

**1034. Electron Spin Resonance Studies of Radical Anions.
Part II.* Aromatic Nitro-compounds.**

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Electron spin resonance spectra observed during chemical or photochemical reduction of a number of substituted nitrobenzenes in aqueous-alcohol indicate that radical anions are formed by addition of an electron to the nitro-compound. Comparison with results for the same species in aprotic solvents suggests that the solvent causes considerable changes in the electron distribution around the nitrogen atom, possibly through hydrogen-bonding. This affects the hyperfine interaction as well as the relaxation times and line-widths for the different nitrogen nuclear-spin states. A similar effect is observed for hyperfine lines corresponding to transitions involving different fluorine and chlorine nuclear-spin states, the implied variation in relaxation time being much greater than that predicted by recent theories.

THE facility with which aromatic nitro-compounds can accept an electron, and the stability of the resulting radical-anion, have been demonstrated in a number of recent electron spin resonance studies. The electron donor may be an alkali metal in an ethereal solvent,¹ a mercury or platinum anode during electrolysis,²⁻⁴ or an alkoxide or hydroxide ion.⁵ However, it is well known that the reduction of aromatic nitro-compounds proceeds through a number of stages, leading, ultimately, to azo-, hydrazo-, or amino-compounds. Some early experiments with conventional chemical methods of reduction, such as zinc or glucose in neutral or alkaline solution, failed to reveal spectra associated with these later stages, although the spectra were observed when nitrosobenzene or phenylhydroxylamine was the starting material.⁶ Other substituted nitrobenzenes have been examined in the same way, with essentially the same results.

During these investigations the publication by Geske and Maki² of their production of radical-anions by electrolysis in acetonitrile or dimethylformamide showed that the same species were being observed but that there were appreciable differences in some of the spectra, differences which must be attributable to the solvent. Further, the spectra we observed in alcoholic solution using chemical and, later, photochemical reduction were generally rather better resolved and displayed a number of features not observed in the electrolytically produced species. It is to these features that we draw attention in this paper, reserving more detailed discussion of subsequent reduction stages until kinetic measurements are complete.

EXPERIMENTAL

The substituted nitrobenzenes were obtained from British Drug Houses Ltd., Messrs. Light and Co., or Eastman Kodak, Ltd., with the following exceptions: Methyl *p*-nitrobenzoate was prepared by adding *p*-nitrobenzoyl chloride to methanol and when recrystallised from methanol, had m. p. 84–86° (lit., 86°). *p*-Nitrobenzamide was precipitated on addition of *p*-nitrobenzoyl chloride to aqueous ammonia (*d* 0.88) and, recrystallised from aqueous ethanol, had m. p. 201° (lit., 200°).

Four methods of reduction were employed: (A) Reduction with zinc powder in aqueous-ethanolic sodium hydroxide; gentle heating gave the yellowish-brown colour characteristic of radical-anions. (B) Reduction with glucose; glucose and a concentrated solution of sodium

* Part I, preceding paper.

¹ Ward, *J. Chem. Phys.*, 1959, **30**, 852; 1960, **32**, 410; 1962, **36**, 1405.

² Geske and Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671.

³ Maki and Geske, *J. Amer. Chem. Soc.*, 1961, **83**, 1852.

⁴ Piette, Ludwig, and Adams, *Analyt. Chem.*, 1962, **34**, 916.

⁵ Ayscough and Sargent, *Proc. Chem. Soc.*, 1963, 94.

⁶ Wilson, Ph.D. Thesis, University of Leeds, 1962.

ethoxide in ethanol were added to a solution of the nitrobenzene in ethanol or aqueous ethanol and the mixture was heated gently (methanol can replace ethanol). (c) Photochemical reduction; a saturated solution (~1 ml.) of sodium ethoxide in ethanol was added to ~0.1M-nitrobenzene in ethanol (10 ml.); samples were then irradiated with light from a medium-pressure arc from which infrared radiation had been removed by means of a water filter.

The Varian V-4500 EPR spectrometer and auxiliary apparatus have been described earlier,⁷ as has the procedure for measuring g -values and hyperfine separations. These give hyperfine splitting constants within 2–3% and g -values to ± 0.0002 .

