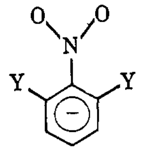
Details of the Steric Interaction in Mono-*ortho*-substituted Nitrobenzene Anion Radicals[1a]

Ted M. McKinney and David H. Geske[1b]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York. *Received August 25, 1966*

Abstract: Previously reported electron spin resonance studies of substituted nitrobenzene anion radicals have provided substantial structural information. The present esr study of nitrobenzene anion radicals with *o*-alkyl substituents permits structural assertions based on both nitrogen and β-proton isotropic coupling constants. As an ancillary matter coupling constants (including thermal coefficients) for nitrobenzene anion radicals with *p*-alkyl substituents are presented. Data for 4- and 5-nitroindan anion radicals, where the methylene protons are essentially fixed with respect to the benzene ring, serve to substantiate the angular dependence of the β-proton coupling constants.

The study of organic free radicals by esr has provided substantial structural and conformational insights.[2] One such example is the work on steric hindrance in nitroaromatic anion radicals. In particular, the effect of mono- and di-*ortho* substituents with threefold symmetry [Y = $-CH_3$, $-C(CH_3)_3$] has already been reported.[3–5]



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The examination of nitrobenzene anion radicals with unsymmetrical mono-*ortho* substituents [Y = $-CH_2CH_3$, $-CH(CH_3)_2$] is reported here. This study is directed to the question of the detailed orientation of the substituent group and of the nitro group with respect to the benzene ring. For the purposes of comparison, the *para* derivatives were also examined. Since coupling constants for the methylene and methine protons of the substituent group are the basis for conformational assertions, it was of interest to examine the temperature dependence of these coupling constants. The examination of two nitroindan anion radicals was relevant because the methylene hydrogens are essentially fixed with respect to the benzene ring.

Experimental Section

2- and 4-ethylnitrobenzenes, as obtained from Aldrich Chemical Company, Inc., were purified by preparative vapor phase chromatography, using a 10-ft column of 20% Carbowax on Chromosorb P. Refractive indices measured at 20° were 1.5353 and 1.5451 for the *ortho* and *para* isomers, respectively. The reported values are 1.5352 and 1.5459, respectively.[6]

4-Isopropylnitrobenzene was prepared by nitration of cumene (Phillips Petroleum "Pure Grade") according to the procedure of Nelson and Brown.[7] The product boiled at 92° at a pressure of approximately 10 mm and had a refractive index of 1.5369 at 20° which was identical with the literature value.[8] The 2-isopropylnitrobenzene was a gift of Professor B. M. Wepster, Delft, The Netherlands.

Nitration of indan (Aldrich) using the procedure described by Newton[8] yielded 4- and 5-nitroindan. The isomers were separated by preparative vapor phase chromatography, using the same conditions employed for the 2- and 4-ethylnitrobenzenes. The melting point of 4-nitroindan was 42.5° and that of 5-nitroindan wat 40°. The literature values are 44–44.5° and 40–40.5°, respectively.[8b]

Acetonitrile and dimethylformamide were purified by previously described procedures.[5] Tetrapropylammonium perchlorate for use as supporting electrolyte was recrystallized three times from water.

The anion radicals were generated electrochemically using the *intra muros* technique.[9] Variable-temperature measurements were made using the Varian V-4557 variable-temperature accessory. Esr signals were normally recorded as the first derivative of the absorption. This mode of presentation usually gave sufficient resolution for complete assignment of the spectrum. However, in some instances the proton hyperfine interactions were of such small magnitude compared to the line width that accurate measurements were impossible. Display of the second derivative greatly facilitated measurements of small splittings and of lines with overlapping components.

Reported coupling constants are averages of at least three individual measurements. For completeness, the parameters used in computed spectra are included in the appropriate figure captions. All computed spectra were simulated with a Lorentzian line shape. Details of electrochemical[10] and electron spin resonance measurements[11] have been described previously.

Results

In order to provide a basis for direct comparison of coupling constants with data secured in the earlier study,[5] acetonitrile (AN) was used as the solvent in this work also. Spectra were also obtained in dimethylformamide (DMF). In general, these spectra were more highly resolved and the lines were narrower than those obtained in AN. Assignment of the spectrum in DMF was often more straightforward and facilitated assignment of the spectrum obtained in AN. The nitrogen coupling constant for a particular anion radical is somewhat larger in AN than in DMF,[12] and there is a corresponding decrease in spin density at the *para* ring position. This reorganization of spin density dis-

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[1] (a) Abstracted in part from the Ph.D. thesis of T. M. McKinney, Cornell University, 1965; (b) Alfred P. Sloan Research Fellow.

