barrier to rotation for this radical has previously been estimated[19] using classical and quantum mechanical analysis of the temperature dependence of a(β–H) as 4·60 kJ mol^{-1}.

(*b*) *Aromatic Radicals*.—Table 2 contains data for the nitrobenzene anion-radical in a variety of solvents,[18,31-33]

---

[30] M. I. Dakhis, A. A. Levin, and V. A. Shlyapochnikov, *J. Mol. Structure*, 1972, **14**, 321.

[31] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 609.

[32] D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671.

[33] W. M. Gulick, jun., and D. H. Geske, *J. Amer. Chem. Soc.*, 1965, **87**, 4049.

including hexamethylphosphoramide (HMPA)[34] in which the ion is thought to be free of solvent and counter-ion interactions. Earlier work has been summarised by Geske.[1] Our INDO calculations for $PhNO_2^{\cdot-}$ employed the following parameters:[28,29] R(N–O) 1·21, R(C–N) 1·48, R(C–C) 1·38, and R(C–H) 1·08 Å. The starting geometry comprised a regular hexagonal structure for the aromatic nucleus, with a planar nitro-group (ONO 124°) in the plane of the ring.

Table 2

Experimental hyperfine splitting constants (mT) for the nitrobenzene anion-radical in various media

Solvent	$a(^{14}N)$	$a(o\text{-}H)$	$a(m\text{-}H)$	$a(p\text{-}H)$	$a(^{17}O)$	Ref.
Water	1·387	0·330	0·112	0·352		18
MeCN	1·032	0·339	0·109	0·397		31, 32
	(+) 1·029				(−) 0·886	33[c]
DMF[a]	0·970	0·336	0·107	0·403		31
	(+) 0·967				(−) 0·884	33[c,d]
HMPA[b]	0·848	0·334	0·101	0·422		34

[a] NN-Dimethylformamide. [b] Hexamethylphosphoramide. [c] See ref. 36 for deductions about the signs of $a(^{14}N)$ and $a(^{17}O)$. [d] An unassigned ^{13}C-splitting (one nucleus) of 0·47 mT was also resolved.

We first studied the effect of bending at nitrogen [*cf.* Figure 1(c); bending is defined similarly]; in marked contrast to the findings for the aliphatic ions the energy *increases* with increasing ϕ. The calculated results for the planar radical ($\phi = 0°$) are displayed in Table 3(a). In addition to the familiar parametrisation schemes due to Pople, Beveridge, and Dobosh (PBD)[15] and to Beveridge and Dobosh (BD),[16] which are appropriate for spin densities calculated before (ba) and after (aa) annihilation of the quartet spin state, respectively, we indicate splittings derived using a direct parametrisation scheme (DP).[35]

Table 3

Total energy (a.u.) and hyperfine splitting constants (mT) calculated for specific geometries of the nitrobenzene anion-radical

Geometry[a]	Total energy	Parametrisation	$a(^{14}N)$	$a(o\text{-}H)$	$a(m\text{-}H)$	$a(p\text{-}H)$	$a(^{17}O)$
(a) Planar nitro-group	−91·185936	PBD[b]-ba[e]	0·900	−0·262	0·123	−0·249	0·467
		DP[c]-ba	1·305	−0·425	0·200	−0·405	−0·866
		BD[d]-aa[f]	0·901	−0·115	0·054	−0·109	0·460
		DP-aa	0·440	−0·141	0·067	−0·135	−0·291
(b) Skeletal distortion	−91·188696	PBD-ba	0·840	−0·293	0·149	−0·311	0·450
		DP-ba	1·217	−0·475	0·242	−0·505	−0·836
		BD-aa	0·839	−0·128	0·066	−0·136	0·444
		DP-aa	0·410	−0·158	0·081	−0·168	−0·281
(c) Twisted (75°) and bent nitro-group ($\phi = 5°$)	−91·175861	PBD-ba	1·438	−0·073	0·081	−0·032	0·501
		DP-ba	2·085	−0·119	0·131	−0·052	−0·930
		BD-aa	2·175	−0·028	0·058	−0·014	0·507
		DP-aa	1·061	−0·034	0·071	−0·017	−0·321

[a] See text for full details. [b] Ref. 15. [c] Ref. 35. [d] Ref. 16. [e] Before annihilation of the quartet spin state. [f] After annihilation.