RESULTS

Reduction of Substituted Nitrobenzenes in Alkaline Solution.—Twenty-two *para*-substituted nitrobenzenes and nine other nitrobenzene derivatives were reduced in aqueous-alcohol by one or more of the methods indicated. The resulting yellow-brown solutions were examined in the electron spin resonance (e.s.r.) spectrometer, and in most cases a complex spectrum was observed which could be attributed to the radical anion of the parent nitro-compound. Reduction with zinc was generally too fast for convenience; where the spectra could be recorded they were seen to have the same characteristics as those recorded when glucose was used as a reducing agent. The latter were stable for periods ranging from several days in the cases of nitrobenzene and *p*-nitrotoluene to a few hours in that of *p*-nitrobenzaldehyde. The use of methanol in place of ethanol for reduction by glucose resulted in rather better resolved spectra in most cases. Photochemical reduction also gave well-resolved spectra, which reached maximum intensity in 20–30 min. and decayed after illumination in a similar time. The spectra were again identical with those obtained on using other methods of reduction in the same solvents. The few cases where one or other method gave anomalous results are discussed below. Table 1 summarises our work and the hyperfine coupling constants derived from it.

Interpretation of the Spectra.—Most of the observed spectra consisted of three well-defined groups of lines corresponding to interaction with the ¹⁴N nucleus. But in contrast to the spectra observed by Geske and Maki the groups were of markedly different intensity and line-width. In particular, the low-field lines corresponding to transition between states for which the nitrogen nuclear spin quantum number $m_1(\text{N})$ was -1 were much smaller and wider than the others. It was generally possible to assign the remaining smaller hyperfine coupling constants to the *ortho*- and *meta*-protons and to magnetic nuclei in the *para*-substituents where interaction takes place. Without deuterium substitution the *ortho*- and *meta*-proton splittings cannot be differentiated but we follow the established custom in assigning the larger splitting to protons *ortho* to the nitro-group. This was confirmed by Ward¹ for the nitrobenzene anion in 1,2-dimethoxyethane.

We include, for comparison, data on the corresponding radical-ions produced electrolytically in acetonitrile.³ The difference in the ¹⁴N hyperfine coupling constants is obvious, amounting to 2–3 gauss. On the other hand, with the exception of *p*-nitrobenzaldehyde, our values for *ortho*- and *meta*-proton splittings agree, within experimental error, with those given by Geske and Maki.³ However, there are small differences between the values for the *para*-proton in nitrobenzene, and the *para*-fluorine atom in *p*-fluoronitrobenzene, which are clearly observable in the spectra. To eliminate possible calibration errors the spectrum of the anion of nitrobenzene was observed after electrolytic reduction in acetonitrile containing tetraethylammonium perchlorate as electrolyte, and it was found to be the same as that reported by Geske and Maki.² No change in the ¹⁴N coupling constant was observed when aqueous methanol replaced aqueous ethanol, but this value increased when water was the solvent. (For the nitrobenzene, *p*-fluoronitrobenzene, and *p*-nitrobenzoic acid anions in water the values of a_N are, respectively, 13.95, 14.3, and 12.7 gauss, each 0.3–0.4 gauss higher than in alcohol.)

Many of these spectra were observed for the first time or were shown to contain additional hyperfine structure obscured in the electrolytically reduced solutions by the greater line-width. Details are given below.

(i) *p*-Alkoxy nitrobenzenes. *p*-Nitroanisole was studied by Geske and Maki. The ethoxy and *n*-butoxy-derivatives give well-resolved spectra in which the hyperfine interaction with the CH₂ protons is clear. The other coupling constants are virtually unaffected by the nature of the alkoxy-radical.

⁷ Ayscough and Thomson, *Trans. Faraday Soc.*, 1961, **57**, 1487.

(ii) *p*-Alkyl- and *p*-Aryl-nitrobenzenes. The nitrogen hyperfine splitting is the same for the three alkyl derivatives studied but decreases appreciably when a phenyl group is in the *para*-position. In this ion, interaction with the *ortho*-, *meta*-, and *para*-protons in the second

TABLE I.
Reduction of nitrobenzene derivatives.

