the esr spectra of the $(C_6H_5)_2CN_2$ intermediates suggest that biradical polymers of different chain lengths coexist. Biradical polymers are known to exhibit esr spectra in which the line width depends on the length of the polymer chain.[38]

It is evident that the radical intermediates bear a direct structural relationship to both the initially formed carbenes and the final decomposition products of the diazo compounds. Furthermore, the observation of radical products formed from the particular diazo compounds included in this study is direct evidence for the triplet-state nature of their carbene intermediates.

Acknowledgments. We thank Mrs. S. B. Wallon for the synthesis of the diazo compounds and Mr. A. R. Cherry for his assistance in analyzing the esr spectra.

Electron Spin Resonance of Oxygen-17 Enriched Pentamethylnitrobenzene and *p*-Dinitrobenzene Anion Radicals

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Abstract: Synthesis of ^{17}O-enriched pentamethylnitrobenzene (PMNB) and *p*-dinitrobenzene (DNB) has been accomplished. Electrochemical reduction of these compounds has permitted observation of the isotropic ^{17}O coupling constants for the resulting anion radicals in several different solvents. The oxygen coupling constant, a_O, for PMNB$^-$ in dimethylformamide was -11.54 G. a_O increased on addition of water to -10.80 G when the water content reached a mole fraction of 0.788. a_O for DNB$^-$ was -3.82 G in dimethylformamide and decreased to -4.36 G on addition of 0.147 mole fraction of water. In addition, PMNB$^-$ was observed in a rigid glass, and anisotropic parameters for both ^{14}N and ^{17}O were obtained. The solvent dependence of a_O suggests that steric interactions are involved in the solvent effect. The ^{17}O data are discussed in relation to previous models for solvent effects and in relation to previous spin-density estimates for nitro aromatic radicals.

It is well known that the magnitude of the isotropic nitrogen coupling constant, a_N, in the electron spin resonance (esr) spectra of nitro aromatic anion radicals is strongly dependent upon the detailed nature of the medium containing the radicals. a_N increases as the solvent is made progressively more polar, say by addition of water to acetonitrile. These observations were explained by Rieger and Fraenkel[2] on the basis of the model proposed by Gendell, Freed, and Fraenkel,[3] that of rapidly exchanging solvent–radical complexes which cause a redistribution of unpaired spin density, primarily at the oxygen atoms of the nitro group. This shift in spin density was approximated in Hückel molecular orbital calculations by making the oxygen atoms more electronegative, *i.e.*, by using larger absolute values of α_O, the oxygen Coulomb integral. This results in progressively larger predicted values of ρ_N^π, the π-spin density on nitrogen, but progressively smaller values of ρ_O^π. In a study[4] of ^{17}O-enriched nitrobenzene anion we found that as the solvent was made more polar a_N increased, but so did $|a_O|$. This observation is explicable within the framework of the model outlined above if a_O can be represented by an equation of the form

$$a_O = Q_1\rho_O^\pi + Q_2\rho_N^\pi \qquad (1)$$

in which the Q's are of comparable magnitude and have the same sign. (The results for nitrobenzene anion could be accommodated with Q's of opposite sign if the dominate contribution to a_O came from the term containing ρ_N^π; it appears that this is not so.) However, if analogy to the theory of Karplus and Fraenkel[5] is applicable, then the contribution to a_O from polarization due to spin on nitrogen may be expected to be of opposite sign to the contribution from spin on ^{17}O itself.

Ling and Gendell,[6] as an outgrowth of a study of the effects of alkali cations on a_N in nitro aromatic anions, pointed out that calculated values of both ρ_O^π and ρ_N^π can be made to increase if α_N is increased, as well as α_O, to simulate increasing solvation or electrostatic interaction with a gegenion.

Thus, an increase in the magnitude of a_O can be predicted from the term $Q_1\rho_O^\pi$ alone and Q_2 in eq 1 could be zero. Data presented in this report, however, show that in pentamethylnitrobenzene anion the magnitude of a_O *decreases* with increasing solvent polarity, a result correctly predicted by increasing only α_O in the MO calculations and not predicted by the method suggested by Ling and Gendell.[6] Our data indicate that changes in a_O with variation in solvent polarity (and presumably also with ion pair formation) are distinctly different for a radical containing a sterically crowded nitro group than for those containing unhindered nitro groups.

The importance of steric considerations has been suggested previously in a slightly different context. In fact, the entire correlation of a_N values with HMO calculations, as exemplified by the work of Rieger and

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[1] (a) Author to whom communications should be addressed. (b) Deceased, Dec 4, 1967.

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

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

[4] W. M. Gulick, Jr., and D. H. Geske, *J. Am. Chem. Soc.*, 87, 4049 (1965).

[5] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, 35, 1312 (1961).

[6] C.-Y. Ling and J. Gendell, *ibid.*, 47, 3475 (1967).

Fraenkel,[2] has been challenged by Fox, Gross, and Symons.[7,8] Data obtained by these authors[7] from rigid glass esr spectra were used to calculate values of ρ_N^π much larger than those obtained from HMO theory, thereby requiring smaller values of the Q parameters for a_N. In addition, Symons, *et al.*,[7] suggested that, as the spin density on nitrogen increased, the nitro group would undergo a distortion toward pyramidal conformation resulting in an increase in the s character of the unpaired electron and an exaltation of a_N.

Clearly, experimental investigation of the spin density on the nitro group oxygen atoms is of value in any attempt to describe the total spin distribution and is highly pertinent to studies of the solvent effects observed for this class of anion radicals. The data previously reported[4] for nitrobenzene anion (NB⁻) were, alone, insufficient. Thus, we regarded acquisition of ^{17}O esr data for nitro aromatic anion radicals which possessed very different values of a_N and therefore very different π-electron spin densities on the atoms of the nitro group as the next logical step in studying the problems set forth above.

p-Dinitrobenzene anion was selected because of the very small[9] value of a_N and the symmetry of the molecule. Pentamethylnitrobenzene anion was chosen because it was known to exhibit a large nitrogen coupling constant and only three resolvable hyperfine components in its esr spectrum.[10] Ease of isotopic enrichment was another important criterion in choosing these radicals.

