crystallized from methanol-ether (yield 20 mg), mp 186°. The methiodide was found to be identical with the methiodide of the nonphenolic fragment in respect to melting poing, mixture melting point, and infrared spectrum.

Registry No.—Hayatin, 1381-51-7.

Acknowledgment.—Our thanks are due to Dr. T. R. Govindachari and Professor A. R. Battersby, F. R. S., for useful discussions and Dr. R. S. Kapil for determination of mass spectra.

A Comparison of the Electron Spin Resonance Spectra of *p*-Nitrotoluene, *p*-Nitroethylbenzene, *p*-Nitrocumene, and 2-Nitrotriptycene Radical Anions in Acetonitrile

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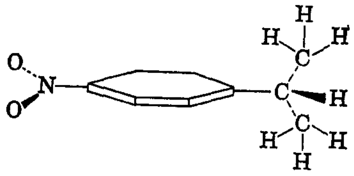
In connection with some studies on the spontaneous, free-radical formation in basic solutions of *o*- and *p*-nitrotoluenes[1] we obtained the esr spectrum of *p*-nitrotoluene, *p*-nitroethylbenzene, and *p*-nitrocumene anion radicals in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) containing potassium *t*-butoxide. The spectra are consistent with 3.81-, 2.92-, and 1.73-gauss splitting for the α hydrogens of the methyl, ethyl, and isopropyl groups, respectively.[2] The ring hydrogens compare well with values previously reported for *p*-nitrotoluene radical anion in acetonitrile (Table I).

The observed decrease in α-hydrogen coupling constant with increased substitution in *p*-methyl-, *p*-ethyl-, and *p*-isopropylnitrobenzene radical anion is undoubtedly due to preferred population of certain conformations for the ethyl and isopropyl groups which are unfavorable for maximum interaction of the α hydrogen(s) with the unpaired electron in the aromatic system. Maximum interaction is possible if the dihedral angle (defined as the angle between the H-C-C plane and the axis of the p orbital containing the unpaired electron) is 0. The angular dependence of α-hydrogen coupling constants is expressed in the following relationship[3]

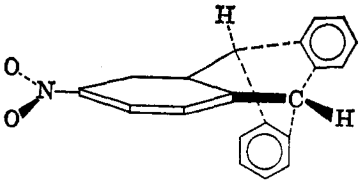
$$A^{\mathrm{H}} = B + A \cos^2 \theta \qquad (1)$$

where θ is the dihedral angle, $B \cong 0$, and $A \cong 50$ for alkyl radicals. Thus when $\theta = 90°$ no proton coupling (or very small coupling) is expected.

The nonuniform population of all possible conformations for alkyl groups larger than methyl in nitrobenzene radical anions and other similar radicals is due to steric hindrance to free rotation.[4-6] The bulky methyl groups of the isopropyl group in isopropylnitrobenzene radical anion, for example, prevent free rotation of the isopropyl group and orientations which place the methyl groups above and below the aromatic ring are favored. Because such orientations have relatively large dihedral angles for the methine hydrogen the coupling constant for this hydrogen is relatively small.



It was thought that further support for this interpretation could be provided from a study of the esr spectrum of 2-nitrotriptycene radical anion. Because of the restrictions imposed by the bonding to the bridgehead carbon the α hydrogen is essentially fixed at a dihedral angle of 90°. This Note reports our results on a comparison of the esr spectra of 2-nitrotriptycene, *p*-isopropylnitrobenzene, *p*-ethylnitrobenzene, and *p*-nitrotoluene radical anions.



Since more studies of substituted nitrobenzene radical anions have been made in acetonitrile than in any other solvent system this solvent was chosen. Esr spectra for *p*-ethyl- and *p*-isopropylnitrobenzene radical anions have previously been obtained in basic ethanol[7] and aqueous acetone.[8]

The electron spin resonance spectra of *p*-nitroethylbenzene and *p*-nitroisopropylbenzene in acetonitrile can be fitted to coupling constants listed in Table I.[9] Essentially the same values are obtained in acetonitrile as found earlier[1,2] in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) containing potassium *t*-butoxide. The spectra in basic *t*-butyl alcohol, ethanol,[7] or aqueous acetone,[8] however, show a sizable increase in the nitrogen coupling constant. This effect has previously been observed in protic solvents and is attributed to solvation and hydrogen bonding of the partially negatively charged nitro group.[10]

2-Nitrotriptycene gave the spectrum in Figure 1. An analysis of the spectrum gives the coupling constants in Table I. The assignment is based on the coupling constants reported for 3,4-dimethylnitro-

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[1] G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962).