Subst.	Hyperfine splitting constants (gauss) *					Method of redn.†			Previous results ³
	a_N	a_1	a_2	a_3	a_4	A	B	C	
<i>p</i> -NH ₂	14.8	3.3	1.1	1.1(b)	1.1(d)		+		12.78, 3.36, 1.12, 1.12, 1.12
<i>p</i> -OBu ⁿ	14.5	3.4	1.1	0.4(b)	—			+	
<i>p</i> -OEt	14.4 ₅	3.4	1.0 ₅	0.4(b)	—		+		
<i>p</i> -OMe	14.3 ₅	3.4	1.1	0.34(c)	—		+	+	11.57, 3.43, 1.11, 0.30
<i>p</i> -Me	14.0 ₅	3.4	1.1 ₅	3.7 ₅ (c)	—	+	+	+	10.79, 3.39, 1.11, 3.98
<i>p</i> -Et	14.0	3.4	1.1	2.8(b)	—		+	+	
<i>p</i> -Bu ^t	14.0	3.4	1.1	—	—		+	+	
<i>p</i> -F	13.8	3.4 ₅	1.1 ₅	8.0 ₅ (a)	—	+	+	+	10.76, 3.56, 1.16, 8.41
<i>p</i> -H	13.6 ₅	3.3 ₅	1.1 ₅	3.6(a)	—	+	+	+	10.32, 3.39, 1.09, 3.97
<i>p</i> -CH ₂ ·OH	13.5	3.4	1.1	2.3(b)	—			+	
<i>p</i> -CH ₂ ·CH ₂ ·OH	13.5	3.4	1.1	2.3(b)	—			+	
<i>p</i> -CH ₂ ·CO ₂ H ...	13.4	3.3	1.1	2.6(b)	—			+	
<i>p</i> -Cl	13.2	3.4 ₅	1.2	0.24(e)	—		+	+	9.83, 3.46, 1.17
<i>p</i> -Br	12.9 ₅	3.4 ₅	1.2	—	—		+	+	9.70, 3.43, 1.15
<i>p</i> -Ph	12.9	3.4	1.1	0.5 ₅ (c)	0.3(b)			+	
<i>p</i> -I	12.6	3.3 ₅	1.2	—	—	—	+	—	
<i>p</i> -CO ₂ H	12.3 ₅	3.3	1.1	—	—		+	+	
<i>p</i> -CO·NH ₂	11.7	3.3	1.0 ₅	—	—		+	+	8.37, 3.20, 0.98
<i>p</i> -CO ₂ Me	11.4 ₅	3.2 ₅	1.0 ₅	0.26(c)	—		+	+	
<i>p</i> -Ac	10.0 ₅	3.1	0.9	0.4 ₅ (c)	—		+	+	7.02, 2.95, 0.66, 0.66
<i>p</i> -CHO	7.9	4.5 ₅ (a)	0.78	1.9(a)	1.1 ₅ (a)		+		5.83, 3.1, 0.44, 2.37, 1.23
<i>p</i> -NO ₂	3.6	1.1	1.1	—	—			+	
<i>o</i> -F								+	
<i>o</i> -Cl	14.1 ₅	3.1 ₅ (a)	1.1 ₅	3.0 ₅ (a)	0.17(e)		+		
<i>m</i> -F	12.6	3.3(b)	1.1(a)	3.7(a)	3.0(a)			+	
<i>m</i> -Cl	12.8 ₅	3.5 ₅	1.1(a)	3.5(a)	—		+		
<i>m</i> -CO ₂ H	13.7	3.4(b)	1.1(a)	3.6(a)	—			+	
<i>m</i> -NO ₂ (<i>m</i> -OMe)†	12.4	3.3(b)	1.1(a)	3.6(a)	—			+	
2,5-Cl ₂	12.8 ₅	3.3 ₅ (a)	1.1(a)	—	—		+		
2,6-Me ₂	20.6	—	0.4(b)	1.2(a)	0.4(f)			+	
2,4,5-Cl ₃	12.1	3.4(a)	1.6(a)	—	—			+	

* Hyperfine splitting constants relate to (a) one spin with $I = \frac{1}{2}$, (b) two spins with $I = \frac{1}{2}$, (c) three spins with $I = \frac{1}{2}$, (d) one spin with $I = 1$, (e) one spin with $I = \frac{3}{2}$, and (f) six spins with $I = \frac{1}{2}$. a_N refers to the nitrogen atom, a_1 to the *ortho*-protons, a_2 to the *meta*-protons, a_3 and a_4 to *para*-protons or *para*-substituents. † See text.

