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Solvent Effects on Hyperfine Coupling Constants in Electron Paramagnetic Resonance Spectra

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The effect of various protic solvents on the nitrogen coupling constant (a_N) of some aromatic and aliphatic nitro radical anions has been examined by electron paramagnetic resonance employing *in situ* electrolytic generation techniques. The degree of variation of a_N of the aromatic nitro compounds qualitatively follows the dissociation constant of the protic solvent. Steric hindrance of and intramolecular hydrogen bonding to the nitro group have been found to affect the degree of change of a_N in the various solvents.

The initial study of the electrolytic generation of anion radicals in *aqueous* solution revealed that N^{14} hyperfine coupling constants of the anions of aromatic nitro compounds were some 3–4 gauss larger in water than in acetonitrile.¹ A further study showed this to be a general effect for the negative ions of aromatic nitro compounds, whereas practically no solvent influence could be detected for the anion radicals of aliphatic nitro compounds.²

These results led to an intensive experimental investigation of solvent effects.

Several reports of solvent effects on hyperfine coupling constants have appeared recently. Stone and Maki reported significant changes in proton splittings for several semiquinone ion radicals measured in aprotic and aqueous solvents.³ Iljasav found marked changes in coupling constants for two complex nitroso compounds when the solvent was varied between toluene and alcohol–water mixtures,⁴ and Deguchi observed both N^{14} and proton splittings in diphenylamine oxide varied with solvents.⁵ Heineken, Bruin, and Bruin observed proton coupling constants changed in the thioindigo radical using ethanol and acetone as solvents.⁶ Recently, Gendell, Freed, and Fraenkel have given an excellent picture of these effects for semiquinones and some nitro anions. They describe the redistribution of π -electron charge and spin density caused by localized solvent–radical ion complexes which undergo rapid exchange.⁷ Our experimental studies, both support and amplify the theoretical work of Fraenkel and co-workers. Most recently Tench and Coppens have reported solvent effects with photochemically generated aromatic nitro anions which are identical with previous findings.⁸

The present report is concerned almost entirely with electrolytically generated anion radicals of nitro compounds. A few other radical ions are included for reference. It should be noted that the electrolytic generation technique is particularly important in this type of study. Chemical reductimetric techniques would have been difficult if not impossible in many of the solvent systems used.

Experimental

The electrochemical generation techniques were those which, by now, are quite conventional.^{9,10} All electron paramagnetic

(1) L. H. Piette, P. Ludwig, and R. N. Adams, *J. Am. Chem. Soc.*, **83**, 3909 (1961).

(2) L. H. Piette, P. Ludwig, and R. N. Adams, *ibid.*, **84**, 4212 (1962).

(3) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **36**, 1944 (1962).

(4) A. W. Iljasav, *Zh. Strukt. Khim.*, **3**, 95 (1962).

(5) Y. Deguchi, *Bull. Chem. Soc. Japan*, **35**, 260 (1962).

(6) F. W. Heineken, M. Bruin, and F. Bruin, *J. Chem. Phys.*, **37**, 452 (1962).

(7) J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.*, **37**, 2832 (1962).

(8) A. J. Tench and P. Coppens, *J. Phys. Chem.*, **67**, 1378 (1963).

(e.p.r.) spectra were obtained with a Varian V-4500 spectrometer using 100-kc. modulation.

It was foreseen that the experimental results would be dependent on the presence of water in the solvents. Two approaches were considered: (a) to dry the solvent systems to the utmost degree and employ special handling during the electrochemical generation, or (b) to use solvent purification and handling methods standard to nonaqueous electrochemical practice. The latter approach was chosen (while the judgment on this decision may be open to question we are confident none of the data or conclusions have been compromised by this choice) because it seemed to provide the best method of acquiring data consistent with the existing literature in the area. Acetonitrile was purified *via* the conventional distillation methods.⁹ Dimethylformamide was Fisher certified reagent grade containing 0.03–0.07% water. It was used without further purification, and water pick-up during handling was such that the total water content was much less than 1%. The supporting electrolyte was 0.1 *M* tetraethylammonium perchlorate (TEAP) in all cases. Reagents were Eastman White Label or specially purified. Coupling constants are given in gauss and are believed to be correct to ± 1 –2%.