[2] This subject has been reviewed by D. H. Geske, *Progr. Phys. Org. Chem.*, 4, 125 (1967).

[3] D. H. Geske and J. L. Ragle, *J. Am. Chem. Soc.*, **83**, 3532 (1961).

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

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

[6] H. C. Brown and W. H. Bonner, *ibtd.*, **76**, 605 (1954).

[7] K. L. Nelson and H. C. Brown, *ibid.*, **73**, 5605 (1951).

[8] (a) A. Newton, *ibid.*, **65**, 2434 (1943); (b) J. Lindner and J. Bruhin, *Ber.*, **60B**, 435 (1927).

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

[10] K. Kuwata and D. H. Geske, *ibid.*, **86**, 2101 (1964).

[11] T. M. McKinney and D. H. Geske, *J. Chem. Phys.*, **44**, 2277 (1966).

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

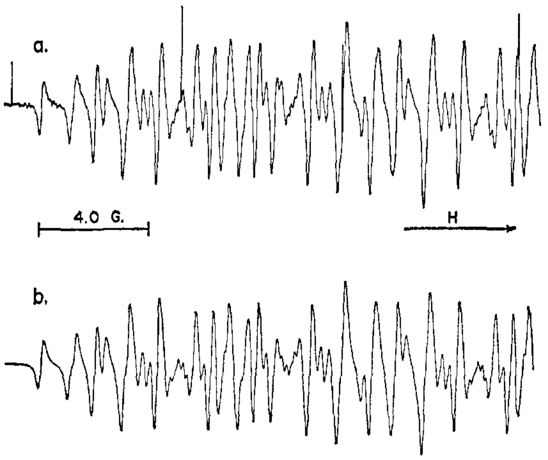

Figure 1. (a) Low-field one-half of esr spectrum obtained by reduction of 0.49 mM solution of 2-ethylnitrobenzene in DMF. (b) Spectrum computed using the values (in gauss) 3.92 (1 proton), 1.125 (1 proton), 0.975 (1 proton), 3.34 (1 proton), 1.805 (2 protons), 10.14 (1 nitrogen), a line width of 1.06, and 0.005-gauss increments.

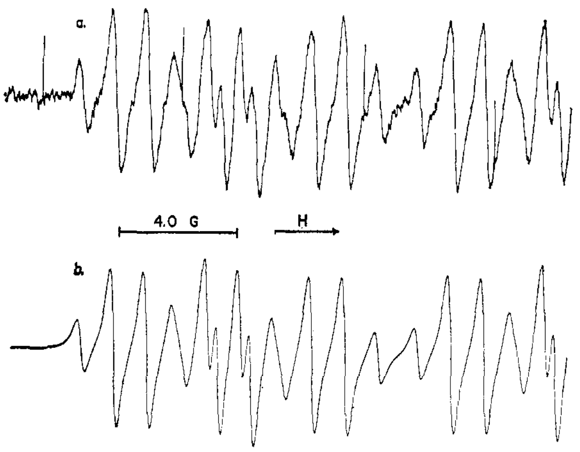

Figure 2. (a) Low-field one-half of esr spectrum obtained by reduction of 0.11 mM solution of 2-isopropylnitrobenzene in AN. (b) Spectrum computed by using the values (in gauss) 3.565 (1 proton), 3.175 (1 proton), 1.125 (3 protons), 11.46 (1 nitrogen), a line width of 0.3, and 0.005-gauss increments.

tribution upon changing the solvent medium was a useful adjunct in the assignment of proton coupling constants to particular molecular positions.

Polarographic and esr data for the compounds examined in this study are given in Table I along with relevant data for related compounds studied earlier. g values were all close to 2.0 but they were not explicitly measured. All of the compounds in Table I meet the necessary condition for reversible, one-electron reduction at 25°, namely, $E_{3/4} - E_{1/4} \approx -56$ mv. The diffusion current constants also indicate the transfer of one electron.