aromatic ring can be observed (see Fig. 1B). The total unpaired spin density in this ring is about 15–20% of that in the ring containing the nitro-group. For the *t*-butyl derivative, resolved structure from the methyl protons cannot be seen, though the broadening of the lines compared with those of the other alkyl derivatives indicates some interaction. In the spectrum observed when reducing 2,6-dimethyl-1-nitrobenzene by photolysis the major triplet was clearly distinguishable (Fig. 1A), corresponding to a nitrogen hyperfine interaction of more than 20 gauss. This is the highest observed in this series. The other striking feature is the smallness of the interaction with both ring and methyl protons, corresponding to a very considerable diminution in unpaired spin density in the aromatic π -orbital.

(iii) *Alcohols*. The two alcohols examined gave almost identical spectra in which hyperfine interaction with the two α -CH₂ protons was observed (a_H is about 70% of that of the methyl protons in *para*-nitrotoluene). No spectra were observed for a solution of *p*-nitrophenol during reduction in alkaline solution, presumably because of rapid condensation reactions.

(iv) *p*-Fluoronitrobenzene. The spectrum of the anion of *p*-fluoronitrobenzene in aqueous ethanol or methanol differs strikingly from that observed in an aprotic solvent (see Figs. 2A and B, and ref. 3). Instead of a simple pattern of lines of relative intensities 1, 2, and 4, the relative intensities and line-widths vary in a much more complex manner, as indicated below. Each line in the spectrum can be assigned to a transition involving radicals with specific nitrogen,

fluorine, and proton nuclear-spin quantum numbers. For example, the lines marked with an asterisk in Fig. 2A all correspond to transitions for which the total proton nuclear spin is zero, but for which $m_I(\text{N})$ and $m_I(\text{F})$ differ. They should be of equal intensity. Instead, the relative intensities (based on peak heights on first derivative curve) are those given in Table 2, starting

TABLE 2.

Results for e.s.r. spectrum of *p*-fluoronitrobenzene.

$m_I(\text{N}), m_I(\text{F})$	$-1, -\frac{1}{2}$	$-1, +\frac{1}{2}$	$0, -\frac{1}{2}$	$0, +\frac{1}{2}$	$+1, -\frac{1}{2}$	$+1, +\frac{1}{2}$
Rel. intensity	1.00	3.1	2.3	3.05	3.75	1.6
Line-width (gauss)	0.39	0.25	0.28	0.26	0.23	0.35

from the high-field end of the spectrum. There is an inverse correlation with line-width (also measures between points of maximum slope). The effect becomes even more pronounced if the temperature of the solution is reduced or the microwave power increased. It may thus be

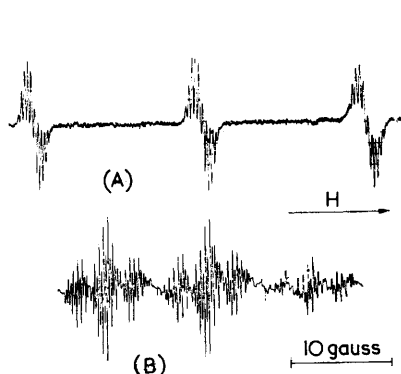


FIG. 1. Electron spin resonance spectra of radical anions formed by reduction of (A) 2,6-dimethyl-1-nitrobenzene and (B) *p*-phenylnitrobenzene.

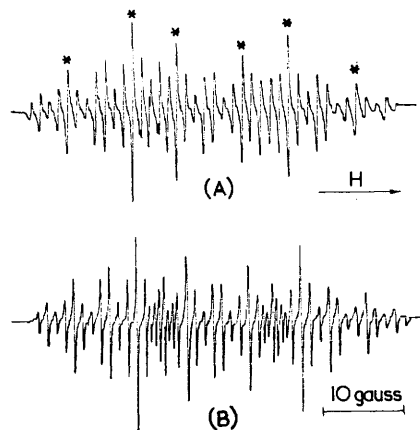


FIG. 2. Electron spin resonance spectra of radical anions formed by reduction of *p*-fluoronitrobenzene in (A) aqueous sodium methoxide and (B) aqueous sodium hydroxide.

caused by differences in the degree of power saturation, corresponding to markedly different relaxation times for species with different orientations of the nitrogen and fluorine nuclear-spin vectors.

