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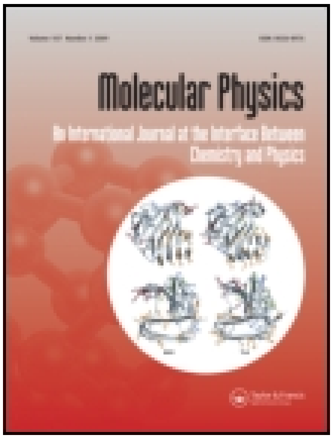

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Electron spin resonance investigation of carbon-13 hyperfine interactions in nitrobenzene anion radical

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Electron spin resonance investigation of carbon-13 hyperfine interactions in nitrobenzene anion radical

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Synthesis of carbon-13 enriched nitrobenzene which contains 22·5 mole per cent of nitrobenzene-1-^{13}C and an equal amount of nitrobenzene-4-^{13}C has been accomplished. We report the carbon-13 hyperfine interactions in the corresponding anion radicals in a variety of solvent media. In hexamethylphosphoramide $a_{C_1} = -7{\cdot}05$ gauss and $a_{C_4} = 6{\cdot}14$ gauss. These couplings change to $-9{\cdot}03$ gauss and 5·31 gauss, respectively, when the solvent medium is dimethylformamide containing 0·598 mole fraction of water. The solvent dependence of a_{C_1} is consistent with the radical remaining planar as opposed to adopting a pyramidal conformation at the nitrogen when hydrogen bonds form between the radical anion and protic solvents. Data reported here provide an experimental means to estimate the spin density distribution in nitrobenzene anion.

1. Introduction

Our continuing interest in the structure and solvation of nitroaromatic anion radicals [1, 2] prompted us to synthesize nitrobenzene enriched with carbon-13 so that the carbon hyperfine couplings in the anion radical could be examined by electron spin resonance (E.S.R.) spectroscopy. Recent molecular orbital calculations [2] suggested that the solvent dependence of a_{C_1} should provide evidence concerning the possibility that a pyramidal distortion of the nitro group accompanies the formation of hydrogen bonds between the radicals and protic solvents. In addition we felt that greater knowledge of the carbon couplings would provide an almost wholly experimental means by which to determine the spin density distribution. The sigma–pi interaction parameters for the nitrogen–carbon bond could also be estimated with these data.

Synthetic considerations showed that it is simpler to prepare molecules which are enriched at position 1 in an equimolar mixture with those enriched at position 4 than to enrich position 1 alone. Observation of a_{C_4} which depends upon spin densities at positions 3, 4 and 5 only, in conjunction with proton splittings for these three positions, yields a means to parameterize the Karplus–Fraenkel [3] and McConnell [4] equations in a self-consistent way.

We report here the synthesis of nitrobenzene which contains 22·5 mole per cent nitrobenzene-1-^{13}C and an equivalent amount of nitrobenzene-4-^{13}C. Hyperfine couplings for the corresponding anion radicals in a variety of solvent media are reported with particular attention to a parallel examination of the solvent dependence of a_{C_1} and a_N. In addition, we report data obtained from a pure sample of nitrobenzene-4-^{13}C anion radical, thus permitting an unambiguous distinction between the C_1 and C_4 splittings.

2. EXPERIMENTAL

Solvents, supporting electrolytes and reagents were, except as specified, commercially available from common sources. As required, these materials were purified by established literature methods. All electrochemical procedures in acetonitrile and *N*,*N*-dimethylformamide (DMF) were carried out using tetraethylammonium perchlorate at 0·1 M concentration as supporting electrolyte†. Electrolytic reduction of nitrobenzene was done in hexamethylphosphoramide (HMPA) containing 40 mM tetrabutylammonium perchlorate (Southwestern Analytical Chemicals, recrystallized from ethyl acetate and vacuum dried) supporting electrolyte.

2.1. *Nitrobenzene*-4-^{13}*C*

4-Nitrobromobenzene-1-^{13}C prepared as described previously [1 (a)] was reduced electrochemically in moist DMF solution at a potential of −1·20 V versus a saturated calomel electrode. Under these conditions, the E.S.R. spectrum which resulted was unequivocally that of nitrobenzene anion. The water content of this DMF was not assayed, but the value of the nitrogen hyperfine splitting obtained (table 1) makes clear that the residual water concentration was considerable.