Results and Discussion

Table I summarizes some of the experimental results for nitrobenzene. Figure 1 gives a graphical representation of the shifts in a_N (for brevity, coupling constants are designated as a_N , a_H , etc.). (Where it is necessary to identify proton splittings, both as to position and nature of splittings, they are designated as $a_{H(d,p)}$, *i.e.*, a doublet splitting from a *para* proton. Similarly, $a_{H(o)}$ and $a_{H(m)}$ are triplet splittings from *ortho* and *meta* protons, respectively. Where the proton assignment is undetermined only the designation $a_{H(d)}$ or $a_{H(v)}$ is given.) By now most of the radical ions examined in this study have been reported in the literature. Except for expected solvent effects on the coupling constants the results are in complete accord with the literature data. Those radical ions we have studied which are believed to involve intrahydrogen bonding are discussed later in the text. The e.p.r. spectrum from reduction of *p*-nitrobenzoic acid in DMF–water or alcohol mixtures is a very well-resolved 27-line pattern with no accidental overlaps. It is readily interpreted in terms of the coupling constants given in Table II, and the observed spectrum agrees with the stick diagram in both position and intensities. The spectrum is presumably that of the dianion radical (*i.e.*, no splitting due to a carboxylate proton is observed). The spectrum from *o*-chloronitrobenzene in pure DMF is best interpreted in terms of a dominant N^{14} (*ca.* 10 gauss) and two slightly dissimilar protons. These give rise to two doublet splittings of 4.12 and 3.27 gauss. The two remaining ring protons are approximately equivalent and give an observed triplet splitting of *ca.* 1 gauss. Nothing can be said about the

(9) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(10) L. H. Piette, P. Ludwig, and R. N. Adams, *Anal. Chem.*, **34**, 916 (1962).

TABLE I
COUPLING CONSTANTS OF NITROBENZENE NEGATIVE ION AS
A FUNCTION OF SOLVENT COMPOSITION

DMF-water				
Water, %	a_N	$a_{H(d,p)}$	$a_{H(t,o)}$	$a_{H(t,m)}$
0	9.83	3.97	3.32	1.09
10	11.35	3.68	3.30	1.07
20	12.06	3.63	3.30	1.10
30	12.56	3.60	3.33	1.10
50	13.15	3.59	3.33	1.11
70	13.55	3.52	3.35	1.11
90	13.87	3.55	3.35	1.12
DMF-ethanol				
Ethanol, % ^a	a_N	$a_{H(d,p)}$	$a_{H(t,o)}$	$a_{H(t,m)}$
30	11.40	3.71	3.31	1.08
60	12.07	3.65	3.31	1.09
80	12.35	3.59	3.30	1.09
DMF-2-propanol				
2-Propanol, % ^a	a_N	$a_{H(d,p)}$	$a_{H(t,o)}$	$a_{H(t,m)}$
30	11.10	3.72	3.36	1.09
70	11.83	3.65	3.34	1.09
MeCN-water				
Water, %	a_N	$a_{H(d,p)}$	$a_{H(t,o)}$	$a_{H(t,m)}$
0	10.48	3.82	3.36	1.09
10	12.78	3.61	3.37	1.12
20	13.20	3.54	3.45	1.11
50	13.59	3.54	3.44	1.12
MeCN-ethanol				
Ethanol, % ^a	a_N	$a_{H(d,p)}$	$a_{H(t,o)}$	$a_{H(t,m)}$
10	11.65	3.67	3.32	1.08
30	12.06	3.61	3.31	1.08
50	12.15	3.62	3.31	1.10
Pyridine-water ^b				
Water, %	a_N	$a_{H(d,p)}$	$a_{H(t,o)}$	$a_{H(t,m)}$
0	10.51	3.86	3.48	1.09
4	11.25	3.76	3.32	1.05
30	12.98	3.60	3.32	1.08

^a For brevity, values for 0% alcohol (100% DMF or MeCN) not repeated. ^b Electrolyte LiClO₄, solubility of tetraethylammonium perchlorate (TEAP) too low; all other solvents contain 0.1 M TEAP as supporting electrolyte.

position assignments of these splittings. As the water concentration is increased the *ca.* 4-gauss single proton coupling decreases until it is practically identical with the other proton (see *o*-chloronitrobenzene in Table III; at >40% water the two "doublet" splittings have the same value and thus merge to an observed triplet). This behavior is almost identical with that reported recently for *o*-chloronitrobenzene in alkaline aqueous media by Ayscough, Sargent, and Wilson. Similarly our spectrum of *p*-nitrobenzoic acid is practically identical with theirs at high water-DMF ratios.¹¹

The general behavior of aromatic nitro compounds is well illustrated by nitrobenzene. As seen in Table I and particularly Fig. 1, a_N increases markedly with increasing water or alcohol content. The solvent effect on a_H is less pronounced. As seen later, a_H values for substituted nitrobenzenes may either increase or decrease with solvent changes.