We report here the synthesis of *p*-dinitrobenzene with one nitro group enriched in ^{17}O and of ^{17}O-enriched pentamethylnitrobenzene; for the corresponding anion radicals we report isotropic coupling constants for ^{14}N and ^{17}O as functions of solvent composition. In addition, rigid glass esr spectra were observed and anisotropic parameters obtained. As a matter of ancillary interest, high-resolution infrared spectra of the heavy oxygen enriched compounds are presented, and the mechanism of the nitration reaction employed to produce enriched dinitrobenzene is examined.

Experimental Section

Reagents. Acetonitrile, N,N-dimethylformamide (DMF), tetraethylammonium perchlorate, and tetrabutylammonium perchlorate were prepared as described previously.[10,11] Pentamethylbenzene, *p*-nitroaniline, and 1,1-diphenyl-2-picrylhydrazyl were obtained from Distillation Products Industries, while anhydrous aluminum chloride, benzene, chloroform, and carbon tetrachloride were Mallinckrodt analytical reagents. Dimethoxyethane was distilled *in vacuo* from potassium–anthracene before use. Thin layer chromatography was carried out using Silica Gel GF (Merck) obtained from Brinkman Instruments, Inc. Nitrations were performed using isotopically enriched NO_2 prepared as described previously[4] from nitric oxide (Matheson) and isotopically enriched oxygen gas (YEDA Research and Development Co., Ltd.).

^{17}O-Pentamethylnitrobenzene. A 4.46-mmole sample of NO_2 (prepared from oxygen gas of composition 35.8 atom % ^{17}O and 34.85 atom % ^{18}O) was condensed *in vacuo* into a reaction vessel containing 1.0 g (5.9 mmoles) of pentamethylbenzene and 2.2 g (15 mmoles) of anhydrous aluminum chloride in 35 ml of chloroform. The flask was sealed and heated at *ca.* 75° for 2 hr with stirring. The mixture was cooled and washed with 125 ml of water. The phases were separated by centrifugation and the aqueous layer was discarded. After concentrating the chloroform solution to *ca.* 20 ml, product separation was effected *via* thin layer chromatography on silica gel using benzene eluent. After recrystallization from methanol, 90 mg (10.5% yield based on molecular oxygen) of pentamethylnitrobenzene was obtained, mp 143–145° (lit.[12] 154°).

^{17}O-*p*-Dinitrobenzene. The most obvious way of preparing *p*-dinitrobenzene with isotopic enrichment of *one* nitro group might appear to be nitration of acetanilide with NO_2 as described by Topchiev[13] followed by hydrolysis and oxidation of the amine with trifluoroperacetic acid. The nitration, however, appears to require a large excess of NO_2, and in our hands only a trace of *p*-nitroacetanilide was obtained by employing only a stoichiometric quantity of this reagent. We found, however, that NO_2 would convert *p*-nitrosonitrobenzene to the desired dinitrobenzene in reasonable yield. *p*-Nitrosonitrobenzene, prepared by Caro's acid oxidation of *p*-nitroaniline according to the method of Bamberger and Hübner,[14] was recovered and purified by repeated steam distillation (mp 117–118°, lit.[14] 118.5–119°).

A 4.46-mmole sample of NO_2 (prepared from oxygen gas of composition 36.47 atom % ^{17}O and 40.17 atom % ^{18}O) was condensed *in vacuo* into a reaction vessel containing 330 mg (2.17 mmoles) of *p*-nitrosonitrobenzene in 50 ml of chloroform. The mixture was heated in the stoppered flask at 70–80° for 3.5 hr. The reaction mixture was cooled and the solvent removed, leaving a yellow-green solid residue which, after recrystallization from 95% ethanol, melted at 169–171° (lit.[15] 173°). The yield was 263 mg or 36.3% based on molecular oxygen.

Electron Spin Resonance. Radical anions were generated in solution by electrolytic reduction of the nitro compounds using the *intra muros* technique.[16] Spectra of pentamethylnitrobenzene anion (PMNB⁻) were obtained using a Varian flat electrolysis cell in a Varian V-4531 multipurpose cavity; spectra of dinitrobenzene anion (DNB⁻) were obtained using a 3-mm o.d. cylindrical cell in the cylindrical cavity described previously.[16]

Radicals for glass spectra were generated by exhaustive controlled-potential reduction of 1–2 m*M* solutions of the nitro compounds in a mixture of two volumes of DMF with one volume of acetonitrile. Electrolyses were carried out in a standard three-compartment cell external to the microwave cavity. The cathode compartment was fitted with a syphon which allowed samples to be withdrawn into an evacuated quartz tube. A three-way stopcock permitted connecting the filled sample tube to the vacuum pump for degassing and seal-off. Varian 5-mm quartz sample tubes were employed and spectra were obtained at 77°K using a Varian liquid nitrogen dewar in the multipurpose cavity. When stored in liquid nitrogen, samples prepared in this manner appeared to be indefinitely stable. No changes in spectra were observed when samples were rotated in the microwave cavity, indicating that the frozen solutions were in fact glassy.

p-Dinitrobenzene anion radical in dimethoxyethane was obtained by electroreduction in a vacuum electrolysis cell similar to that described by Johnson and Chang.[17] Tetrabutylammonium perchlorate supporting electrolyte was employed in this experiment. All other solutions for electrochemical reduction were made 0.1 *M* in tetraethylammonium perchlorate supporting electrolyte.

The Varian esr spectrometer employed has been described by Kuwata and Geske.[11] Magnetic-field calibration was achieved as described previously.[18] The g-value measurements were made *vs.* DPPH for which we took $g = 2.0036$.

Infrared Spectra. Both the natural and oxygen-labeled nitro compounds were studied as 3% solutions in carbon tetrachloride

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[7] W. M. Fox, J. M. Gross, and M. C. R. Symons, *J. Chem. Soc., A*, 448 (1966).

[8] J. M. Gross and M. C. R. Symons, *ibid.*, 451 (1966).

[9] A. H. Maki and D. H. Geske, *J. Chem. Phys.*, 33, 825 (1960).

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[13] A. V. Topchiev, "Nitration of Hydrocarbons and Other Organic Compounds," C. Mathews, translator, Pergamon Press, New York, N. Y., 1959, p 243.

[14] E. Bamberger and R. Hübner, *Chem. Ber.*, **36**, 3803 (1903).