2.2. 1-^{13}*C and* 4-^{13}*C-nitrobenzene mixture*

Condensation of acetone-2-^{13}C (Merck Chemical Division of Merck, Sharpe, and Dohme, Ltd.) with sodium nitromalonaldehyde monohydrate incorporated the label into the aromatic ring and yielded 4-nitrophenol-1-^{13}C (**I**). Conversion of **I** to 4-nitroaniline-1-^{13}C (**II**) was effected using 4-chloro-2-phenylquinazoline (' AMexOL ', Aldrich Chemical Co.). Oxidation of **II** to 1,4-dinitrobenzene (**III**) randomized the ^{13}C label and reduction of **III** to 4-nitroaniline produced a mixture of 1-^{13}C and 4-^{13}C material (**IV**) with the label equally divided. Diazotization of **IV** followed by reduction with hypophosphorous acid yielded the mixture of 1-^{13}C and 4-^{13}C-nitrobenzene which we desired. The synthesis is described in detail elsewhere [5].

2.3. *E.S.R. spectroscopy*

E.S.R. spectra were obtained with a Varian E–12 X-band E.S.R. spectrometer using 100 kHz field modulation. Spectra of nitrobenzene anion-4-^{13}C were calibrated using Fremi's salt in saturated aqueous sodium carbonate solution for which the nitrogen coupling was taken as 13·091 ± 0·004 G‡ [6] as described previously [1 (a)]. All other spectra were calibrated using a Spectromagnetic Industries Model 5200 proton resonance fluxmeter.

All spectra were obtained using the *intra muros* [7] method of electrolytic radical generation. Computer simulations of spectra were carried out using a

† $M = mol\ l^{-1}$.

‡ $G = 10^{-4}$ T.

Solvent	$-a_{H_2}$	a_{H_3}	$-a_{H_4}$	a_N	$-a_{C_1}$	a_{C_4}
			Nitrobenzene anion, ^{13}C-enriched at positions 1 and 4			
HMPA‡	3·341 ± 0·009	1·038 ± 0·003	4·18 ± 0·02	8·96 ± 0·01	7·05 ± 0·02	6·14 ± 0·02
MeCN§	3·357 ± 0·009	1·079 ± 0·007	3·969 ± 0·009	10·419 ± 0·008	7·93 ± 0·02	5·76 ± 0·03
DMF‖	3·34 ± 0·02	1·059 ± 0·006	4·014 ± 0·006	9·71 ± 0·01	7·62 ± 0·02	5·95 ± 0·02
DMF–water¶ $X_{H_2O} \times 10^3$						
4·3	3·36 ± 0·02	1·065 ± 0·006	3·981 ± 0	9·91 ± 0·01	7·72 ± 0·01	5·89 ± 0·02
8·6	3·349 ± 0·008	1·058 ± 0·008	3·98 ± 0·01	9·89 ± 0·01	7·75 ± 0·03	5·89 ± 0·03
17·2	3·352 ± 0·004	1·059 ± 0·006	3·95 ± 0·01	10·111 ± 0·009	7·86 ± 0·01	5·83 ± 0·03
33·7	3·354 ± 0·006	1·067 ± 0·007	3·95 ± 0·01	10·288 ± 0·007	7·93 ± 0·02	5·78 ± 0·02
65·3	3·35 ± 0·01	1·073 ± 0·004	3·93 ± 0·01	10·58 ± 0·01	8·07 ± 0·04	5·78 ± 0·04
123	3·36 ± 0·01	1·08 ± 0·01	3·87 ± 0·02	10·896 ± 0·009	8·30 ± 0·03	5·68 ± 0·03
218	3·34 ± 0·02	1·078 ± 0·004	3·82 ± 0·01	11·33 ± 0·01	8·52 ± 0·04	5·60 ± 0·02
263	3·35 ± 0·03	1·061 ± 0·004	3·81 ± 0·01	11·36 ± 0·01	8·58 ± 0·06	5·62 ± 0·06
373	3·35 ± 0·02	1·071 ± 0·006	3·75 ± 0·01	11·750 ± 0·009	8·75 ± 0·04	5·55 ± 0·04
472	3·35 ± 0·02	1·088 ± 0·005	3·73 ± 0·02	12·10 ± 0·01	8·88 ± 0·04	5·46 ± 0·03
543	3·36 ± 0·01	1·106 ± 0·008	3·70 ± 0·01	12·35 ± 0·01	8·99 ± 0·03	5·41 ± 0·02
598	3·36 ± 0·03	1·11 ± 0·01	3·68 ± 0·02	12·538 ± 0·008	9·03 ± 0·04	5·31 ± 0·05
			Nitrobenzene anion, ^{13}C-enriched at position 4			
Moist DMF	3·33 ± 0·01	1·057 ± 0·007	3·94 ± 0·01	10·12 ± 0·04	—	5·82 ± 0·03