The greatest change in a_N occurs in the region of small concentrations of water or alcohol. As indicated by the slopes of the curves in Fig. 1, the rate and total

(11) P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963).

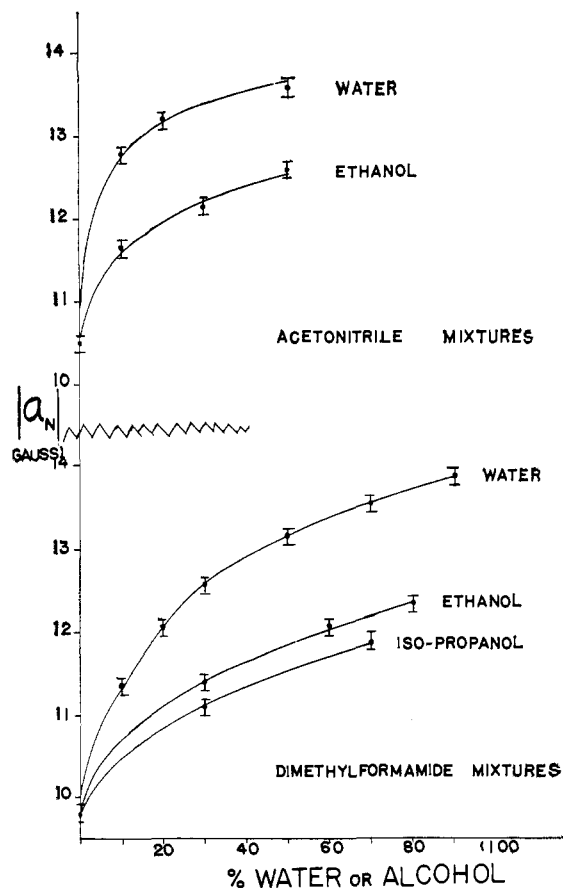


Fig. 1.—Solvent dependence of a_N in nitrobenzene anion.

magnitude of change in a_N decreases in the order: water, ethanol, and 2-propanol. Relatively little significance should be attached to a_N values in inert solvents which are alleged to be pure. (The arbitrary solvent classification inert refers to acetonitrile (MeCN), dimethylformamide (DMF), pyridine (Py), etc.) MeCN, DMF, etc., purified by whatever means always contain about mmolar water concentrations as determined say, *via* Karl Fischer titration. In view of the strong a_N dependence on small amounts of "active" solvents like water, the a_N value for "pure" MeCN, DMF, etc., is always somewhat doubtful. We believe a_N values for nitro anion radicals may vary by 0.2 to 0.5 gauss in "pure" solvents like DMF and MeCN. This is borne out by comparisons of most careful measurements for nitrobenzene negative ion in "0% water" by several workers.

The behavior of substituted nitrobenzenes varies from little or no change in a_N with solvent as is the case with *o*-nitrobenzoic acid in ethanol, to the most pronounced shift in the case of nitromesitylene. The wide range of typical responses is shown in Fig. 2 for solvent mixtures of DMF and water (alcohol in the case of the *o*-nitrobenzoic acid). The exact data are given in Tables II-IV.

General Nature of Solvent Interaction

A survey of the data indicates that the interaction between radical ion and solvent which markedly affects a_N values is closely related to the possibility of hydrogen-bond (H-bond) formation. As seen from Tables I-IV large variations in a_N only occur when the solvent can act as a proton donor. (This does not imply the radical ion does not solvate with MeCN,