It is more appropriate to compare calculated results with experimental observations on the 'isolated' radical in HMPA. Inspection of Tables 2 and 3(a) reveals that there is reasonably good agreement for a(N) with a planar nitro-group using both PBD and BD parametrisation, though the former gives somewhat better agreement with the ring-hydrogen splittings. The DP scheme (before annihilation) gives good agreement for $a(^{17}O)$ and approximates quite reasonably the a(N) and a(H) values. However, for all schemes, $a(p\text{-}H)$ is calculated to be rather less than $a(o\text{-}H)$, the reverse of the experimental observation, and $a(m\text{-}H)$ is generally overestimated. Calculated ^{13}C-couplings are unable to assist in the unambiguous assignment of the 0·47 mT splitting.[33] The $2p:2s$ ratio for the unpaired electron on nitrogen is calculated (before annihilation) as 17·7, which is comparable with the ratios for a range of aromatic nitro-anion-radicals deduced[4a] from anisotropic spectra (15—24; see footnote 36, ref. 36 and ref. 4*b*).

Since INDO calculations[37,38] for the benzyl radical $PhCH_2^{\cdot}$ are in better agreement with experiment if a 'distorted' structure is assumed for the ring (emphasising the p-quinonoid character), we also investigated the appropriate geometrical variation for $PhNO_2^{\cdot-}$. As a preliminary to this, however, the relief of any possible steric compression between the nitro-group and the *ortho*-protons was allowed for by twisting the planar nitro-group out of the plane of the ring in steps of 2°. We found that a shallow minimum in the total energy did occur at 2° and maintained this angle of twist in calculations of skeletal distortion. Shortening of the C(2)–C(3) and C(5)–C(6) bonds (from 1·38 Å) resulted in the total energy becoming less negative; however, if, instead, the C(1)–C(2), C(3)–C(4), C(4)–C(5), and C(6)–C(1) bonds were simultaneously lengthened (*i.e.* again accentuating quinonoid character), a minimum in the energy was found to occur at a bond length of 1·40 Å. Results at this energy minimum are displayed in Table 3(b) which reveals that the nitrogen splitting (PBD and BD) is in even better agreement with experiment than

---

[34] G. R. Stevenson, L. Echegoyen, and L. R. Lizardi, *J. Phys. Chem.*, 1972, **76**, 1439.

[35] M. F. Chiu, B. C. Gilbert, and B. T. Sutcliffe, *J. Phys. Chem.*, 1972, **76**, 553.

[36] W. M. Gulick, jun., W. E. Geiger, jun., and D. H. Geske, *J. Amer. Chem. Soc.*, 1968, **90**, 4218.

[37] D. L. Beveridge and E. Guth, *J. Chem. Phys.*, 1971, **55**, 458.

[38] H. G. Benson and A. Hudson, *Mol. Phys.*, 1971, **20**, 185.

previously. Further, the correct sequence of *o*- and *p*-hydrogen splittings is now reproduced, although numerical agreement with experiment is still not good. No doubt more extensive calculations could achieve closer agreement between calculated and experimental splittings.

A detailed study of a wide range of alkylnitrobenzene anion-radicals [39] has revealed that with *ortho*-substituents of increasing size, and especially with di-*o*-alkylation, the nitro-group becomes forced out of the plane of the aromatic ring. Spin delocalisation from the nitro-group into the ring is consequently reduced, so that a(N) increases while at the same time the ring-hydrogen splittings decrease [for *e.g.*,[39] for the anion-radicals of 2,3,5,6-tetramethylnitrobenzene and 2,6-dimethylnitrobenzene a(N) is 2·04 and 1·78, respectively, and, for the latter, a(*o*-Me) = 0·085, a(*m*-H) = 0·088, and a(*p*-H) = 1 14 mT].