Table 1. Coupling constants in gauss†.

† Uncertainties given at the 95 per cent confidence level.
‡ Hexamethylphosphoramide.
§ Acetonitrile.
‖ *N*,*N*-Dimethylformamide.
¶ X_{H_2O} = mole fraction of water in DMF.

Varian 620i computer interfaced with the E.S.R. spectrometer and a simulation programme supplied by Varian.

3. Results

Electrochemical reduction of a solution containing 1·06 mM 4-nitrobromobenzene-1-^{13}C in moist DMF as described above yielded nitrobenzene anion. Carbon lines appeared at an intensity consistent with the enrichment of the compound, 30 atom per cent [1 (a)]. Coupling constants measured for this species are given in table 1.

Electrochemical reduction of solutions containing 1–2 mM total concentrations of the mixture of 1-^{13}C and 4-^{13}C-nitrobenzene in a variety of solvent media yielded radical anions which exhibited E.S.R. spectra which contain two sets of carbon-13 satellite lines, each of which had an integrated intensity consistent with the isotopic enrichment. Coupling constants measured in these experiments are summarized in table 1.

Assignment of the spectrum of the mixed label nitrobenzene anions in dry DMF was verified by computer simulation of the experimental spectrum; excellent agreement with experiment was obtained. Typical of the results of this investigation is the low-field region of a spectrum obtained in DMF containing 0·373 mole fraction of water shown in figure 1.

The variation of the coupling constants with water content of DMF solutions was measured over the range of mole fraction of water zero to 0·598 (table 1). The variations of the nitrogen and C_1 splittings with water content are displayed graphically in figure 2. Unweighted linear least squares fits to the data give for nitrogen a slope of 4·40 G/mole fraction, an intercept of 10·07 G, and a

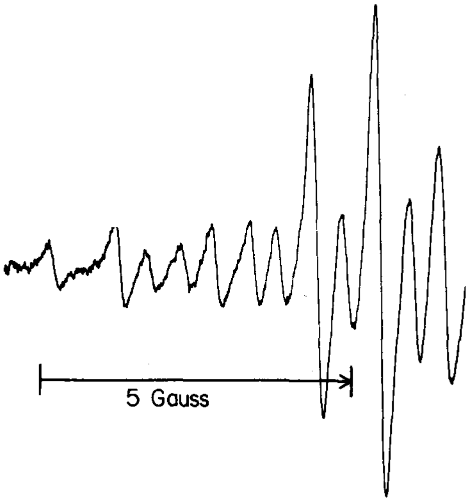

Figure 1. Low-field end line region of the E.S.R. spectrum of mixed label nitrobenzene anions in a solution of dimethylformamide containing 0·373 mole fraction of water. The three large lines at the right are those due to unlabelled radicals. From the left, the first, second, and fourth lines are the low-field triplet from radicals labelled at C–1 ; the third and fifth lines are the low-field portion of the low-field triplet from radicals labelled at C–4.