[2] G. A. Russell and E. G. Janzen, *ibid.*, **89**, 300 (1967).

[3] C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

[4] A. Carrington and P. F. Todd, *Mol. Phys.*, **8**, 299 (1964).

[5] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

[6] T. M. McKinney and D. H. Geske, *ibid.*, **44**, 2277 (1966), and references therein.

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

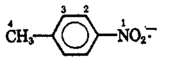
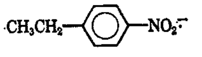
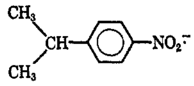
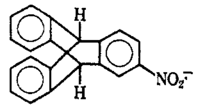
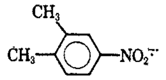
[8] P. L. Kolker and W. A. Waters, *ibid.*, 1136 (1964).

[9] McKinney and Geske (*J. Am. Chem. Soc.*, in press) have obtained the following coupling constants for *p*-nitroethylbenzene: $a_{\mathrm{N}} = 10.71$; $a_{2,6}{}^{\mathrm{H}} = 3.37$; $a_{3,5}{}^{\mathrm{H}} = 1.11$; $a_{\alpha}{}^{\mathrm{H}} = 2.96$; and for *p*-isopropylnitrobenzene $a_{\mathrm{N}} = 10.66$; $a_{2,6}{}^{\mathrm{H}} = 3.36$; $a_{3,5}{}^{\mathrm{H}} = 1.10$; $a_{\alpha}{}^{\mathrm{H}} = 1.74$ in acetonitrile. We are grateful to Professor Geske for sending us a preprint of this work and allowing us to quote data obtained in his laboratories previous to publication.

[10] L. H. Piette, P. Ludwig, and R. N. Adams, *ibid.*, **83**, 3909 (1961); **84**, 4214 (1962); P. Ludwig, T. Layloff, and R. N. Adams, *ibid.*, **86**, 4568 (1964); J. Q. Chambers, T. Layloff, and R. N. Adams, *J. Phys. Chem.*, **68**, 661 (1964); P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963), and ref 1.

TABLE I

HYPERFINE COUPLING CONSTANTS OF SUBSTITUTED NITROBENZENE ANION RADICALS

Radical	Solvent	Position				Ref
		1	2	3	4	
	CH_3CN	10.79	3.39	1.11	3.98	*a*
	DMSO (80%)-*t*-BuOH (20%)	10.55	3.40	1.11	3.81	2
	t-BuOH	12.7	3.4	1.1	3.4	1
	CH_3CN	10.66	3.23	1.08	2.92	This work
	DMSO (80%)-*t*-BuOH (20%)	10.30	3.31	0.99	2.92	2
	t-BuOH	12.85	3.18	1.10	2.84	2
	CH_3CN	10.54	3.36	1.01	1.64	This work
	DMSO (80%)-*t*-BuOH (20%)	10.56	3.31	1.04	1.73	2
	CH_3CN	10.07	2.99, 3.62	1.09	0.00	This work
	CH_3CN	10.09	3.35	1.05	3.95	*a*

[a] A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83,** 1852 (1961).

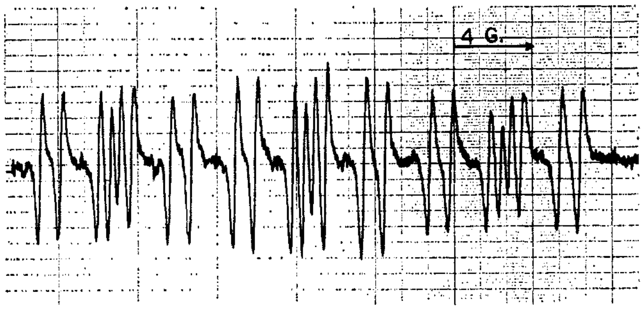
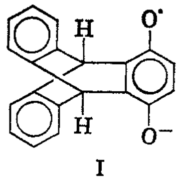
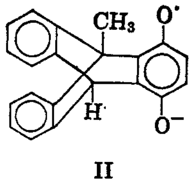


Figure 1.—Electron spin resonance spectrum of 2-nitrotriptycene radical anion in acetonitrile.

benzene[11] (Table I). The 10.07- and 1.09-gauss splittings are of the same magnitude as found for nitrogen and *meta* hydrogens of 3,4-dimethylnitrobenzene. The remaining 2.99- and 3.62-gauss splittings are assigned to the *ortho* hydrogens of 2-nitrotriptycene since the average of these values (3.32 gauss) is the same as the 3.35-gauss *ortho* hydrogen splitting in 3,4-dimethylnitrobenzene. No splitting from the bridgehead hydrogens is observed. This is in agreement with a number of other studies of radical anions having bridgehead hydrogens in a β position to a site of high spin density. In the semiquinones I and II[12] no evidence for bridgehead proton splitting is found.