Replacement of the methanolic solvent by aqueous alkali further reduces the line-width and increases the nitrogen splitting (cf. Figs. 2A and B). The variation in line-width is still present.

(v) *o*- and *m*-Fluoronitrobenzene. Both anions may be observed during photolytic reduction of the parent compounds, and both show the same kind of variation in line-width as the *para* fluoro-derivative. However, the *ortho*-compound rapidly loses a fluorine atom and the spectrum has not been fully interpreted. With the *meta*-compound there is a possible ambiguity in the allocation of splitting constants to the *para*-proton and the fluorine atom, but the general observation that ring-substitution causes very little change in the ring-proton interactions favours the allocation given in the Table.

(vi) *p*-Chloronitrobenzene. The best resolved spectra were recorded from methanolic solutions (see Fig. 3A). A striking feature observed in this solvent only is that each of the 27 principal lines (from interaction with one nitrogen atom, two *ortho*- and two *meta*-protons) is further split into a quartet, the central lines of which are narrower and more intense than the outer pair. We attribute this four-fold splitting to interaction with the chlorine nucleus ($I = 3/2$), not previously observed in an aromatic system. The unequal intensities of these lines cannot be attributed entirely to the difference in the nuclear moments of the chlorine isotopes, though this will tend to make the inner lines appear narrower. We believe that it

implies a different relaxation time for radicals in which the chlorine nuclear-spin quantum number is $\pm\frac{1}{2}$ during the electronic transition, and for those for which it is $\pm\frac{3}{2}$. Further comment on this point is made elsewhere. [The possibility that the chlorine atom had been replaced by methoxyl, as happens on heating, was eliminated by comparison with the spectra of *p*-methoxynitrobenzene (Fig. 3B).]

(vii) *o*-Chloronitrobenzene. Methods (B) and (C) gave a spectrum corresponding closely to that expected from interaction with one nitrogen atom and two pairs of equivalent protons, with additional splitting of the outermost lines, again attributed to a small interaction with chlorine.

(viii) *m*-Chloronitrobenzene. The chlorine splitting is expected to be about one-third of that of *ortho*- and *para*-chlorine atoms and is not resolved, though some distortion, apparent at slow sweep speeds, suggests its presence.

(ix) *p*-Iodonitrobenzene. A rather weak and poorly resolved spectrum was observed on reduction with glucose in aqueous methanol; iodine was liberated. No spectrum was observed

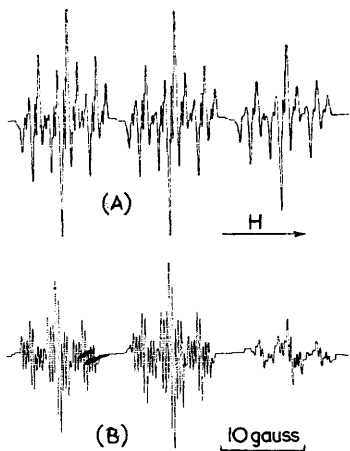


FIG. 3. Electron spin resonance spectra of radical anions formed by reduction of (A) *p*-chloronitrobenzene and (B) *p*-nitroanisole.

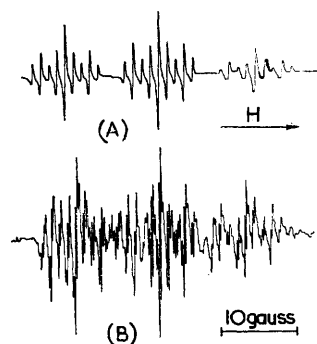


FIG. 4. Electron spin resonance spectra of radical anions formed by reduction of (A) *p*-nitrobenzoic acid and (B) methyl *p*-nitrobenzoate.

in ethanolic solution, during reduction by zinc, or during electrolytic reduction. Photolytic reduction, on the other hand, caused loss of iodine, the spectrum observed being that of the nitrobenzene anion.

(x) *Other halogenated nitrobenzenes*. No chlorine interaction was seen with the di- and trichlorinated derivatives, or with bromo- or iodo-nitrobenzene. The line-widths for all these species were much greater than for the monochloro-derivatives. Slow changes in the spectra suggest replacement of chlorine and, perhaps, some ring-protons by methoxyl or ethoxyl in the anions of 2,5-dichloro- and 2,4,5-trichloro-nitrobenzene. For example, the spectrum of the latter compound changes to one of three lines only, after 15 hours at room temperature. The change is accelerated by heat.