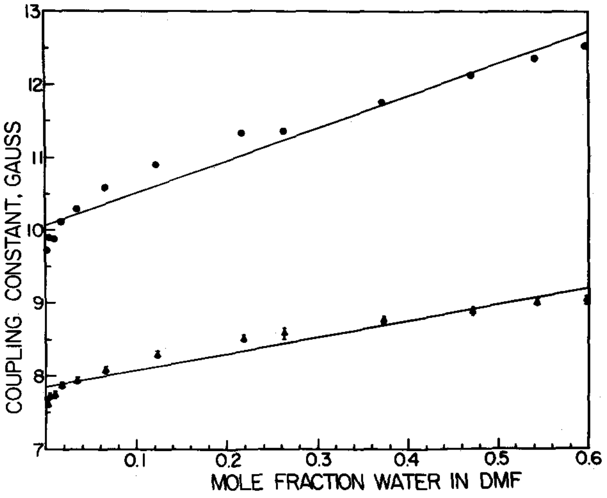

Figure 2. Nitrogen splitting (circles) and carbon-13 splitting from position 1 (triangles) as a function of mole fraction of water added to dimethylformamide solution.

correlation coefficient of 0·979 ; while for C_1 the slope is 2·25 G/mole fraction, the intercept is 7·84 G, and the correlation coefficient is 0·966.

In two solvent systems we observed satellites which we believe arise from carbon-13 in natural abundance. In HMPA satellites were detected and assigned to spin 0·5 nuclei with a coupling constant of $4{\cdot}58 \pm 0{\cdot}06$ G ; the integrated intensities of these satellites are 1·3–1·5 per cent of the intensities of the parent lines. In acetonitrile similar satellites lines were observed with a coupling constant $4{\cdot}60 \pm 0{\cdot}03$ G and integrated intensities 1·6–1·9 per cent of the proton lines. In the latter solvent an additional set of satellites was observed which had intensities of *ca.* 0·5 per cent ; the value of the coupling, $\simeq 7{\cdot}9$ G, suggests that these lines arise from natural abundance carbon-13 at position 1.

The ratio of heights between derivative extrema was determined for the low- and high-field end proton lines from spectra obtained in HMPA. The ratio of low/high field line heights is 1·52. A similar measurement for well resolved lines from C_1 gives 1·76, while the ratio for C_4 lines is 2·10.

4. Discussion

In interpreting the data obtained in this study, it is first necessary to affix the sign of a_{C_1} and then to assign the natural abundance splitting to the appropriate molecular position. It is then possible for the first time to give a description of the spin density distribution in the nitrobenzene anion based almost completely on experiment.

4.1. *Sign of* a_{C_1}

Unequivocal assignment of the signs of carbon hyperfine splittings may be made on the basis of variations of line width when the intramolecular electron–nuclear dipolar interactions are dominated by local spin densities [8] ; in fact, the line widths are often proportional to the square of the local spin density [9].

All theoretical estimates [2, 10] suggest that the spin density at C_1 in nitrobenzene anion is very small; empirical estimates [11] of spin densities at the other positions in the radical substantiate this view. Thus the observation that lines from C_1 have nearly the same width variation as the proton lines rules out a large spin density at position 1. In contrast there is a definite additional broadening of the high field lines which arise from C_4, a site at which the spin density is *ca.* 0·16. Accordingly, we presume that a_{C_1} is negative and find that this choice as used with the available experimental data forms a reasonable and self-consistent picture.

4.2. *Natural abundance splitting*

Since the integrated intensities observed for the natural abundance carbon splitting† are larger than the value of 1 per cent expected from a two-fold degenerate site, the possibility that more than a two-fold degeneracy is involved is suggested. Both INDO calculations [2, 10 (a)] and estimates based on reasonable spin densities and the Karplus–Fraenkel [3] relationships suggest that $a_{C_2} \simeq -a_{C_3}$. If, for example, we assume that $a_{C_2} = 4{\cdot}6$ G, using the experimentally determined spin densities (*vide infra*) we calculate $a_{C_3} = -4{\cdot}72$ G in acetonitrile and $-4{\cdot}89$ G in HMPA. Two such sets of satellites are likely not to be resolved; but since they are not perfectly superimposed, one would expect intensities in the 1–2 per cent range. Apparently overlap obscures lines due to C_4. The stick diagram given in figure 3 supports these assertions.

4.3. *Sigma–pi parameters*

It is necessary to decide whether to take $Q_{CH}{}^{H}$ as a variable, or following Bolton [13] and Strom *et al.* [14] to alter the parameters calculated by Karplus and Fraenkel [3]. While the question is not currently subject to experimental test, we note that Bolton's [13] observations for benzene anion may be influenced by a large dynamic Jahn–Teller distortion. Later work by Bolton and Fraenkel [8] and by Das and Fraenkel [15] suggests that it is preferable to retain the original parameters for carbon [3] and to determine $Q_{CH}{}^{H}$. In both of the latter cases [8, 15] $Q_{CH}{}^{H} = -27$ G was found suitable.