The large nitrogen coupling is the dominant feature of all of the esr spectra reported here. The proton coupling constants were assigned by analogy to the unequivocal assignment of the *m*-monodeuterionitrobenzene anion,[5] but in certain instances there is uncertainty as to which nucleus is responsible for a given coupling constant. Hence, the assignments are discussed briefly below.

4-Ethylnitrobenzene. The spectrum of the 4-ethylnitrobenzene anion radical in DMF had a line width of 0.14 gauss and was readily assigned using the coupling constants shown in Table I. By analogy to the nitrobenzene anion radical, the smallest splitting constant was attributed to the *meta* protons. The 3.37-gauss splitting from two equivalent nuclei with a spin of $^1/_2$ was comparable to the coupling constants for the *ortho* protons in the nitrobenzene and *p*-nitrotoluene radicals[5] and was therefore assigned to the *ortho* protons. This is corroborated by the observation of the same value in 4-isopropylnitrobenzene anion where there is no possible ambiguity in assignment of *ortho* and *para* coupling constants since the latter gives rise to a doublet splitting. The remaining 2.96-gauss triplet was assigned to the methylene protons of the ethyl group. The data in Table I show that the protons of the *para* substituent in the 4-ethylnitrobenzene radical do indeed have a larger coupling constant in DMF than in AN, and this adds reliability to the assignment of coupling constants to molecular positions. The coupling constants for this anion radical in ethanol[13] and aqueous acetone[14] are given in Table I for comparison.

2-Ethylnitrobenzene. Figure 1 shows the low-field half of the spectrum of the 2-ethylnitrobenzene anion radical in DMF together with a computed spectrum. This is a relatively complicated spectrum since the ring protons are not strictly equivalent in pairs. The close similarity of the experimental and computed spectra is substantial evidence for the validity of the assignment. By analogy to the nitrobenzene spectrum, the two smallest coupling constants were assigned to the positions *meta* to the nitro group. The proton coupling constants for the 3 and 5 positions were slightly different. There is no basis for distinguishing which position is associated with the larger constant, a fact indicated in Table I by bracketing the constants.

The triplet proton splitting was immediately assignable to the methylene protons of the ethyl substituent since they are the only two protons in the radical which are fully equivalent. The remaining two proton doublets were assigned to positions *ortho* and *para* to the nitro group; by analogy to the nitrobenzene radical, the larger value was assigned to the *para* ring proton. Moreover, this splitting showed the larger solvent variation.

4-Isopropylnitrobenzene. Since the methine proton is the only nucleus in the isopropyl group which shows a resolvable splitting, the esr spectrum for the 4-isopropylnitrobenzene anion radical bears a formal resemblance to that for the nitrobenzene anion radical. Accordingly, the smallest coupling constant was attributed to the *meta* protons. Assignment of the 1.8-gauss constant to the methine proton is unequivocal. The line width for the esr spectrum in DMF was 0.33 gauss. The coupling constants for this anion radical in aqueous acetone are also given in Table I.

2-Isopropylnitrobenzene. Figure 2 shows the low-field half of the experimental spectrum for the 2-isopropylnitrobenzene anion along with a spectrum computed using the coupling constants given in the figure caption.

The outstanding features of the proton hyperfine structure are the extreme low-field lines which indi-

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[13] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 4518 (1963).