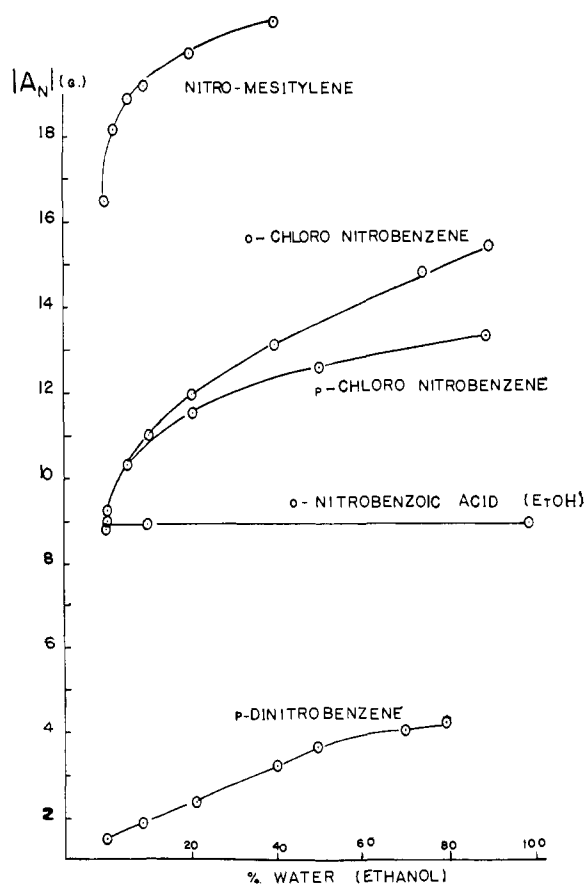


Fig. 2.—Solvent dependence of a_N for substituted nitrobenzene anions.

DMF, etc., but only that H-bond or hydroxylic solvation is much stronger.) Further, large changes in coupling constants occur only when the radical ion can act as an acceptor. The effect of 2% water in MeCN changed the a_H values of anthracene negative ion by only 0.01 gauss. Similarly the a_H values of phenanthrene anion radical in pure MeCN and 10% water-MeCN differ by only 0.06 gauss. (These hydrocarbon anions were generated *via* the standard *in situ* technique. While the anions have shorter lifetimes in the water mixtures, the e.p.r. spectra are otherwise not significantly different.) An obvious conclusion is that the nitro anions (and other radical ions primarily with functional groups) are suitable acceptors for H-bonding with hydroxylic solvents. Similar interactions with hydrocarbons are certainly very weak.

The H-bond hypothesis is strengthened when one observes the solvent effects on *ortho*-substituted nitrobenzene anions where intra-H-bonding is possible. In Fig. 2 and Table III (entry 4) one sees that the a_N of *o*-nitrobenzoic acid shows almost no shift from pure DMF to 100% ethanol. Strong intra-H-bonding could occur in *o*-nitrobenzoic acid. That the e.p.r. spectrum one observes with electrolytic reduction of *o*-nitrobenzoic acid in ethanol is the monoanion with the intra-H-bonded carboxylate proton retained is strongly suggested by the fact that a proton doublet with rather large a_H is obtained. If the electrolysis is carried out in either water or D_2O , the doublet splitting disappears. It is most reasonable that this doublet is due to the carboxylic acid proton. The solvent behavior of *o*-nitrobenzoic acid is in marked contrast

TABLE II
SOLVENT EFFECTS ON SOME *para*-SUBSTITUTED NITROBENZENE ANION RADICALS

(1) <i>p</i> -Dinitrobenzene, DMF-water				
Water, %	a_N^a	a_H^b		
0	1.47	1.16		
10	1.89	1.13		
20	2.31	1.11		
40	3.14	1.07		
70	3.98	1.09		
80	4.16	1.15		
(2) <i>p</i> -Nitrobenzotrile, DMF-water				
Water, %	$a_N(NO_2)$	$a_N(CN)$	$a_H(t)$	$a_H(l)$
0	6.60	0.77	3.23	0.76
6	8.04	0.77	3.30	0.76
20	9.45	0.71	3.36	0.97
(3) <i>p</i> -Nitrobenzoic acid, DMF-water				
Water, %	a_N	$a_H(t)$	$a_H(l)$	
0	9.63	3.25	1.08	
5	9.81	3.24	1.07	
20	10.71	3.24	1.08	
90	12.68	3.32	1.13	
(4) <i>p</i> -Nitrobenzoic acid, DMF-ethanol				
Ethanol, %	a_N	$a_H(t)$	$a_H(l)$	
0	9.63	3.25	1.08	
10	10.25	3.23	1.06	
20	10.65	3.28	1.07	
40	11.09	3.26	1.08	
80	11.69	3.27	1.09	
90	11.86	3.27	1.08	
(5) <i>p</i> -Chloronitrobenzene, DMF-water				
Water, %	a_N	$a_H(t)$	$a_H(l)$	
0	9.16	3.42	1.11	
5	10.26	3.43	1.15	
20	11.50	3.40	1.18	
50	12.53	3.39	1.20	
90	13.29	3.43	...	
(6) <i>p</i> -Nitroaniline, DMF-water				
Water, %	a_N			
0	11.59			
10	13.19			
20	13.63			
40	14.16			
80	14.50			

^a Interaction with two equivalent N^{14} nuclei. ^b Interaction with four equivalent protons.

to that of *p*-nitrobenzoic acid. Here, where no intra-H-bonding is possible, a_N shifts markedly with alcohol and water additions (Table II, entries 3, 4).