(xi) *Carboxylic acids*. Reduction of *p*-nitrobenzoic acid by glucose in aqueous ethanol produces a well-resolved spectrum corresponding to interaction of the ^{14}N nucleus and two pairs of equivalent protons (see Fig. 4A). The species is presumably the reduced carboxylate ion in a strongly alkaline solution. An unusual feature observed during reduction in methanol is the adsorption of a paramagnetic species on the particles of undissolved glucose. The single line, about 5 gauss in width, associated with this species almost completely obscures the spectrum of the normal radical anion.

The spectrum observed during photolytic reduction of *p*-nitrophenylacetic acid is much less well resolved. The hyperfine splitting constants are very close to those of other compounds with α -methylene groups, *e.g.*, alcohols. In such species the methylene group effectively blocks the electron-withdrawing characteristics of the carboxyl group.

(xii) *Methyl p-nitrobenzoate*. In addition to the major splitting into three broad triplets reported by Geske and Maki, splitting by the *meta*-protons is observed, and also an even smaller interaction with the methyl protons (see Fig. 4B). This observation is remarkable since these protons are separated from the aromatic π -orbital by three intervening atoms (C-O-C).

(xiii) *p-Nitrobenzonitrile*. None of the four reduction procedures produced a spectrum which could be interpreted. All the spectra were markedly asymmetric, presumably a result of partial hydrolysis in the alkaline media.

(xiv) *4-Nitroacetophenone*. Chemical reduction gave asymmetric spectra, but photolysis gave a reasonably symmetrical spectrum from which the hyperfine interaction constants were estimated, though the values given for the *meta*- and methyl protons are not certain.

(xv) *p-Nitrobenzaldehyde*. As in the ion formed during electrolytic reduction, interaction with five protons is observed and only two are equivalent. Maki and Geske³ explained the asymmetry in the hyperfine coupling constants in terms of the loss of two-fold symmetry of the molecular orbital when the formyl group is locked in the plane of the aromatic ring. This asymmetry should be observed in the coupling constants for the protons *meta* to the nitro-group, as well as for those in the *ortho*-position, but it is obscured by the line-width and complexity of the spectra. Without deuterium substitution it is not possible to make positive assignments of the observed coupling constants, but if we follow Maki and Geske in attributing the smallest single proton splitting to the aldehydic proton the asymmetry of the *ortho*-proton splittings is even more produced (4.55 and 1.9 gauss compared with 3.10 and 2.37 gauss). If this is simply a question of restricted rotation it is very surprising that a similar effect is not observed in the anions of 4-nitroacetophenone and methyl *p*-nitrobenzoate. In the aqueous-alcoholic solutions that we used, interaction of the solvent and the aldehydic protons may lead to the unsymmetrical configuration in this species but not in the ketone or ester. This question is discussed in more detail in a recent paper by Rieger and Fraenkel.⁸

(xvi) *p-Dinitrobenzene*. The spectrum observed initially during photochemical reduction in methoxide solution consists of five groups of lines corresponding to two equivalent nitrogen atoms. It is replaced during 10–20 min. by the spectrum of *p*-nitroanisole. The second nitro-group is not labile under these conditions.

(xvii) *m-Dinitrobenzene*. One nitro-group is even more readily replaced by methoxide than from the *para*-compound. The spectrum observed during photochemical reduction cannot be interpreted in terms of interaction with two nitrogen atoms. There are two almost equivalent protons (*ortho*) and two different protons (*meta* and *para*). The *meta*-methoxy-protons cause a splitting estimated from the line-width to be about 0.1 gauss.

DISCUSSION

There can be no doubt that all the spectra described in Table I and in the text are those of first species in the reduction sequence formed by addition of one electron to the parent compound. The distribution of the unpaired electron between the *ortho*-, *meta*-, and *para*-positions has already been commented upon by Geske and Maki,² as has the relation between the nitrogen hyperfine splitting and the Hammett σ -values for the various substituents. Our observations on these points, including those for some *para*-substituted anions not observed before, are in substantial agreement. There appears to be a further correlation, as yet only semiquantitative, between the stability of the radical-anion and a_N . Table I lists the anions in decreasing order of reaction with nitrogen: this is also substantially the order of decreasing stability to further reduction, although the nature of the subsequent reduction steps is unknown. The only other paramagnetic species observed are those resulting from substitution by methoxide or ethoxide of, probably, the parent nitro-compound.