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

Table I. Polarographic and Esr Data for Nitroaromatic Anion Radicals

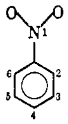
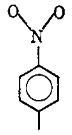
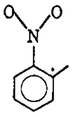
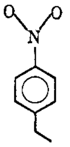
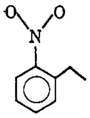
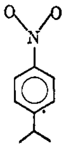
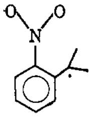
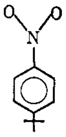
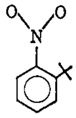
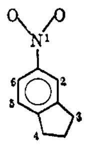
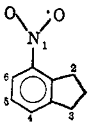
Compound and structure	$-E_{1/2}{}^{a}$	$-(E_{3/4} - E_{1/4})$, mv	I^{b}	Solvent^{c}	$\lvert a_1\rvert^{d}$	$\lvert a_2\rvert$	$\lvert a_3\rvert$	$\lvert a_4\rvert$	$\lvert a_5\rvert$	$\lvert a_6\rvert$	R
Nitrobenzene 	1.14_7	56	4.1	A^{e}	10.32	3.39	1.09	3.97	1.09	3.39	
				D^{f}	9.70	3.36	1.07	4.03	1.07	3.36	
				AA^{g}	13.30	3.40	0.90	3.40	0.90	3.40	
				E^{h}	13.65	3.35	1.15	3.35	1.15	3.35	
4-Methylnitrobenzene 	1.20_3	56	4.0	A^{i}	10.70	3.39	1.11	3.98^{j}	1.11	3.39	
				D	10.40	3.40	1.10	3.94^{j}	1.10	3.40	
				AA^{g}	14.10	3.50	1.10	3.80^{j}	1.10	3.50	
				E^{h}	14.05	3.40	1.15	3.75^{j}	1.15	3.40	
2-Methylnitrobenzene 	1.26_3	56	4.6	A^{k}	11.00	3.12^{j}	1.04	3.91	1.04	3.12	
				D	10.19	3.24^{j}	1.06	3.87	1.06	3.37	
4-Ethylnitrobenzene 	1.19_9	58	4.3	A^{m}	10.71	3.37	1.11	2.96^{l}	1.11	3.37	0.74
				D	10.18	3.34	1.09	3.01^{l}	1.09	3.34	0.76
				AA^{g}	14.15	3.45	1.15	3.05^{l}	1.15	3.45	0.80
				E^{h}	14.00	3.40	1.10	2.80^{l}	1.10	3.40	0.75
2-Ethylnitrobenzene 	1.25_1	57	4.3	A	11.03	1.76^{l}	$[1.00^{n}]$	3.76	$[1.15^{n}]$	3.29	0.56
				D	10.20	1.81^{l}	$[0.98^{n}]$	3.92	$[1.13^{n}]$	3.34	0.56
4-Isopropylnitrobenzene 	1.19_4	57	4.3	A^{m}	10.66	3.36	1.10	1.74^{o}	1.10	3.36	0.44
				D	10.05	3.40	1.07	1.76^{o}	1.07	3.40	0.45
				AA^{g}	14.20	3.40	1.15	1.80^{o}	1.15	3.40	0.47
2-Isopropylnitrobenzene 	1.28_5	56	4.0	A	11.47	1.13^{o}	1.13	3.66	1.13	3.20	0.36
				D	10.41	1.13^{o}	1.13	3.75	1.13	3.18	0.35
4-*t*-Butylnitrobenzene 				AA^{g}	14.25	3.40	1.10	$\ldots^{p}$	1.10	3.40	
				E^{h}	14.00	3.40	1.10	$\ldots^{p}$	1.10	3.40	
2-*t*-Butylnitrobenzene 	1.35_5	54	2.9	A^{k}	14.90	$\ldots^{p}$	1.10	2.50	1.10	2.50	
				D	12.73	$\ldots^{p}$	1.10	3.10	1.10	2.80	
5-Nitroindan 				A	10.84	[3.30]	1.38^{q}	5.40^{q}	1.11	[3.54]	1.36
				D	10.32	[3.22]	1.41^{q}	5.42^{q}	1.09	[3.52]	1.35
4-Nitroindan 				A	10.49	4.86^{q}	1.15^{q}	3.92	1.15	3.38	1.56
				D	9.84	4.93^{q}	1.09^{q}	3.99	1.09	3.38	1.53

Table I (*Footnotes*)

[a] Half-wave potentials are reported for acetonitrile solution with respect to the aqueous saturated calomel electrode. Data are tabulated for only the least negative half-wave potential for each compound. [b] Diffusion current constant, $i_d/m^{2/3}t^{1/6}C$, where the maximum diffusion current i_d is measured in microamperes, m in milligram per second, t is seconds, and C in millimoles per liter. [c] Notation: A, acetonitrile; D, dimethylformamide; AA, 10–15% aqueous acetone; E, ethanol. [d] Nitrogen coupling constant. [e] Data from ref 9. [f] Data for *D* from P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963). [g] Data for AA from ref 14. [h] Data for E from ref 13. [i] Data from A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961). [j] Coupling constant for three equivalent nuclei with spin of $^1/_2$. [k] Data from ref 5. [l] Coupling constant for two methylene protons of ethyl group at this position. [m] After completion of this work essentially the same coupling constants were reported by E. G. Janzen and J. L. Gerlock, *J. Org. Chem.*, **32**, 820 (1967). [n] The ring protons *meta* to the nitro group are nonequivalent, but there is no straightforward way of determining which position has the larger coupling constant. [o] Splitting from the methine proton of the isopropyl substituent at this position. [p] No splitting resolved from the *t*-butyl group. [q] Coupling constants for methylene protons.