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[16] D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960).

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[18] W. M. Gulick, Jr., and D. H. Geske, *J. Am. Chem. Soc.*, **88**, 4119 (1966).

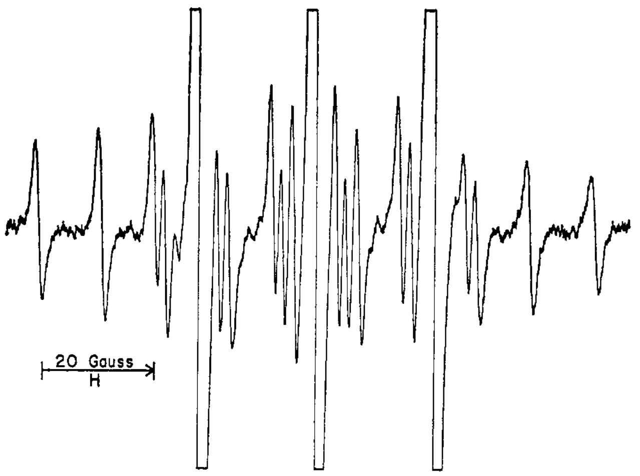

Figure 1. First-derivative esr spectrum of ^{17}O-enriched pentamethylnitrobenzene anion radical. Radicals were produced by electroreduction of an acetonitrile solution initially 1.9 m*M* in enriched pentamethylnitrobenzene. All 18 lines from radicals containing a single ^{17}O nucleus are easily identified. The three lines from unlabeled radicals are off scale. Several small lines from radicals containing two ^{17}O nuclei are visible.

(PMNB) and chloroform (DNB). Spectra were obtained using a Perkin-Elmer Model 521 grating infrared spectrophotometer which had been calibrated with indene.

Results

Electron Spin Resonance in Solution. PMNB⁻. The esr spectrum of ^{17}O-enriched PMNB⁻ produced by electrolytic reduction of an acetonitrile solution 1.9 m*M* in enriched PMNB is given in Figure 1. All 18 lines anticipated from interaction of the odd electron with one ^{17}O nucleus ($I = ^5/_2$) and one ^{14}N nucleus are readily observable. The three lines from unlabeled radicals (no proton splittings are resolvable) are off scale in the figure. Comparison of the integrated intensities of the isotopic lines with those from unlabeled radicals gave the population of radicals containing one ^{17}O as 32.2% in good agreement with 29.4%, the value calculated from the stated enrichment of the O_2 gas assuming statistical distribution of oxygen isotopes during the synthesis of NO_2.

Table I. Solvent Effects for PMNB⁻

Solvent composition	Coupling constants, G[a] a_N	$-a_O$
A. Mole fraction of water in acetonitrile		
0.000	21.13 ± 0.09	11.50 ± 0.05
0.162	21.61 ± 0.24	11.11 ± 0.11
0.279	21.86 ± 0.21	11.06 ± 0.09
0.368	21.91 ± 1.44	10.92 ± 0.19
B. Mole fraction of water in DMF		
0.000	20.31 ± 0.19	11.54 ± 0.07
0.125	20.85 ± 0.19	11.17 ± 0.11
0.223	21.12 ± 0.04	11.12 ± 0.08
0.364	21.30 ± 0.05	11.11 ± 0.12
0.463	21.36 ± 0.10	11.04 ± 0.06
0.588	21.43 ± 0.10	10.90 ± 0.10
0.696	21.50 ± 0.17	10.86 ± 0.11
0.788	21.66 ± 0.19	10.80 ± 0.31
C. DMF/acetonitrile, 2:1 (v/v)	20.69 ± 0.13	

[a] Uncertainties given at the 95% confidence level.

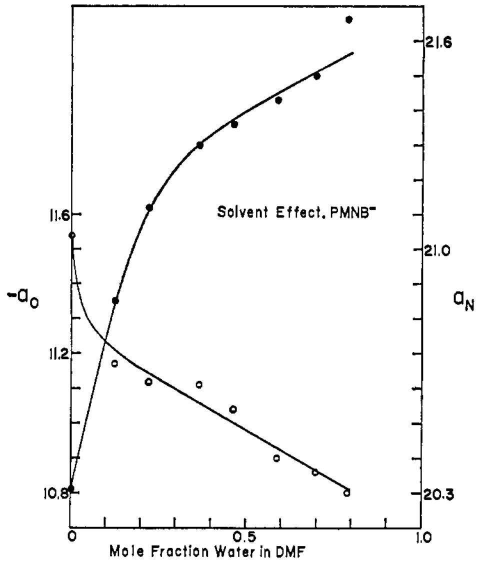

Figure 2. Isotropic nitrogen coupling constant (solid circles) and ^{17}O coupling constant (open circles) in pentamethylnitrobenzene anion as a function of mole fraction of water added to dimethylformamide.

Table I summarizes the isotropic nitrogen and oxygen coupling constants observed as water is added to DMF or acetonitrile solutions of PMNB⁻. The data for the DMF–H_2O system are displayed graphically in Figure 2. Although radical stability decreased markedly at water contents above *ca.* mole fraction 0.25, it was possible to secure reproducible data. In pure acetonitrile, radical stability was sufficient that, with use of a Varian C-1024 Computer of Average Transients, we were able to detect all of the extreme low-field lines predicted for the PMNB⁻ species containing two ^{17}O atoms. On the basis of random isotope distribution the abundance of this species is 3.2%.

A magnetic-field-dependent line-width variation was observed in spectra of PMNB⁻. In spectra at reduced gain, the relative derivative amplitudes of the three ^{14}N hyperfine components were observed to be (in order of increasing magnetic field) 0.935, 1.00, and 0.888. As can be noted in Figure 1, only the two extreme low-field and two extreme high-field ^{17}O hyperfine lines are fully resolved. The relative derivative amplitudes of these lines were observed to be (again with increasing applied field) 0.86, 1.00, 0.86, and 0.70. Normalizing all seven lines with respect to the center ^{14}N line (the width of this line is 1.040 G) and expressing the results as relative line widths, we obtain, in order of increasing external field, 1.380, 1.187, 1.070, 1.000, 1.126, 1.380, and 1.696. The variation in width of the ^{17}O components as estimated from the relative derivative amplitudes will be used to determine the sign of the isotropic ^{17}O coupling constant.