Changes in Hyperfine Splitting Constants.—The increase in a_N observed in protic solvents corresponds to an increase in the unpaired spin density in the nitrogen 2s orbital, since only that part of the unpaired spin density which is in an s-type orbital can interact directly with the nitrogen nuclear spin to give the observed isotropic interaction. Such an increase could arise by withdrawal of electron density from the aromatic ring or by a change in the mixture of orbitals defining the character of the hybrid orbital around the nitrogen atom.

⁸ Rieger and Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2811.

The *ortho*- and *meta*-proton splittings, which reflect the unpaired spin density at the adjacent aromatic carbon atoms, suggest that there is little or no change in the unpaired spin density in the aromatic system. We therefore assume that the change in electronic distribution in the nitro-group is more important. This could result from specific interaction with a proton linking the aromatic anion with the solvent molecules (*i.e.*, hydrogen-bonding) or from a polarising effect of the orientated ionic atmosphere which is likely to exist in the polar solvents used. The further increase in a_N when water, with a higher dielectric constant, is used in place of ethanol or methanol, is significant in this respect. Similar observations concerning the effect of solvent on the spectra of aromatic ketyls suggest that the effect is general.

Variation in Line-width.—(1) *Effect of nitrogen nuclear-spin state.* The major triplet splitting observed in all the radical anions examined is caused by interaction with ^{14}N . The three groups correspond to electron-spin transitions during which $m_I(\text{N})$ remains constant. The low-field group corresponds to $m_I(\text{N}) = +1$, the centre group to $m_I(\text{N}) = 0$, and the high-field group to $m_I(\text{N}) = -1$. In all cases the high-field group of lines was broader and less intense. Some typical values of line-width and relative intensity of the biggest peak in each group are given in Table 3.

TABLE 3.

Subst.	Line-width * (between points of max. slope) (gauss)			Relative intensity * (for peak heights on first derivative curve)		
	$m_I(\text{N}) = +1$	0	-1	+1	0	-1
<i>p</i> -H	0.23	0.22	0.29	0.94	1	0.49
<i>p</i> -OMe	0.16	0.15	0.20	0.81	1	0.24
<i>p</i> -Cl	0.16	0.16	0.18	0.98	1	0.76
<i>p</i> -Br	0.36	0.37	0.43	1.06	1	0.64
<i>p</i> -Me	0.23	0.22	0.27	0.88	1	0.40

* Estimated $\pm 10\%$; relative intensities $\pm 5\%$.

The effect of microwave power saturation is to decrease the total intensity of the line, *i.e.*, the integrated area of the absorption curve. This can be related in a simple manner to the change in peak height on the first derivative curve, giving a parameter which is more readily measured. Further, because the effect of saturation is greatest at the centre of the peak where the absorption of power is a maximum, one observes an increase in line-width measured between points of maximum slope. Although no attempt has been made to obtain an accurate comparison between different species, our values were obtained under conditions of approximately constant microwave power. The concentration was such that dipolar broadening was negligible. The differences in intensity are much greater than the differences in line-width, and the effect is clearly one of greater saturation for the transitions for which $m_I(\text{N}) = -1$, *i.e.*, longer relaxation times. Thus, increasing the microwave power increases the differential intensity.

The theory of saturation in free radicals has been discussed by various workers,^{9,10} and a careful examination of the spectra of the *p*-benzosemiquinones has substantiated the main points of the theory. Differences in saturation were, however, rather small ($<10\%$), whereas for the *p*-nitroaniso radical anion the ratio of intensity for the "0" lines to the "-1" lines is more than 4:1. Such a large effect does not seem accountable in terms of the theories of Stephen and Fraenkel,⁹ though they specifically exclude the effect of relaxation *via* modulation of the nuclear quadrupole interaction. It is, however, interesting that, by considering two types of spin-lattice relaxation, namely, (i) motional modulation of the intramolecular anisotropic dipole-dipole interaction between the unpaired electron and the magnetic nuclei in the free radical and (ii) motional modulation of the anisotropic

⁹ Stephen and Fraenkel, *J. Chem. Phys.*, 1960, **32**, 1435.