cate the presence of quartet splittings with intensity ratios of approximately 1:3:3:1. Since there are not three symmetrically equivalent protons in the molecule, this implies that the coupling constant for the methine proton of the isopropyl group is accidentally nearly the same as that for the two ring protons *meta* to the nitro group. The larger of the two remaining doublet splittings is assigned to the *para* ring proton by analogy to the nitrobenzene case. Furthermore, this coupling constant increases when the solvent is changed from AN to DMF. The other doublet is assigned to the ring proton *ortho* to the nitro group.

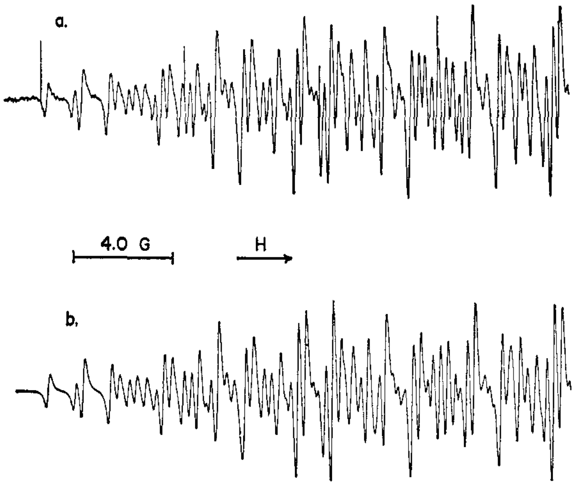


Figure 3. (a) Low-field one-half of esr spectrum obtained by reduction of 0.96 m*M* solution of 5-nitroindan in DMF. (b) Spectrum computed by using the values (in gauss) 3.52 (1 proton), 3.22 (1 proton), 1.09 (1 proton), 5.42 (2 protons), 1.41 (2 protons), 10.34 (1 nitrogen), a line width of 0.16, and 0.005-gauss increments.

2-*t*-Butylnitrobenzene. Unresolved hyperfine structure from the nine methyl protons in the *t*-butyl group contributes to the line width in this spectrum. The assignment of the spectrum of this radical in AN as reported earlier[5] distinguished no difference in coupling constants for the *ortho* and *para* ring protons. During the present investigation the spectrum was examined in DMF. Use of a second derivative display revealed two different doublet splittings, the larger of which was assigned to the *para* ring proton. No difference was resolved between the *meta* proton coupling constants.

5-Nitroindan. Experimental and computed spectra for the anion radical of 5-nitroindan are given in Figure 3. Assignment of the larger of the two methylene proton coupling constants to the protons at the 4 position (numbering defined in Table I) is based on the larger spin density at the *para* carbon atom. The two *ortho* proton coupling constants are distinguished as different; the arbitrary nature of the assignment between positions 2 and 6 is indicated in Table I by brackets.

4-Nitroindan. The experimental esr spectrum for the anion radical of 4-nitroindan in DMF is shown in Figure 4 along with a computed spectrum. The quartet structure for the smallest coupling constant was attributed to accidental coincidence of the coupling constants for the *meta* ring and methylene protons (positions 3 and 5, Table I). The triplet splitting of 4.9 gauss has been assigned to the *o*-methylene protons, and the larger of the two remaining proton coupling constants was assigned to the *para* proton.