Nitroresorcinol (2,6-dihydroxy-1-nitrobenzene) and nitromesitylene (2,4,6-trimethyl-1-nitrobenzene) present an interesting comparison. The former compound has the possibility of forming two intra-H-bonds with the *ortho* hydroxyl functions. Although a_N is initially large, it is hardly affected by large amounts of hydroxylic solvent. (In this case D_2O was used to aid in interpreting proton splittings and provides an unequivocal assignment. Thus the 0.49-gauss triplet splitting is only observed with 0% D_2O and is due to the phenolic protons. Since the other proton splittings in nitroresorcinol are a solvent-invariant triplet (*ca.* 0.96 gauss) and a doublet (*ca.* 3.4 gauss), they can be assigned to the *meta* and *para* protons, respectively.) In contrast to nitroresorcinol, nitromesitylene (no intra-H-bonding) shows a large shift in a_N . This case is discussed in more detail later. It appears that

TABLE III
SOLVENT EFFECTS ON SOME *ortho*-SUBSTITUTED NITROBENZENE ANION RADICALS

(1) <i>o</i> -Chloronitrobenzene, DMF-water				
Water, %	a_N	$a_{H(d)}$	$a_{H(t)}$	$a_{H(t)}$
0	9.06	4.12	3.27	1.14
5	10.38	3.84	3.27	1.14
10	10.87	3.41	3.21	1.14
40	13.09	3.12	3.10	1.14
75	14.78	2.84	2.84	1.14
90	15.4	2.77	2.77	1.13
(2) Nitromesitylene, DMF-water				
Water, %	a_N		Σa_H^a	
0		16.4		12.3
2		18.2		9.9
5		19.0		8.9
10		19.6		7.6
20		20.0		6.7
40		20.7		5.2
80		21.3		4.6
(3) <i>o</i> -Nitrobenzoic acid, DMF-ethanol				
Ethanol, %	a_N	$a_{H(d)}^b$	$a_{H(t)}$	$a_{H(t)}$
0	8.89	11.67	3.24	1.04
10	8.90	11.80	3.24	1.05
20	8.87	11.85	3.25	1.05
100	8.93	11.96	3.28	1.06
(4) 2,6-Dihydroxynitrobenzene (nitroresorcinol), DMF-D ₂ O				
D ₂ O, %	a_N	$a_{H(t,OH)}$	$a_{H(t,m)}$	$a_{H(d;p)}$
0	14.19	0.49	0.94	3.43
10	14.51	..	0.96	3.41
30	14.81	..	0.97	3.38
50	15.02	..	0.97	3.38

^a Σa_H measured as total width of each N¹⁴ splitting (unable to resolve as individual splittings). ^b In either aqueous or D₂O solutions, this doublet splitting is not observed; hence, it is believed that this is due to the carboxylic proton.

TABLE IV
COUPLING CONSTANTS OF 2-NITROPROPANE IN DMF-WATER MIXTURES^a

% Water	a_N	$a_{H(d)}$	$a_{H(CH_3)}$
0	25.1 ± 0.2	4.92 ± 0.26	...
10	25.4 ± 0.3	4.92 ± 0.09	...
100	25.6 ± 0.5	4.66 ± 0.02	0.24 ± 0.01
20% <i>t</i> -butyl alcohol-DMF	25.5 ± 0.4	4.78 ± 0.12	...

^a In pure DMF, the septet splitting from the six methyl protons is not resolvable. All values listed are the mean of at least two upfield and two downfield sweeps.

hydroxylic solvents interact only weakly, if at all, with those anion radicals where the nitro function is already involved in strong intra-H-bonding.

It is significant that the literature contains very few reports on inter-H-bonding of aromatic nitro compounds. Hammond and Modic assigned the red shift of the nitrobenzene ultraviolet absorption to H-bonding.¹² The classical study of Bayliss and McRae also attributes the red shift of the 2900-Å absorption of nitrobenzene in hydroxylic solvents to H-bonding.¹³ A few other investigations mention H-bonding of nitrobenzene in connection with optical spectra studies.¹⁴⁻¹⁶ Infrared data supporting inter-H-bonding of aromatic nitro compounds are equally meager.

(12) G. S. Hammond and F. J. Modic, *J. Am. Chem. Soc.*, **75**, 1385 (1953).

(13) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1006 (1954).

(14) K. Semba, *Bull. Chem. Soc. Japan*, **34**, 722 (1961).