¹⁰ Schreurs, Blomgren, and Fraenkel, *J. Chem. Phys.*, 1960, **32**, 1861; Kivelson, *ibid.*, 1960, **33**, 1094.

g -tensor, they show the observed saturation parameters (and hence relative intensities) of the hyperfine lines to depend on nuclear spin in such a way as to produce both a symmetrical effect about the centre of the spectrum and a linear variation from end to end. The saturation parameters, or the related relative peak heights as given in Tables 2 and 3, might then be expressed by an equation of the form $Z = Km^2 + Lm + M$, where m is the nuclear magnetic quantum number for the particular transition involved, and K , L , and M are parameters (not the same as those used by Stephen and Fraenkel⁹) depending on the g -tensors, the hyperfine interaction tensors, and the correlation time in the particular solvent. Our results would fit such an equation but, at the moment, neither theoretical nor experimental information is sufficient to justify a more detailed analysis.

(2) *Effect of fluorine nuclear-spin state.* The spectrum of the anion of *p*-fluoronitrobenzene in alcoholic or aqueous solution can be interpreted only by assuming that it is possible to assign a characteristic relaxation time to each group of anions with particular nitrogen and fluorine nuclear-spin quantum numbers, and that these relaxation times differ markedly from one another. If the relaxation times are such that partial saturation occurs at the microwave power levels used, the absorption lines in the spectrum, corresponding to changes in electron spin of one unit with no change in nuclear spins, will be reduced in intensity to different extents. Those lines corresponding to long relaxation times will saturate most and have the smallest intensity and the greatest line-width.

Although the effect may be attributed to the presence of a nuclear quadrupole moment in the case of the nitrogen atom, this is clearly not possible for fluorine. If the effect of $m_1(\text{F})$ is eliminated by taking the average size of each pair of lines $(+1, \pm\frac{1}{2})$, $(0, \pm\frac{1}{2})$, and $(-1, \pm\frac{1}{2})$, the relative intensities corresponding to differences in $m_1(\text{N})$ only are 1.0 : 1 : 0.76, almost identical with those obtained for *p*-chloronitrobenzene under the same conditions. This suggests that the contributions are additive and that some insight into the relaxation mechanisms may be obtained by trying to separate them.

However, it is apparent that in order to obtain a relation between relative intensities and $m_1(\text{N})$ and $m_1(\text{F})$ similar to that quoted earlier for $m_1(\text{N})$ only, it is necessary to include cross-terms such as $m_1(\text{N}).m_1(\text{F})$ and $m_1^2(\text{N}).m_1(\text{F})$ as well as $m_1(\text{N})$, $m_1^2(\text{N})$, and $m_1(\text{F})$. The necessity for including such terms can be appreciated qualitatively in terms of the theory of line-widths outlined by Carrington and Longuet-Higgins,¹¹ who extended the treatment given by Stephen and Fraenkel.⁹ A more detailed quantitative correlation appears justifiable. It is already clear, however, that one reason for the magnitude of the effect of the fluorine atom is the very considerable anisotropy of the hyperfine coupling constants. (The values given for the three principal axes in the radical $\cdot\text{CHF}\cdot\text{CO}\cdot\text{NH}_2$ are, for example, 189, 17, and 8 gauss.¹²) This effect is perhaps accentuated by the extreme electronegativity of fluorine, which will result in stronger interaction with the solvent sheath. The effect of temperature, previously noted, supports this view.

Similar observations relating to the anion of *m*-fluoronitrobenzene, and, with a less convincing interpretation, to that of *o*-fluoronitrobenzene, suggest that their behaviour may be interpreted in the same manner.

(3) *Effect of chlorine nuclear-spin state.* The variation in line-width and intensity between the lines of the chlorine quartet observed in the anion of *p*-chloronitrobenzene shows a somewhat similar effect, though accurate measurements were not possible. This system will also be complicated by the nuclear quadrupole moment of the chlorine nucleus and by the existence of two abundant isotopes.

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¹¹ Carrington and Longuet-Higgins, *J. Mol. Phys.*, 1962, **5**, 447.

¹² Cook, Rowlands, and Whiffen, *Proc. Chem. Soc.*, 1962, 252.