Equation (1) embodies the Karplus–Fraenkel formulation and parameters [3],

$$a_{C_4} = 35{\cdot}6\rho_{C_4}{}^{\pi} - 27{\cdot}8\rho_{C_3}{}^{\pi} \qquad (1)$$

this may be combined with McConnell's relation [4] to yield the expression for $Q_{CH}{}^{H}$ given in equation (2):

$$Q_{CH}{}^{H} = (35{\cdot}6a_{H_4} - 27{\cdot}8a_{H_3})/a_{C_4}. \qquad (2)$$

Values of $Q_{CH}{}^{H}$ calculated using this relationship fall in the range‡ $-28{\cdot}94$ G to $-30{\cdot}48$ G for the solvent media used here. These values are nearly identical

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† Gulick and Geske [12] measured this splitting in DMF and in DMF containing up to 4 volume per cent water. It was found to be independent of water content and *ca.* 4·7 G. The relative intensities of those satellite lines were observed to be about 1 per cent of the parent lines; however, those authors erroneously assigned the splitting to a single carbon-13 nucleus, rather than to a position of two-fold degeneracy.

‡ Parrish *et al.* [1 (a)] stated that $a_{C_4} = 5{\cdot}8$ G is well reproduced when $Q_{CH}{}^{H} = -22{\cdot}5$ G. This is a numerical error; the data then available actually give a value of $-29{\cdot}5$ G, very similar to our current results.

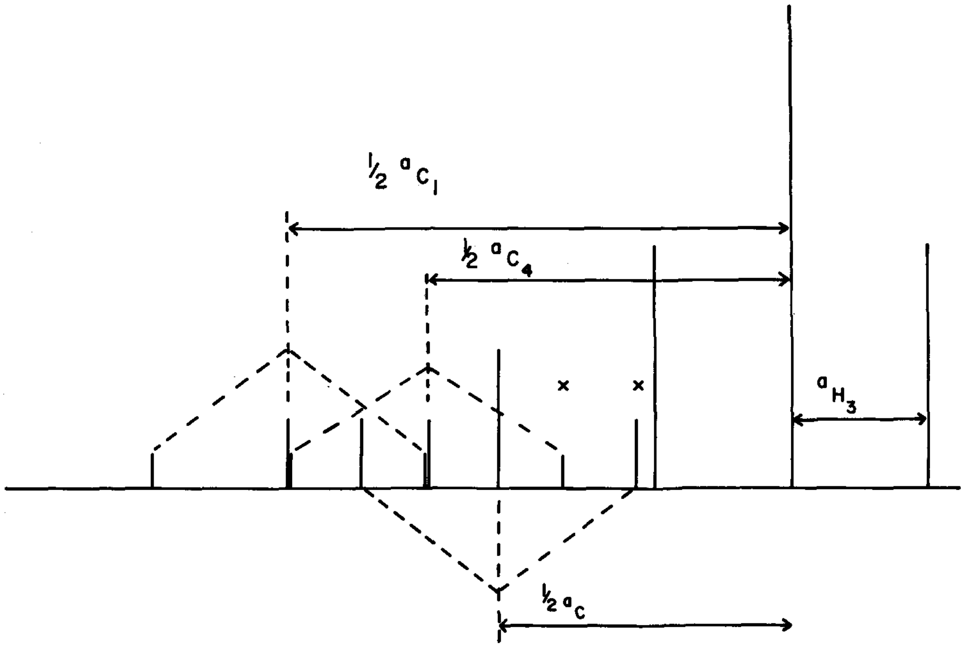

Figure 3. Stick diagram assignment of the natural abundance carbon-13 splittings observed for nitrobenzene anion radical. The splitting which is not labelled with a position is believed to arise from superposition of lines from C–2 and from C–3. The two lines marked X were obscured by the lowest field proton line. The proton lines are not drawn to scale and should, of course, be much larger.

to the value suggested by Bolton and Fraenkel [8] ; moreover, Das and Fraenkel [15] state that values ' above ' −27 G appear to be the most appropriate, although they use −27 G in their calculations. In the evaluation of spin density distributions, we have used the $Q_{\mathrm{CH}}^{\mathrm{H}}$ calculated for each different solvent composition.