It is important to point out that in this study we are concerned not with the parent nitrobenzene molecule but with the negatively charged anion radical. The behavior of it as an acceptor in a H-bond pair should be greatly enhanced over that of the parent molecule by the increased localized charge on the nitro group. Thus it is firmly believed that H-bonding (solvation) with the hydroxylic solvents is responsible for the large changes in e.p.r. hyperfine couplings observed here. Furthermore, in most solvent systems, like DMF and MeCN, the anion radical is, in all probability, complexed with the particular solvent. Thus, one would deal with interchanges of the type



where IS and SOH represent inert and hydroxylic solvents, respectively. The term inert solvent clearly does not imply that interactions with the anion radical are nonexistent—only that these solvents do not change a_N as much as hydroxylic donors. At present there is little information on the solvation numbers involved.

Interpretation of Coupling Constant Changes

The interpretation by Gendell, Freed, and Fraenkel⁷ proposes localized solvent complexes with the functional group of the radical ion. Since these complexes undergo rapid exchange, hyperfine splittings with magnetic nuclei in the solvent are not observed but a marked redistribution of charge and π -electron spin density in the functional group may occur. Neglecting the contribution from the carbon to which the nitro N¹⁴ is bonded, Fraenkel and co-workers have given the expression^{17,18}

$$a_N = 99.0\rho_N^\pi - 71.6\rho_O^\pi$$

where the ρ^π values are the π -electron spin densities on the respective nitrogen and oxygen atoms. This equation emphasizes that small changes in, say, ρ_O^π which will occur due to solvent interaction will alter a_N materially since the Q values are large in magnitude and opposite in sign. Alterations of coupling constants in the solvated complex may result only from charge interactions of the oxygen *via* H-bonding, but the changes may be primarily due to geometric and spatial characteristics of the solvation complex or, most likely, a combination of both effects. Some physical models of the solvent interaction are considered below in light of the present experimental data.

A. Twisting of Nitro Group.—While mechanical pictures to represent molecular interactions are open to much criticism, they are often helpful. One geometric representation of the complex might consider the solvated nitro group to be twisted around a line in the plane of the ring. Such a twisting effect in sterically hindered nitro compounds has been shown conclusively by Geske and Ragle to cause a large increase in the N¹⁴ coupling constant.^{19a} This is consistent with the effect of hydroxylic solvents on

(15) M. Godfrey and J. N. Murrell, *Proc. Chem. Soc.*, 171 (1961).

(16) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962.

(17) J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1881 (1962).

(18) P. H. Rieger and G. K. Fraenkel, *ibid.*, **39**, 609 (1963).

(19) (a) D. H. Geske and J. L. Ragle, *J. Am. Chem. Soc.*, **83**, 3532 (1961);

(b) D. H. Geske, J. L. Ragle, M. A. Bannbenek, and A. L. Balch, *ibid.*, **86**, 987 (1964).

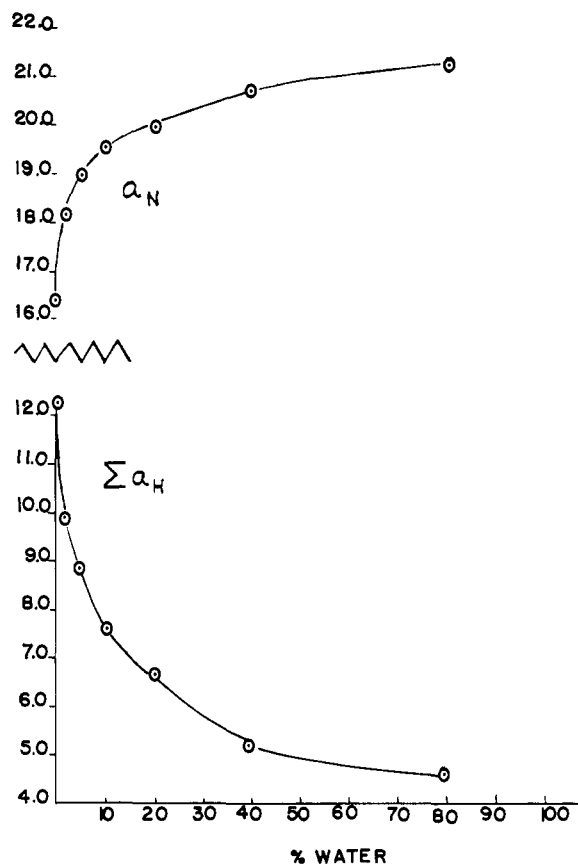


Fig. 3.—Variation of a_N and Σa_H for nitromesitylene anion.