DNB⁻. The esr spectrum of ^{17}O-enriched DNB⁻ generated by vacuum electrolysis of a dimethoxyethane solution *ca.* 0.8 m*M* in DNB is given in Figure 3. Under all of the experimental conditions examined, the ^{17}O hyperfine structure remained insufficiently resolved to obtain a reliable integrated intensity. However, DNB itself was analyzed by mass spectrometry[19] and

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(19) We are indebted to Professor F. W. McLafferty for the mass spectral analysis.

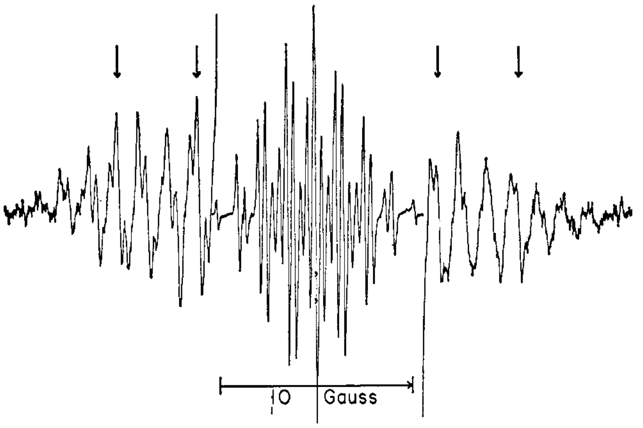

Figure 3. First-derivative esr spectrum of ^{17}O-enriched *p*-dinitrobenzene anion radical in dimethoxyethane solution. Radicals were generated by electroreduction *in vacuo* of a solution initially *ca.* 0.8 m*M* in enriched dinitrobenzene. The center lines of the four visible ^{17}O multiplets are indicated by arrows. The center portion of the spectrum, that due to unlabeled radicals, was recorded at reduced gain and modulation amplitude. These were $^1/_{20}$ and $^1/_3$, respectively, of the values employed to observe the isotopic structure.

found to contain 23.2% molecules containing a single ^{17}O and 25.8% molecules containing a single ^{18}O. In Figure 4 the low-field portion of the esr spectrum of ^{17}O-enriched DNB$^-$ is compared with a computed spectrum.[20] Because of the rapid decrease in stability of DNB$^-$ with added water, the solvent effect study was restricted to rather small quantities of added water. Coupling constants in various solvent media are summarized in Table II. The data were of insufficient quality to permit quantitative measure of line-width variations; however, as shown in Figure 3, the high-field ^{17}O satellites are clearly broader than those at low field. Thus the sign of a_O is obtainable.

Table II. Solvent Effects for DNB$^-$

Solvent composition	Coupling constants, G[a]		
	$-a_H$	a_N	$-a_O$
A. Mole fraction of water in acetonitrile			
0.000	1.09 ± 0.03	1.67 ± 0.03	4.34 ± 0.04
0.055	1.18 ± 0.03	2.08 ± 0.02	4.40 ± 0.01
0.104	1.11 ± 0.02	2.22 ± 0.02	4.43 ± 0.01
B. Mole fraction of water in DMF			
0.000	1.18 ± 0.01	1.41 ± 0.04	3.82 ± 0.02
0.079	1.15 ± 0.02	1.56 ± 0.03	4.29 ± 0.04
0.147	1.11 ± 0.01	1.66 ± 0.01	4.36 ± 0.03
C. Dimethoxyethane	1.11 ± 0.01	1.47 ± 0.01	4.28 ± 0.04

[a] Uncertainties given at the 95% confidence level.

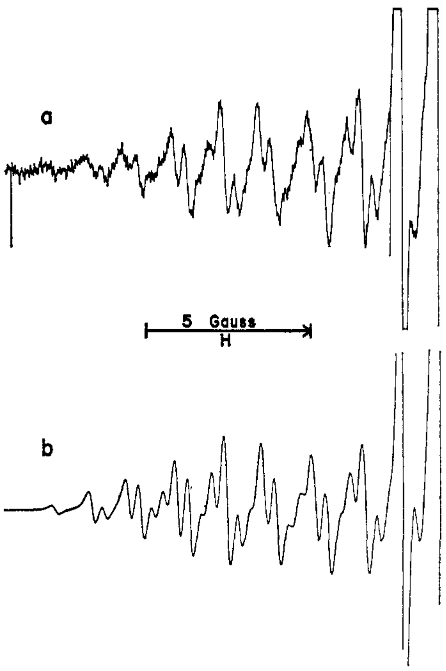

Figure 4. (a) Low-field portion of the esr spectrum of ^{17}O-enriched *p*-dinitrobenzene in dimethoxyethane solution. Two of the lines are from unlabeled radicals and are off scale. (b) Computer simulation of the spectrum assuming a Lorentzian line shape and employing the following parameters: unlabeled species, $a_H = 1.13$ G, $a_N = 1.51$ G, line width = 0.140 G; labeled species, a_H and a_N as above, $a_O = 4.28$ G and line width = 0.230 G. The greater width of the ^{17}O lines is presumed to arise from a larger anisotropic intramolecular dipolar interaction of this nuclear spin with the electron spin.

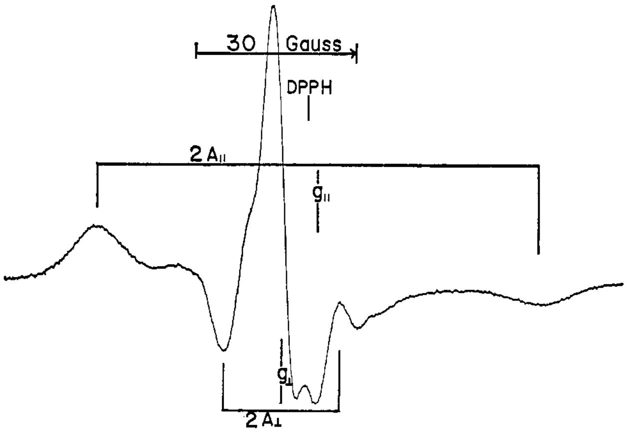

Figure 5. First-derivative esr spectrum of pentamethylnitrobenzene anion in a rigid glass at 77°K. The assignment of ^{14}N parameters is indicated in the figure. Radicals were produced by controlled-potential reduction of pentamethylnitrobenzene in a mixture of dimethylformamide and acetonitrile (see text).