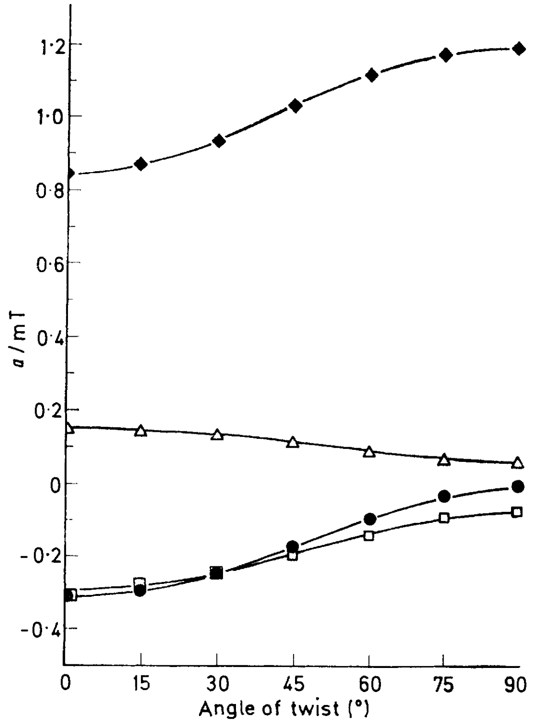

FIGURE 3 Dependence of calculated nitrogen and hydrogen hyperfine coupling constants (before annihilation-PBD parametrisation [15]) for $\mathrm{PhNO_2}^{-\cdot}$ on the angle of twist of the nitro-group out of the plane of the aromatic ring: a(N) ◆; a(*o*-H) □; a(*m*-H) △; a(*p*-H) ●

Calculations were therefore performed for $\mathrm{PhNO_2}^{-\cdot}$ with the nitro-group rotated (*i.e.* twisted) out of the plane of the ring, in steps of 15° (the deformed geometry being maintained). The results (PBD–ba) are depicted in Figure 3; the calculations correctly predict the direction (though not the magnitude) of the change in a(N) and give a reasonable account of the ring-proton splittings. Thus, for the 2,6-dimethylnitrobenzene anion-radical an angle of twist of *ca.* 60° seems appropriate [though a(*p*–H) is overestimated]. The calculations also predict a limiting order of a(*m*–H) $\geqslant$ a(*o*–H) > a(*p*–H), which is probably typical of an aromatic system twisted out of conjugation with an unpaired electron (see, *e.g.*, results for hindered nitroxides [40]). The appropriate experimental data for a test of this hypothesis are not available.

We anticipated that the nitro-function would also become increasingly ' aliphatic-like ' as it is rotated out of the plane of the benzene ring (see also ref. 4) and consequently that bending should be induced, with the appropriate increase in a(N). We thus fixed the nitro-group at an out-of-plane angle of 75° [this is close to the value estimated for the 2,3,5,6-tetramethylnitrobenzene anion-radical from consideration of the magnitude of a(N)] and performed calculations for bending about nitrogen (ϕ = 5 and 10°). The calculated energy is lower for ϕ = 5° (*i.e.* a slightly pyramidal nitro-group) than for ϕ = 0° (planar) and 10°; it can be seen [Table 3(c)] that the large nitrogen splitting is now reproduced. The small extent of bending has little effect on the calculated ring-proton splittings.

Conclusions.—INDO Calculations for $\mathrm{MeNO_2}^{-\cdot}$ and $\mathrm{EtNO_2}^{-\cdot}$ provide corroborative evidence for conclusions based on ^{14}N and ^{13}C hyperfine splittings that the nitro-function in these radicals is pyramidal (bending *ca.* 6°). In both examples the appropriate energy minimum has been located and the calculated splittings are in reasonable agreement with experimental observations.

In contrast, INDO results for $\mathrm{PhNO_2}^{-\cdot}$ suggest that the radical is planar with a small extent of distortion in the ring to accommodate some *p*-quinonoid character. Good agreement is then obtained between experimental and calculated splittings (especially those derived before annihilation). For aromatic nitro-anion-radicals which are alkylated in the *ortho*-positions the trends in the hyperfine splittings are reproduced by a model in which twisting of the nitro-group out of the plane of the ring also induces some bending at nitrogen. For the anion-radical of 2,3,5,6-tetramethylnitrobenzene we find that good agreement with experiment is obtained for a twist angle of 75° and 5° bending at nitrogen.

We conclude that nitro-anion-radicals provide further examples of the importance of geometrical variations, as well as of electronic effects, on e.s.r. spectra and that INDO MO calculations provide a useful means for their investigation.

We are grateful to Dr. M. F. Chiu, for assistance with the INDO programme and for helpful discussions, and to the S.R.C. for computing facilities at Chilton and a Research Studentship (for M. T.).

[3/1292 *Received*, 19*th June*, 1973]

---

[39] D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Amer. Chem. Soc.*, 1964, **86**, 987.

[40] A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481.