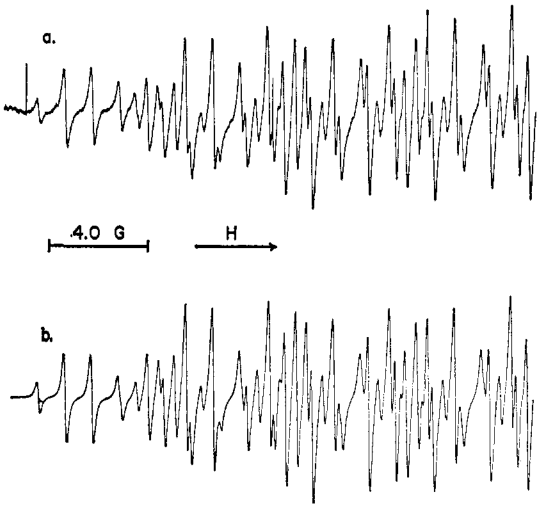


Figure 4. (a) Low-field one-half of esr spectrum obtained by reduction of 1.1 m*M* solution of 4-nitroindan in DMF. (b) Spectrum computed by using the values (in gauss) 4.015 (1 proton), 3.38 (1 proton), 4.93 (2 protons), 1.09 (3 protons), 9.80 (1 nitrogen), a line width of 0.14, and 0.005-gauss increments.

Temperature Dependence. Data for the temperature dependence of the alkyl proton coupling constants are given in Table II. Equation 1 describes the temperature dependence of the methine proton coupling constant, $a_{\text{iso}}^{\text{H}}$, in the 4-isopropylnitrobenzene anion

$$a_{\text{iso}}^{\text{H}} = 1.389 + (1.23 \times 10^{-3})T \qquad (1)$$

radical as a function of absolute temperature, T, with a correlation coefficient of 0.994.

Discussion

We wish to examine the above data with the intention of extracting those structural inferences which are warranted.

Table II. Temperature Dependence of Proton Coupling Constants for Alkyl Substituents[a]

Radical	Temp, °K	n^b	$a_\beta^{H\,c}$
4-Isopropylnitrobenzene	233	12	1.672 ± 0.015
	263	11	1.712 ± 0.014
	283	20	1.757 ± 0.019
	333	12	1.793 ± 0.020
2-Isopropylnitrobenzene	233	12	1.120 ± 0.017
	333	16	1.128 ± 0.011
4-Methylnitrobenzene	233	6	3.965 ± 0.011
	296	6	3.942 ± 0.034
	333	6	3.949 ± 0.069
4-Ethylnitrobenzene	233		3.01
	333		3.01

[a] Data for anion radicals in acetonitrile solution. [b] Number of measurements. [c] Uncertainties designated at the 95% confidence levels.

Nitrogen Coupling Constants. Attention is first of all focused on the nitrogen coupling constants. Previous work[5] has established that introduction of bulky substituent groups *ortho* and di-*ortho* to the nitro group in nitrobenzene anion radicals results in a substantial increase in the isotropic nitrogen coupling constant, a_N. Thus with acetonitrile as solvent, a_N increases from 10.3 gauss for nitrobenzene anion radical to 23.6 gauss for one conformational isomer of the 2,3,5,6-tetraisopropylnitrobenzene anion radical.[11] In qualitative terms, this increase in a_N can be regarded as the result of the transfer of spin density from the phenyl group to the nitro group as the nitro group is twisted out of the plane of the ring by *ortho* substituents. A rationalization of nitro group nitrogen coupling constants on the basis of semiempirically calculated nitrogen and oxygen π-spin densities has been developed by Rieger and Fraenkel;[4] twisting of the nitro group was accommodated in their molecular orbital calculations by a decrease of the carbon–nitrogen resonance integral. On the basis of examination of the anisotropic nitrogen coupling constants, Fox, Gross, and Symons[15,16] have suggested that twisting of the nitro group along the carbon–nitrogen axis is accompanied by pyramidal distortion of the nitro group.

The nitrogen coupling constants for the nitrobenzene anion radicals (Table I), where the 2-substituent (Y) is successively $-H$, $-CH_3$, $-CH_2CH_3$, $-CH(CH_3)_2$, and $-C(CH_3)_3$, are 10.3, 11.0, 10.7, 11.5, and 14.9 gauss, respectively (in AN). The point of particular interest is that there is only a minimal effect on a_N for Y = methyl, ethyl, and isopropyl; for the symmetrical *t*-butyl group there is an abrupt increase in a_N.[17] We interpret these data as evidence that the 2-ethyl and 2-isopropyl substituents are oriented for *minimum* interaction with the nitro group. A simplified view would state that, if the ethyl and isopropyl groups were rotating freely, the a_N values would be expected to be the same as for the 2-*t*-butylnitrobenzene anion radical. The a_N of 10.5 gauss for the 4-nitroindan anion, where the methylene protons are essentially fixed in relation to the ring, is consistent with this interpretation.