Rigid-Glass Esr Spectra. PMNB$^-$. Figure 5 depicts the ^{14}N anisotropic esr spectrum of PMNB$^-$ obtained in acetonitrile–DMF glass at 77°K. Assignments of parameters from this spectrum are indicated in the figure and based on theoretical calculations for a single nucleus of $I = 1$ as summarized by Atkins and Symons.[21] A broader sweep at high gain revealed ^{17}O satellites as shown in Figure 6. The values of the isotropic ^{14}N coupling constant (Table I) and $\langle g \rangle$ were determined in the mixed solvent in a separate experiment at room temperature.

DNB$^-$. The esr spectrum of DNB$^-$ in the rigid glass is characterized by a single line of 4.5-G width between derivative extrema with unresolved shoulders on both

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[20] The computation was achieved using the program devised by E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 38, 1999 (1963); the spin of $^5/_2$ was accommodated as described in ref 4.

[21] P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier Publishing Co., New York, N. Y., 1967, p 268 ff.

Table III. Anisotropic Parameters for Acetonitrile-Dimethylformamide Glass at 77°K

	Values in gauss			Measured *vs.* DPPH		
	$A_{\parallel}$[a]	$A_{\perp}$[a]	B[a]	$g_{\parallel}$	$g_{\perp}$	$\langle g \rangle$[b]
PMNB⁻						
^{14}N	42.2 ± 0.7	10.9 ± 0.2	10.4 ± 0.2	2.0025	2.0066	2.0054
^{17}O	−39.0 ± 0.6	2.25 ± 0.30[c]	−13.8 ± 0.3[c]			
DNB⁻						
^{14}N[d]	$A_{\parallel} \leq 4$	$0.5 \leq A_{\perp} \leq 1.7$	$B \leq 1.2$		$g = 2.0070$	

[a] Standard deviations from the mean of four or more measurements are indicated; calculated values given with *computed* standard deviations. [b] Measured in fluid solution of the same mixed solvent. [c] Computed from $A_{\parallel}$ and a. [d] Single line; no ^{17}O structure observed; see text for details.

the high- and low-field sides. We were unable to detect any satellite lines outside these shoulders using a sample enriched in ^{17}O. We have, therefore, only attempted to place limits on the ^{14}N parameters as required by the separation of *ca.* 16 G between the shoulders. If these shoulders represent the outer ^{14}N parallel features, then, since there are two equivalent ^{14}N nuclei in the radical, the value of $A_{\parallel}$ must be ≤4 G. The anisotropic parameters are given in Table III.

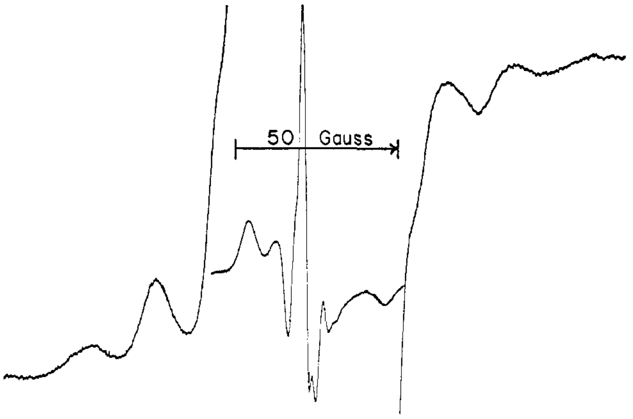

Figure 6. First-derivative esr spectrum of ^{17}O-enriched pentamethylnitrobenzene anion in a rigid glass at 77°K. Two ^{17}O lines are easily distinguished on each end of the spectrum. A third ^{17}O line appears on each side as a shoulder just before the signal goes off scale. The center portion of the spectrum was recorded at one-sixth the gain and one-eight the modulation amplitude used to observe the ^{17}O lines.

Infrared Spectroscopy. PMNB. Labeled PMNB exhibited a spectrum which is different from the unlabeled species in three areas in the 3550–700-cm^{-1} region. The strong band at 1527 cm^{-1}, attributed to the N–O asymmetric stretching motion,[22,23] was split into three partially resolved bands in the labeled material. The symmetric N–O stretching frequency[22,23] was not resolved in either the labeled or unlabeled species from the C–H bending mode in the 1385–1360-cm^{-1} region.[24,25] An area of absorption containing at least three bands and centered at 1370 cm^{-1} in the unlabeled species was split into a minimum of five bands in the labeled material. The isotopic enrichment of the labeled species was demonstrated most dramatically in the splitting of the band at 837 cm^{-1} in the unlabeled material into three bands at 837, 832, and 826 cm^{-1} in the enriched compound. The pertinent sections of the spectra of labeled and unlabeled PMNB are compared in Figure 7a. A complete list of the bands observed in this investigation is given in Table IV.

Table IV. Infrared Bands (cm^{-1}) of PMNB

Isotopically natural		^{17}O and ^{18}O enriched	
3000	Weak	3000	Weak
2935	Medium	2935	Medium
2870[a]	Shoulder	2870[a]	Shoulder
1527	Strong	1526	Strong
		1520[a]	
		1517[a]	
1465	Medium	1465	Medium
1381[a]	Medium	1386	Shoulder
1373[a]	Medium	1381	Medium
1370	Strong	1367[a]	Medium
		1360[a]	Medium
1269	Weak	1270	Weak
1228	Weak	1230	Weak
1069	Weak	1069	Weak
1033	Weak	1033	Weak
837	Strong	837	Medium
		832	Medium
		826	Medium

[a] Incompletely resolved.

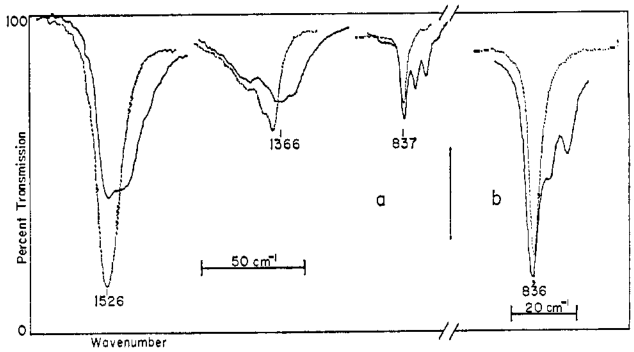

Figure 7. Comparison of selected portions of the infrared spectra of the ^{17}O-enriched nitro compounds (solid lines) with isotopically natural materials (dotted lines). See text for details: (a) pentamethylnitrobenzene, (b) dinitrobenzene.