Unfortunately, in the most extensive previous investigation of spin densities in nitroaromatic anion radicals, Rieger and Fraenkel [16] fitted their Huckel–McLachlan [17] calculations to E.S.R. data for nitrobenzene anion using $Q_{\mathrm{CH}}^{\mathrm{H}} = -23{\cdot}7$ G. The current finding that a larger value appears more appropriate points to the necessity to re-examine the sigma–pi parameters previously determined for nitrogen [16]. Gross and Symons [11 (b)] have already criticized these parameters as too large.

4.4. *Calculation of spin densities*

Spin densities may now be calculated for carbons bound to protons and assignment of the natural abundance carbon splitting to position 2 permits estimation of the spin density at C_1 using equation (3) :

$$a_{C_2} = 35{\cdot}6\rho_{C_2}^{\pi} - 13{\cdot}9\rho_{C_3}^{\pi} - 13{\cdot}9\rho_{C_1}^{\pi}. \qquad (3)$$

The oxygen spin density may be determined to reasonable accuracy using equation (4) with $Q^{O} = -41 \pm 3$ G,

$$a_{O} = Q^{O}\rho_{O}^{\pi}, \tag{4}$$

a relation which now has ample experimental support [1 (b, c), 12, 18].

Oxygen-17 data are available for nitrobenzene anion in DMF, DMF–10 per cent water ($X_{H_2O} = 0{\cdot}322$), and acetonitrile [12]. In addition, we assume $a_{O} = -8{\cdot}8$ G in HMPA and extrapolate the data of [12] to obtain $a_{O} = -9{\cdot}12$ G when the mole fraction of water $= 0{\cdot}598$.

These experimental data and the conservation of electron spin make possible a complete description of the spin density in this radical. We have carried out such calculations for a representative selection of solvent media and the results are presented in table 2. We present also, for comparison, spin densities calculated by the Hückel–McLachlan [16, 17] method and also spin densities and coupling constants calculated using INDO [2, 10 (a)]. In making our calculations, we assumed that a_{C_2} is the same in dry DMF as in HMPA and that in DMF-water mixtures it is the same as in acetonitrile ; values of a_{C_4} and a_{H_4} for 10 per cent water in DMF were calculated from least squares fits to our data.

4.5. *Sigma–pi parameters for carbon*

Figure 4 shows a plot of $|a_{C_1}|$ versus a_{N}. The solid line represents a least squares fit of the data and gives a slope of 0·543, an intercept of 2·32, and a correlation coefficient of 0·994. Since the spin density at C_1 is very small and the solvent dependence of a_{H_2} is minor, it appears that a_{C_1} depends strongly on ρ_{N}^{π}. In the framework of the Karplus–Fraenkel development [3] we can express a_{C_1} by equation (5) and the experimental spin densities may then be used to evaluate Q_{NC}^{C} :

$$a_{C_1} = 16{\cdot}1\rho_{C_1}^{\pi} - 27{\cdot}8\rho_{C_2}^{\pi} + Q_{CN}^{C}\rho_{C_1}^{\pi} + Q_{NC}^{C}\rho_{N}^{\pi}. \tag{5}$$

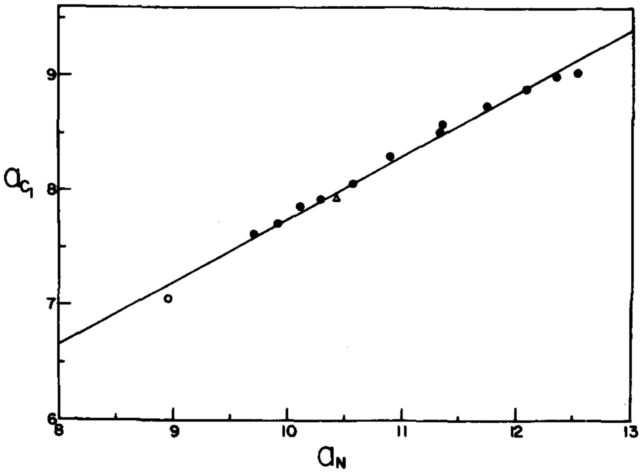

Figure 4. Absolute value of a_{C_1} plotted versus a_{N}. The solid circles represent values from solutions of dimethylformamide–water. The open circle is for hexamethylphosphoramide and the open triangle is for acetonitrile.