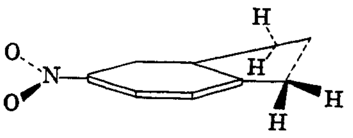
I



II

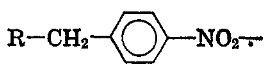
This observation points to a value of 0 for B in eq 1 for nitrobenzene radical anion.

McKinney and Geske[9] have also obtained the esr spectrum of 5-nitroindan where the orientation of the



α-methylene hydrogens is essentially fixed at a dihedral angle of 30°. The methylene coupling constants are 5.40 and 1.38 gauss in the *para* and *meta* positions, respectively. A plot of the *para* and *meta* α-hydrogen coupling constants in 2-nitrotriptycene, *p*- and *m*-nitrotoluene,[11,13] and 5-nitroindan[9] *vs.* $\cos^2 \theta$ gives a fairly good straight-line relationship, (Figure 2) as expected if eq 1 holds for these radicals. Inherently it is assumed that the spin density distribution in the aromatic system is negligibly different for these compounds. The plots predict approximately 8- and 2-gauss coupling to an α hydrogen held fixed at a 0 dihedral angle in the *para* and *meta* positions, respectively.

It was furthermore of interest to obtain a series of substituted *p*-nitrobenzene radical anions having a large variety of R groups with varying steric and electronic properties. The coupling constants of the



methylene hydrogens should be expected to reflect both the steric and direct inductive effect of the attached group. With this aim in mind the reduction of methyl *p*-nitrophenylacetate, *p*-nitrophenylacetonitrile, *p,p'*-dinitrodiphenylmethane, *p*-nitrophenyldiphenylmethane, and tris(*p*-nitrophenyl)methane [R = $COOCH_3$, CN, *p*-$NO_2C_6H_4$, $(C_6H_5)_2$, and $(p\text{-}NO_2C_6H_4)_2$]

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(11) D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.*, **86,** 987 (1964).

(12) L. M. Stock and J. Suzuki, *ibid.*, **87,** 3909 (1965); *Proc. Chem. Soc.*, 136 (1962).

(13) See Table I, footnote *a*.

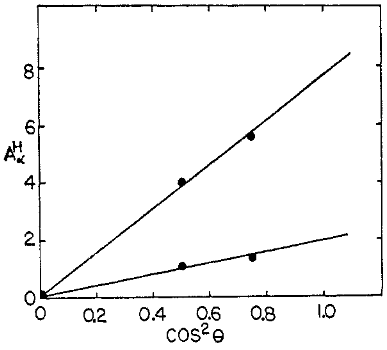

Figure 2.—Plots of *para* and *meta* α-hydrogen coupling constants *vs.* $\cos^2 \theta$ for 2-nitrotriptycene (0 gauss, 90° and 0 gauss 90°), *p*-nitrotoluene (3.98 gauss, 45°), *m*-nitrotoluene (1.10 gauss, 45°), and 5-nitroindan (5.40 gauss, 30° and 1.38 gauss, 30°).

was attempted. Only very transient, free-radical species were obtained or no signal at all. However, the bright red or blue color characteristic of the carbanion was observed immediately after electrolysis was begun. It appears that the initially formed radicals act as strong bases and immediately remove the acidic proton from the parent *p*-nitrobenzyl derivative. Since the neutral reduced nitrobenzene radical formed by the protonation of nitrobenzene radical anion is not stable[14] no radicals are seen and simultaneously the unreduced *p*-nitrobenzyl derivative is removed from the solution and converted to the carbanion, *e.g.*

$$(C_6H_5)_2\text{—}CH\text{—}C_6H_4NO_2^{-}\cdot + (C_6H_5)_2\text{—}CH\text{—}(C_6H_4NO_2) \longrightarrow$$

$$\underset{\text{unstable}}{(C_6H_5)_2\text{—}CH\text{—}C_6H_4\dot{N}O_2H} + \underset{\text{stable carbanion}}{(C_6H_5)_2\text{—}\ddot{C}\text{—}C_6H_4NO_2^{-}}$$