DNB. The two N–O stretching bands were merely broadened in the case of labeled DNB. However, the 836-cm^{-1} band was split into three nearly resolved bands in the enriched compound. This band is compared for the labeled and unlabeled compounds in Figure 7b. The infrared spectrum of the natural material has been reported previously.[26]

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(22) R. Randle and D. H. Whiffen, *J. Chem. Soc.*, 4153 (1952).
(23) S. Dohne and H. Stanko, *Spectrochim. Acta*, **18**, 561 (1962).
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(25) R. Nakashima, S. Watarai, and T. Kinugasa, *Bull. Chem. Soc. Japan*, 34, 1740 (1961).
(26) C. P. Conduit, *J. Chem. Soc.*, 3273 (1959).

Discussion

Sign of a_O. The parameter most easily and unequivocally derived from this study is the sign of the isotropic oxygen coupling constant. In DNB$^-$ only examination of Figure 3 is required: the lines marked by arrows indicate the center lines of the four ^{17}O multiplets which fall outside the spectrum of unlabeled radicals. In this fortunate circumstance in which a_O is the largest coupling constant in the radical, the four indicated lines all arise from the same nitrogen and proton nuclear spin states, namely $M_N = 0$ and $M_H = 0$. The field-dependent variation in intensity and resolution of these lines was reproducible over many spectra, and the over-all intensity of the esr signal did not diminish noticeably with time. Thus, the variation in intensity and resolution is interpreted as a variation in line width associated with the oxygen nuclear spin quantum number, M_O. The observation of broader lines at higher external magnetic field strength is indicative of a negative sign for a_O by the arguments presented previously.[18] The validity of this reasoning depends upon knowledge of the relative magnitudes of the components of the g tensor, namely that $g_z < {}^1/_2(g_x + g_y)$, where g_z is the component perpendicular to the plane of the aromatic ring. For the *p*-dinitrobenzene anion Freed and Fraenkel[27] have shown that this condition is fulfilled and also have shown that a positive sign obtains for a_N.

The case of PMNB$^-$ is more complicated because the four ^{17}O lines which are uniquely resolved and suitable for line-width measurement arise in pairs, each pair from a different ^{14}N nuclear spin state. Thus, the variation in width must be treated after the manner of Kaplan, *et al.*,[28] who give the line-width parameter, Δk, as

$$\Delta k = A + \sum_i B_i\tilde{M}_i + \sum_i C_i\tilde{M}_i^2 + \sum_{i \neq j} E_{ij}\tilde{M}_i\tilde{M}_j \quad (2)$$

where the $\tilde{M}_i$'s are the spectral index numbers introduced previously.[27] We obtained the ^{14}N parameters directly from examination of spectra at low gain. The line-width variation observed is quite well reproduced by the following values of the constants (given in gauss): $A = 1.040$, $B_N = 0.029$, $C_N = 0.102$, $B_O = 0.051$, $C_O = 0.054$, and $E_{ON} = 0.048$.

There is ample reason to expect that the spin density on both nitrogen and oxygen is positive. Since the sign of the product $a_N\rho_N$ is the same[28] as the sign of B_N, as anticipated, a positive sign for a_N is indicated. Considering the negative nuclear moment of ^{17}O, the positive[29] value of B_O indicates that a_O is negative. This conclusion is confirmed by the positive[29] value of E_{ON} which indicates that a_N and a_O have opposite signs.

Although previous data did not permit evaluation of the sign of a_O for nitrobenzene anion, the present finding that a_O is negative in both DNB$^-$ and PMNB$^-$ virtually assures that it is also negative in NB$^-$.

Solvent Effects. Since the ^{17}O coupling constant observed in PMNB$^-$ changes with solvent polarity in the manner predicted by Gendell, *et al.*,[3] and the variations in both a_N and a_O are large compared with experimental errors, it is possible to estimate the ^{17}O σ–π parameters for this radical. We use the relation

$$a_N = (99.0 \pm 10.2)\rho_N^\pi - (71.6 \pm 11.8)\rho_O^\pi \quad (3)$$

given by Rieger and Fraenkel[2] which employs spin densities calculated by the method of McLachlan.[30] We fit a_N in dry DMF using the MO parameters of ref 2, with β_{CN} reduced to 0.36. The calculated spin densities are $\rho_N^\pi = 0.3910$ and $\rho_O^\pi = 0.2553$. The change in a_N observed for similar radicals on going from dry DMF to pure water was accommodated[2] by changing the oxygen Coulomb parameter, δ_O ($\alpha_O = \alpha_C + \delta_O\beta_{CC}$), from 1.4 to 1.8. Our data extend only to mole fraction of water (N_{H_2O}) equal to 0.788; thus the required δ_O is 1.715 and the spin densities obtained are $\rho_N^\pi = 0.4557$ and $\rho_O^\pi = 0.2443$. We then write two equations in the form of eq 1 employing the experimental values of a_O and the calculated spin densities for the two water contents, $N_{H_2O} = 0$ and $N_{H_2O} = 0.788$. Simultaneous solution gives $Q_1 = -49.7$ and $Q_2 = +2.92$, values which, on the basis of the theory of Karplus and Fraenkel,[5] are not unreasonable. Use of these Q values and McLachlan spin densities to calculate a_O for DNB$^-$ and NB$^-$ yields only moderate agreement with experiment.

On the basis of experimental data for only limited changes in solvent polarity (from DMF to acetonitrile), Rieger and Fraenkel[2] concluded that twisting the nitro group does not alter the solvent effect; however, for PMNB$^-$ with $N_{H_2O} = 0.788$, the calculated a_N is 27.6 G, a value much larger than that observed experimentally. Further, this model does not account for the observed solvent effect upon a_O in DNB$^-$ or NB$^-$. On the other hand, the suggestion by Ling and Gendell[6] that one can reproduce the solvent dependence of a_O in NB$^-$ by increasing both α_N and α_O in the MO calculation fails to account for the observed behavior of PMNB$^-$.