	Source							
Position	HMPA†	MeCN†	DMF†	DMF–$X_{H_2O}=0{\cdot}322$†	DMF–$X_{H_2O}=0{\cdot}598$†	Hückel, ρ^{π}‡	INDO, ρ^{P_z}§	INDO, a_i‖
1	0·0020	−0·0055	0·0010	−0·0050	−0·0123	0·0071	−0·0277	−5·26
2	0·1154	0·1129	0·1153	0·1132	0·1102	0·1414	0·1403	6·08
3	−0·0359	−0·0363	−0·0366	−0·0360	−0·0364	−0·0480	−0·0848	−5·18
4	0·1445	0·1335	0·1386	0·1284	0·1207	0·1704	0·1619	7·14
N	0·2673	0·2866	0·2718	0·2836	0·2992	0·2381	0·3353	7·10
O	0·2146	0·2161	0·2156	0·2193	0·2224	0·1988	0·2098	−4·18

† Calculated from experimental data, see text.
‡ From [16].
§ From [2, 10 (a)].
‖ Carbon splittings given for positions 1–4.

Table 2. Spin densities.

In making such calculations, we ignore the term $Q_{CN}{}^{C}\rho_{C_1}{}^{\pi}$ since any reasonable value for the Q parameter would yield an insignificant contribution to the total hyperfine splitting. The values of $Q_{NC}{}^{C}$ obtained from data in various solvent media range from $-16\cdot3$ G to $-19\cdot3$ G with an average of $-17\cdot8$ G. The consistency is gratifying and suggests that this parameter may be taken between -16 and -20 G with some confidence.

These values should be compared with those obtained from dinitrobenzene-1-^{13}C anion, $Q_{NC}{}^{C} = -1\cdot8$ to $-14\cdot6$ G [1 (a)]. As pointed out previously, the bonding in the nitro group of dinitrobenzene may differ from that in other nitroaromatics because of unusually strong resonance interactions. Nonetheless, data for dinitrobenzene anion can be used to make a crude estimate of $Q_{CN}{}^{C}$ since $\rho_{C_1}{}^{\pi}$ is not negligible in that radical. Using the average value of $Q_{NC}{}^{C}$ with a_{C_1} for dinitrobenzene (2·36 G in dry DMF [1 (a)]) and the experimental spin densities, equation (5) yields $Q_{CN}{}^{C} = 43\cdot5$ G ; using McLachlan [17] spin densities the result is 52·0 G.

4.6. *Structure of the radical*

Nitrobenzene itself has been shown to be planar in the gas phase [19]. This finding has, of course, only limited implications for the anion radical in solution ; however, it suggests a presumption of planarity the invalidation of which requires experimental evidence. On the basis of INDO calculations, Gilbert and Trenwith [20] have suggested that the radical is slightly non-planar (2° twist of the nitro group) and that there is a small quininoidal asymmetry of the aromatic ring. They found an energy minimum with C_2–C_3 and C_5–C_6 maintained at the usual value of 1·38 Å, but the remaining C–C bonds lengthened to 1·40 Å. It has been noted [3] that the sigma–pi polarization parameters depend on bond length and that larger values are favoured by longer bonds. Thus, the implications of such a distortion include the possibility of perturbing the value of $Q_{CC'}{}^{C}$.

Our previous INDO calculations [2] suggested that the solvent dependencies of the hyperfine coupling constants in nitrobenzene anion are better reproduced if formation of an hydrogen bond between water and the nitro group is accompanied by distortion of the nitro group toward a pyramidal conformation. A singular feature of this added distortion is the qualitatively different behaviour of a_{C_1}. If the radical remains planar, as hydrogen bonds form a_{C_1} assumes larger negative values ; whereas, if the distortion is introduced simultaneously, a_{C_1} becomes more positive. The experimental results presented here suggest that the radical does not, in fact, become pyramidal and that some other way is needed to understand the discrepancies between experiment and the INDO calculations in which no distortion is used. The study of additional carbon-13 enriched radical anions will assist in resolving those areas still in question. Such studies are in progress in our laboratory.

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