the nitrobenzene anion. However, as a consequence of the twisting, the π -system of the nitro group and the ring tend to decouple, and the increased spin density on the N^{14} occurs at the expense of decreasing density on the ring proton.^{19a,b} This type of effect does not account entirely for the a_N change with nitrobenzene anion. While a_N increases by some 40%, $a_{H(d,p)}$ decreases by ca. 10% while the remaining protons hardly change (Table I).²⁰ Similar effects are noted for all *para*-substituted nitrobenzenes in Table II; the changes in ring proton couplings are very small in general. In *p*-dinitrobenzene (Table II, entry 1) the two equivalent N^{14} nuclei show a relatively small $a_N = 1.47$ gauss in pure DMF. This changes by a very large percentage to about 4 gauss with large water additions, but the ring proton couplings are practically unchanged. It may be concluded then that the formation of the solvation complex does not show evidence of significant twisting of the nitro group provided that the nitro group is essentially isolated spatially from other ring substituents.

That the twisting effect is operative in some cases can be seen in the data of Table III. With *o*-chloronitrobenzene a particularly large change in a_N occurs—a total change of ca. 6.5 gauss, as compared to 4.2 gauss for *p*-chloronitrobenzene (see Fig. 2) or 4.1 gauss for nitrobenzene with similar amounts of water added. In addition a large decrease of about 1.3 gauss is seen in $a_{H(d)}$ with *o*-chloronitrobenzene (entry 1, column 3). The other proton doublet also decreases significantly. These results are just what one expects if twisting of the nitro group occurs. The chlorine

atom is about as effective as a methyl with regard to its steric influence on an adjacent nitro group. In the case of 1-nitro-2-methylbenzene the twist angle of the nitro group has been estimated at 34° by Wepster.²¹

In view of Geske and Ragle's results one would expect the a_N of *o*-chloronitrobenzene anion to be greater than that of the *p*-chloronitrobenzene anion in the same solvent. One notes however that the a_N values in pure DMF are almost identical (from Tables II and III, $a_N = 9.06$ and 9.16 gauss, respectively). We suggest the similarity of the a_N values for *o*- and *p*-chloronitrobenzene is due to the fact that formation of the anion radical, with its resulting tendency toward coplanarity, overcomes the expected increase in a_N for the *ortho* compound because of twisting in the ground state. Similar conclusions on the planar character of nitro anion radicals have been expressed by Rieger and Fraenkel.¹⁸ Nonetheless, if an H-bond complex is formed, the nitro group must be dislocated to accommodate the added bulky group and is reflected in the "extra" sensitivity of a_N and the decrease in ring proton couplings when hydroxylic solvents are added. (It can be noted that the a_N data given above for *o*- and *p*-chloronitrobenzene are in accord with studies of *o*- and *p*-nitrotoluene.^{19b})

The twisting effect is most pronounced in nitromesitylene where, upon adding 80% water to DMF, a_N increased from 16.4 to 21.3 gauss (Table III, entry 2). It has not been possible to resolve the individual proton splittings in this spectrum. However, by taking the total width of each of the three nitrogen lines one obtains an estimate of Σa_H , and this value decreases markedly as expected with the twisting effect. The pronounced increase of a_N concurrent with the decrease of Σa_H is illustrated in Fig. 3. It is interesting to note that the limiting effect of water on nitromesitylene anion is to increase a_N to a value comparable to that of the most sterically hindered aromatic nitro compounds.^{19b}

B. Out-of-Plane Bending of Nitro Group.—There is at least another physical deformation which may be caused by solvation of the nitro anion radical. This is a bending of the nitro group out of the plane of the ring and was discussed by Geske and Ragle.^{19a} In this case a_N may increase due to increasing s-character of the nitrogen. However, since extensive decoupling of the two π -systems does not occur, spin density on the ring is relatively unaffected. This effect could be operative in the case of nitrobenzene anion and other nonsterically hindered nitro anions (*i.e.*, *para*-substituted nitrobenzenes). The present data do not allow one to make any judgments on this effect. To elucidate some of these factors studies of the solvent effect on the visible and infrared spectra of nitro anion radicals have been examined and will be reported later.

Aliphatic Nitro Compounds

Previous studies showed that the N^{14} couplings of aliphatic nitro compounds were practically solvent independent. This is surprising, and, as a typical example, 2-nitropropane was re-examined carefully. Table IV summarizes the data for DMF-water mixtures. The reproducibility of coupling constants for this compound is, in general, less than that obtained

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with the aromatic compounds. While we had hoped to obtain more reproducible data for aliphatic nitro compounds, it is obvious that the changes in a_N are so small as to be negligible in comparison to aromatic nitro compounds.