Reduction of the carbanion is not possible by electrolysis. *p*-Nitrobenzyl bromide and *p*-nitrobenzyl phenyl ether also did not give stable radicals presumably because of elimination of bromide and phenoxide and ions.[15] The only useful spectrum was obtained from *p*-nitrophenylacetic acid. The coupling constants for this radical in acetonitrile are $a_N = 10.78$, $a_{2,6}{}^H = 3.23$, $a_{3,5}{}^H = 1.03$, $a^H = 2.84$. The radical is undoubtedly *p*-nitrophenylacetate dianion radical. Since the coupling constant of the α-methylene hydrogen is essentially the same as in *p*-ethylnitrobenzene, it would appear from this limited data that the carboxylate group is sterically and electronically similar to the methyl group in this solvent. This result is unexpected.

Electron spin resonance spectra were obtained with a Varian 4502 epr spectrometer with 12-in. magnet and "Fieldial" magnetic field control. Radicals were generated electrolytically in a Varian flat cell in acetonitrile containing tetraethylammonium perchlorate as carrier electrolyte. The electrode potential was increased slowly by small increments until radicals were detected. Since at similar potentials the well-known spectrum for nitrobenzene radical anion could be obtained no attempt was made to determine accurate reduction potentials for the nitrobenzene derivations discussed here. Representative values can be found in ref 11 and 13. The method for generating substituted nitrobenzene radical anions in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) has been previously described.[16]

p-Nitrotoluene, *p*-nitroethylbenzene, and *p*-nitrocumene were obtained from commercial sources. A generous sample of 2-nitrotriptycene was obtained from Dr. R. L. Little.[17]

Registry No.—Acetonitrile, 75-0-58; 2-nitrotriptycene, 4628-55-1; *p*-nitrotoluene, 99-99-0; *m*-nitrotoluene, 99-08-1; 5-nitroindan, 7436-07-9; *p*-nitroethylbenzene, 100-12-9; *p*-isopropylnitrobenzene, 1817-47-6; methyl *p*-nitrophenylacetate, 2945-08-6; *p*-nitrophenylacetonitrile, 555-21-5; *p*-*p*′-dinitrodiphenylmethane, 1817-74-9; *p*-nitrophenyldiphenylmethane, 2945-12-2; tris(*p*-nitrophenyl)methane, 603-49-6; *p*-nitrobenzyl bromide, 100-11-8; *p*-nitrobenzyl phenyl ether, 3048-12-2; *p*-nitrophenylacetic acid, 104-03-0; tetraethylammonium perchlorate, 2567-83-1; 3,4-dimethylnitrobenzene, 99-51-4.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[14] R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963).

[15] R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, **87**, 4520 (1965).

[16] G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964); G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, A. Mak, and E. T. Strom in "Selective Oxidation Processes," Advances in Chemistry Series, 51, American Chemical Society, Washington, D. C., 1965, p 112.

[17] We acknowledge Dr. Little's original suggestion which prompted the investigation of the esr spectrum of 2-nitrotriptycene anion radical.

Infrared Spectra of N^{15}-Substituted Schiff Bases

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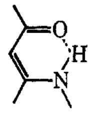
The interpretation of the infrared spectra of chelated α,β-unsaturated β-ketamines has been difficult owing to strong interactions between the carbonyl, the carbon–carbon double bond, and the amino vibrations which may render the concept of group frequencies unapplicable in these systems.[1–4]



Kinseley, *et al.*,[3] demonstrated that N^{15} labeling provided valuable information for the interpretation of the spectra of amides as the band shift between the N^{14} and N^{15} compounds established the C–N frequencies.[3,5] Accordingly, the infrared spectra of several N^{15}-labeled Schiff bases[6] have been obtained

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[1] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

[2] J. Dabrowski. *Spectrochim. Acta*, **19**, 475 (1963).

[3] R. N. Kniseley, V. A. Fassel, E. L. Farquhar, and L. S. Gray, *ibid.*, **18**, 1217 (1962).

[4] H. Holtzclaw, J. P. Collman, and R. M. Alire, *J. Am. Chem. Soc.*, **80**, 1100 (1958).

[5] M. Tsuboi, *Spectrochim. Acta*, **16**, 505 (1960).

[6] G. Dudek and E. P. Dudek, *J. Am. Chem. Soc.*, **86**, 4283 (1964); *ibid.*, **88**, 2407 (1966).