It is difficult to understand why this dichotomy should exist if the solvent effect (and, presumably, the gegenion effect) operates through a purely electrostatic effect on the oxygen atoms. Thus, we now have a fairly clear-cut indication that steric considerations must play some role in solvent variations of a_N and a_O, an indication not obtainable from nitrogen coupling constants alone. By way of comparison, a number of ^{17}O semiquinones have now been investigated, and, in all cases reported[18,31] $|a_O|$ *decreased* when the medium was changed from an aprotic solvent to water. These results are in keeping with the model of Gendell, *et al.*;[3] of course, no steric perturbation is expected in the case of semiquinone radicals. On the basis of this evidence, we feel that the suggestions of Ludwig, Layloff, and Adams[32] are worthy of further consideration. These authors suggested that the solvent effect might be, at least in part, a solvent-induced twisting of the nitro group, or an out-of-plane deformation. Combinations of these two effects with purely coulombic effects

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(27) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 1815 (1964).

(28) M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *ibid.*, **42**, 955 (1965).

(29) The negative nuclear moment of ^{17}O enters the expressions for both B_O and E_{ON} and inverts their signs.

(30) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(31) M. Broze, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, **46**, 4891 (1967).

(32) P. Ludwig, T. Layloff, and R. N. Adams, *J. Am. Chem. Soc.*, **86**, 4568 (1964). The observation that the solvent-induced increase in a_N is *not* accompanied by a decrease in ring proton coupling constants, a phenomenon known to occur with gross twisting of the nitro group, led these authors to reject twisting as the major component of the solvent effect.

cannot be excluded from consideration. An alternative possibility is that in the unhindered radicals both the nitrogen and the oxygen atoms are solvated, whereas in the hindered radical solvation of nitrogen is not possible. In any case, division of the solvent effect into two or more parts, at least one of which depends upon geometric factors, permits rationalization of the ^{17}O data and should improve the quantitative fit of a_N for hindered molecules; the calculated increase in a_N could then be smaller than that calculated above.

Solid-State Spectra

The anisotropic parameters given in Table III for PMNB$^-$ are internally consistent and therefore regarded as correct. Thus, calculation of a_N from $^1/_3(A_{\parallel} + 2A_{\perp})$ yields 21.35 ± 0.25 G, a value in good agreement with the experimental result measured in fluid solution in the same solvent. Similarly the value of $\langle g \rangle$ calculated from the solid-state spectra is in good agreement with the value measured in solution. Assignment of the satellite lines (Figure 6) to the parallel splitting of ^{17}O is quite certainly correct, and the choice of sign is consistent with the known sign of the isotropic splitting. Choosing the opposite sign, or attempting to assign this 39-G splitting (with either sign) to a perpendicular component, results in prediction of a second large splitting. Since no other splitting is observed, the calculation from our assignment of $A_{\perp} = 2.25$ G, a value much smaller than the line widths, is consistent with the assignment.

Spin populations can be estimated from the isotropic coupling constants and from the anisotropic parameter B, the former yielding an estimate of unpaired spin in the appropriate s orbital, the latter giving the spin density in a p orbital. The accuracy of such estimates depends upon the values of A_0 and B_0, the "one-electron hyperfine parameters," which in turn depend upon selection of the proper wave functions for, respectively, calculation of $\Psi^2(0)$ and $\langle r^{-3} \rangle$.

Symons and coworkers[7,8] have used anisotropic parameters to estimate spin densities for a number of nitro aromatic anion radicals. They found uniformly larger spin densities than those predicted from HMO calculations and therefore suggested that the Q parameters given by Rieger and Fraenkel[2] are too large. One can ascertain from these results[7] that the one-electron parameters employed are identical with those tabulated by Morton.[33] Application of those parameters to data from PMNB$^-$, however, leads to an estimate of more than 1.1 unpaired electrons on the nitro group atoms. Hence, we regard the parameters given more recently by Hurd and Coodin[34] as more satisfactory since they are 14–17% larger (^{14}N: $A_0 = 643$ G, $B_0 = 19.8$ G; ^{17}O: $A_0 = 1893$ G, $B_0 = 60.0$ G) than those computed previously. Use of these new parameters with the data for PMNB$^-$ yields $\rho_N^{2s} = 0.032$, $\rho_N^{2p} = 0.525$, $\rho_O^{2s} = 0.006$, $\rho_O^{2p} = 0.230$, values which sum to 1.03. These results are at variance with the predictions of HMO calculations but do bring the estimated nitro group spin density roughly to within experimental error of unity. Thus, we suggest that the spin densities given by Symons[7,8] are too large.[35]

Symons, *et al.*,[7] obtained nitrogen p/s ratios for several radicals which indicate a trend toward lower values of the ratio for radicals with larger nitrogen coupling constants. These values range from 24 for *m*-dinitrobenzene anion to 15.0 for nitromesitylene anion.[36] This trend toward smaller p/s ratios is associated by these workers[7] with a pyramidal distortion of the nitro group as more unpaired electron density is placed on the nitrogen atom. Our data do not entirely confirm this trend. The p/s ratio for PMNB$^-$ is 16.2 using the same one-electron parameters as used in ref 7 and 16.4 using the Hurd–Coodin[34] values, while the value of a_N is nearly identical with that for nitromesitylene anion.

If we employ the same approach for DNB$^-$ using the largest estimate of B_N, 1.2 G, and the acetonitrile value of a_N, we obtain $\rho_N^{2s} = 0.003$ and $\rho_N^{2p} \leqq 0.061$. From a_O we obtain $\rho_O^{2s} \cong 0.002$. If we assume that we did not detect ^{17}O lines in the glass spectrum of DNB$^-$ because the coupling constants are too small with respect to the line width, then the value of the oxygen anisotropic parameter is almost certainly less than 3 G. This results in $\rho_O^{2p} \leqq 0.050$. Using $Q_{CH}^{H} = -23$ G, we obtain $\rho_{C_2}^{\pi} = 0.048$. In this way we account for only ~0.53 electron. In this model, $\rho_{C_1}^{\pi} \cong 0.23$ by difference. These results are in poor agreement with HMO-type calculations.[37] Such a large spin density at C_1, however, coupled with a negative value of Q_{CN}^{N} as previously suggested,[10] might account in part for the anomalously[38] low value of a_N in DNB$^-$.