A satisfactory interpretation of the absence of a_N solvent dependence for the aliphatic compounds is complicated by a lack of understanding at present of the nature of the hyperfine interactions in these compounds.

The lack of solvent dependence of a_N in aliphatic nitro compounds could be explained if they showed far less tendency to H-bond than their aromatic counterparts. On the contrary, nitroalkanes appear to H-bond (both intra- and inter-) as well as aromatics as evidenced by several spectral studies.^{13,16,22-24} Thus, with evidence to support H-bonding in the parent nitroalkanes, it is to be expected that the anion radicals will H-bond at least as strongly as nitroaromatics.

Assuming that H-bonding does occur with the aliphatic nitro anion radicals, then certainly some degree of charge redistribution in the nitro group should occur. Provided the relation given by Fraenkel and co-workers for a_N is applicable to an aliphatic nitro group, one would expect a decided solvent dependence of a_N . This is not found experimentally.

There is one other important distinction between aliphatic and aromatic nitro compounds, namely, that there is essentially unrestricted rotation of the nitro groups about the CN bond. Calculations by Stone and Maki²⁵ show the barrier to hindered rotation to be quite small, and one experimental study indicated this may be less than calculated. Thus, an aliphatic nitro compound should be relatively insensitive to distortions of molecular geometry which might accompany solvation. In fact, it may be that the solvent-insensitive nature of N^{14} couplings in aliphatic nitro compounds strengthens the view raised in this work that the a_N shifts with solvent in aromatic nitro compounds is perhaps associated with geometrical changes. These changes then are reflected in the MO parameters, which, in fact, provide valid calculations of the magnitude of the effect.

Potential Advantages of Solvent Effects

At first glance it would appear that the solvent effect on hyperfine coupling constants only makes more difficult any correlations of experiment and theory in e.p.r. spectroscopy. In practice we have found several situations where the solvent effect is advantageous.

In those substituted nitrobenzene anion radicals where there is a very strong N^{14} coupling, the e.p.r. spectrum shows a dominant triplet of 1:1:1 intensity, but if a_N is small and comparable to other ring splittings, considerable overlaps occur. It often helps in deciphering the spectrum to add a few per cent water to "spread out" the N^{14} splittings, possibly eliminating some overlaps. At very least, the N^{14} splitting is identified as that with the large solvent dependence.

While there is very little question about the proper assignment of the two N^{14} coupling constants in *p*-nitro-

benzotrile,^{26,27} as indicated by Fraenkel, *et al.*,²⁷ the assignments are not uniquely determined by the experiments. If one compares the solvent dependence of a_N for nitrobenzene, benzonitrile, and *p*-nitrobenzotrile over the same range of water in DMF (Table V,

TABLE V
SOLVENT DEPENDENCE OF $a_N(NO_2)$ AND $a_N(CN)$ IN
DMF-WATER MIXTURES

(1) Nitrobenzene				
% water	$a_N(NO_2)$	$a_N(CN)$		
0	9.79			
10	11.40			
20	11.90			
(2) Benzonitrile				
0		2.16		
10		2.18		
20		2.20		
(3) <i>p</i> -Nitrobenzotrile				
0	6.60	0.76		
6	8.04	0.76		
20	9.45	0.70		
(4) 4-Nitropyridine				
% water	a_{N^1}	a_{N^2}	$a_{H(t)}$	$a_{H(t)}$
0	6.75	2.85	2.62	0.33
5	8.40	3.00	2.55	0.45
15	9.30	3.04	2.62	0.52

entries 1-3), it is easy to see the nitrile N^{14} splitting in benzonitrile is relatively unaffected. In *p*-nitrobenzotrile it is the small (0.76 gauss) coupling which is solvent insensitive while the larger coupling shifts strongly. Thus the previous assignments of the 0.76-gauss splitting to the CN nitrogen is rendered even more reasonable.

The spectrum of 4-nitropyridine has apparently not been reported previously. The coupling constants are listed under entry 4 in Table V. There is considerable doubt as to the assignment of the N^{14} splittings to ring nitrogen *vs.* nitro group. While the *ca.* 7-gauss splitting listed as a_{N^1} at first glance seems reasonable for a nitro group, ring nitrogens in diazines are about of this magnitude.²⁸⁻³² The strong increase of a_{N^1} with added water leads us to suspect this is the nitro function. This is not unequivocal since one has as yet no idea of the solvent dependence of the pyridine nitrogen. Unfortunately, attempts to make the pyridine anion radical have resulted in the 4,4'-bipyridyl anion.³³ All measurements of the diazine negative ions have been made in either dimethoxyethane or tetrahydrofuran.

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