Conclusions from the Esr Spectra

For all the ^{17}O radicals studied to date, it seems general that the ^{17}O coupling constants are negative and determined primarily by spin on ^{17}O itself. All of the radicals studied can be described approximately with an equation of the form

$$a_O = Q_O \rho_O^{\pi} \qquad (4)$$

using values of Q_O between −33 (DNB$^-$) and −45 (PMNB$^-$); Broze, Luz, and Silver[31] find $Q_O = -45 \pm 6$ fits a number of ^{17}O semiquinones reasonably well.

It is clear that the effect of added polar solvent is strikingly different for a hindered nitro group than for those which are unhindered when a_O is examined. This observation gives support for the idea of a steric

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(33) J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

(34) C. M. Hurd and P. Coodin, *J. Phys. Chem. Solids*, **28**, 523 (1967).

(35) The HMO–McLachlan[30] calculation gives $\rho_N^{\pi} = 0.2381$ and $\rho_O^{\pi} = 0.1988$ for NB$^-$, whereas Symons[7] obtains $\rho_N^{2p} = 0.411$ for the same radical. An initial, unrefined calculation by the Pople (J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966)) CNDO method gives intermediate, and therefore plausible, values: $\rho_N^{2p_z} = 0.3625$, $\rho_{OH}^{2p_z} = 0.2060$. Ring spin densities obtained are $\rho_{C_1}^{2p_z} = 0.0024$, $\rho_{C_2}^{2p_z} = 0.1023$, $\rho_{C_3}^{2p_z} = -0.0550$, and $\rho_{C_4}^{2p_z} = 0.1286$: P. A. Clark, personal communication. Note that the data of ref 7 in conjunction with the parameters of ref 34 give $\rho_N^{2p} = 0.355$ in good agreement with the calculation.

(36) The p/s ratio for nitromesitylene anion is stated in ref 7 as 12.1. This is a numerical error; the given spin densities follow from the coupling constants given, but their ratio is actually 10.8. In a personal communication, Dr. W. M. Fox advises us that errors were made in the data and that the correct p/s ratios are 15.0 for nitromesitylene anion and 24 for *m*-dinitrobenzene anion. (The stated ratio for *m*-dinitrobenzene anion is 26.)

(37) Initial Pople CNDO calculations for *p*-dinitrobenzene anion appear to agree reasonably well with the experimental results: $\rho_N^{2p_z} = 0.0225$, $\rho_O^{2p_z} = 0.0662$, $\rho_{C_1}^{2p_z} = 0.2535$, $\rho_{C_2}^{2p_z} = 0.0458$: P. A. Clark, personal communication.

(38) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 304 (1963).

interaction associated with the solvent effect. Unfortunately, the detailed nature of this effect cannot yet be specified.

Infrared Spectra

The band centered at *ca.* 837 cm^{-1} in both the PMNB and DNB split into three bands in the labeled materials. The assignment of this absorption band to a molecular vibration has been the subject of a continuing controversy. It has been assigned both to a $C-NO_2$ stretching motion[24,25,39–41] and to the $-NO_2$ symmetric deformation.[42,43] Since one would expect that a C–N stretching frequency would be perturbed only slightly by isotopic oxygen substitution (see calculations by Pinchas, *et al.*[42]), our observations that these splittings are of the same magnitude as those observed for the N–O stretching bands support the latter assignment.

Synthesis of Enriched DNB

It is of interest to consider briefly the mechanism of the reaction of NO_2 with *p*-nitrosonitrobenzene. Two distinctly different mechanisms can be formulated: (a) transfer of an oxygen atom from NO_2 to the nitroso group (with or without subsequent oxygen exchange); (b) displacement of the nitroso group by NO_2. The former necessarily leads to a dilution of the isotopic enrichment while the latter leads to no isotope dilution. Including the dilution of enriched oxygen gas with natural NO, and assuming statistical distribution of isotopes, we calculate that 22.5 mole % of the NO_2 was present as $N^{16}O^{17}O$ and 24.8 mole % as $N^{16}O^{18}O$. Mass spectrometric analysis of the DNB finds 23.2 mole % containing one ^{17}O (mass 169) and 25.8 mole % containing one ^{18}O (mass 170), in excellent agreement with the results anticipated for path b.

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Electron Nuclear Double Resonance in Solutions. Spin Densities in Triarylmethyl Radicals

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Abstract: Electron nuclear double resonance (ENDOR) and electron paramagnetic resonance (epr) spectra have been obtained of a series of four triarylmethyl radicals [triphenylmethyl, *p*-biphenylyldiphenylmethyl, bis-(*p*-biphenylyl)phenylmethyl, and tris(*p*-biphenylyl)methyl] in solution. The hyperfine coupling constants, obtained directly from the ENDOR spectra, were assigned to specific protons with the aid of observed and calculated epr spectra. The experimental spin density distributions in the π systems are compared to those from a Hückel molecular orbital calculation including McLachlan's perturbation correction.

Electron nuclear double resonance (ENDOR) was first introduced by Feher in 1956 for the study of paramagnetic defects in solids.[2] By means of this technique, nuclear spin transitions may be detected by their effects on the electron paramagnetic resonance (epr) signal. ENDOR thus has become especially useful for investigation of the energy levels of nuclei coupled to unpaired electrons. Until recently, the technique has been limited to investigations in single crystals at or near 4°K. In 1963, Cederquist[3] reported detection of ENDOR signals in alkali metal ammonia solutions in the liquid phase. The nuclear Zeeman transitions which were detected (^{14}N, ^{15}N, ^{1}H, and ^{23}Na) each occurred at essentially its unperturbed Larmor frequency, since the hyperfine coupling with the electron spin is averaged out. In 1964, Hyde and Maki[4] reported the first successful ENDOR measurement of an organic radical in liquid solution in which the bridgehead proton and ring proton nuclear resonance transitions of Coppinger's radical[5] were detected. Later, this work was continued by Hyde,[6] who, using improved instrumentation, was able to observe the weaker *t*-butyl proton ENDOR of Coppinger's radical. Hyde also observed ENDOR of several other repre-

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