Within this context it is of interest to examine a_N for several other *ortho*-substituted nitrobenzene anion radicals. In the *o*-nitrobiphenyl anion radical where a_N is 8.7 gauss in DMF,[18] a compromise of twisting the nitro group out of the plane of the ring and delocalization of spin density into the *ortho*-ring substituent much be reached. Essentially the same conclusions have been reached for the anion radical of 2-nitroterphenyl.[19] From the data of Carrington, Hudson, and Longuet-Higgins,[20] it is clear that the nitro group is hindered in the hydrogen adducts of the tetrafluoro- and pentafluoronitrobenzene anion radicals. However, a_N in the 2-fluoronitrobenzene anion radical[20] gives no evidence of steric hindrance.

Alkyl Proton Coupling Constants. Examination of the alkyl proton coupling constants in the *ortho*-substituted anion radicals for conformational implications requires a brief review of the angular dependence of transmission of spin density to β protons (β protons are defined as those protons on an sp^3 carbon which is in turn bonded to a π system). This concern was initiated by the observation of methyl proton coupling constants in methylated semiquinones by Venkataraman and Fraenkel[21] in 1955.

Bersohn[22] proposed a hyperconjugative mechanism which involved the mixing of the methyl group pseudo-π orbital with the π system on the adjacent trigonal carbon atom. Over the past 10 years an extensive literature has developed on the theory of β-proton coupling constants.[23–32] In the main, Bersohn's proposal of hyperconjugation has been substantiated. The point of interest for derivation of conformational information is the angular dependence of the β-proton coupling constants, a_β^H, as stated in eq 2 where $\rho_{C'}^{\pi}$ is the π-electron spin density on the trigonal carbon, C′, to

$$a_\beta^H = \rho_{C'}^{\pi}(B_0 + B\cos^2\theta) \qquad (2)$$

which the alkyl group is attached, B_0 and B are constants, and θ is the angle between the C′–C–H plane and the axis of the p_z orbital on the trigonal carbon atom. The value of B_0 has been variously estimated as -1.1[31] and 4.33 gauss.[33] Estimates of B range from 40 to 53 gauss.[34–36]

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(17) As in earlier studies[5] comparison of the coupling constants for the *para*-substituted anion radicals with constants for nitrobenzene anion radical demonstrates the minor extent of the nonsteric effects of the *ortho* substituent. Although we have not secured esr data for the 4-*t*-butylnitrobenzene in AN and DMF, it is clear from the data in Table I for ethanol and aqueous acetone that the inductive effect of the *p*-*t*-butyl group is negligible.

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

(35) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962); **38**, 1254 (1963).

(36) R. W. Fessenden, *J. Chim. Phys.*, **61**, 1570 (1964).

Equation 2 has been widely used in the rationalization of the spectra of alkyl radicals in irradiated solids.[27,37–40] The first conformational assertions for alkyl radicals in solution were made by Stone and Maki[35] in 1962. They interpreted the β-proton coupling constants[41] for a series of nitroalkane anion radicals in terms of a preferred orientation of the alkyl group resulting from a finite barrier to rotation. Since the alkyl groups in the nitroalkane anions are not rigidly oriented $a_\beta{}^H$ is actually a time-averaged quantity as stated in eq 3, where $\rho_N{}^\pi$ is the π-electron spin density on the nitrogen atom. Evaluation of the average quantity $\langle\cos^2\theta\rangle$ in eq 3 was done quantum mechanically

$$a_\beta{}^H = \rho_N{}^\pi(B_0 + B\langle\cos^2\theta\rangle) \qquad (3)$$

by Stone and Maki[35] under the assumption of a simple twofold sinusoidal barrier with a maximum barrier height of V_0. On the basis of evaluation[42] of this model, a graphic representation of $\langle\cos^2\theta\rangle$ *vs.* V_0 was presented for the four different equilibrium conformations in Figure 5. For the 2-nitropropane anion radical,[41] V_0 was estimated as 1.1 kcal mole^{-1} with **1a** (Figure 5) as the equilibrium conformation. For the nitroethane anion radical,[41] V_0 was estimated as 0.34 kcal mole^{-1} with **2a** (Figure 5) as the equilibrium conformation. Temperature coefficients, $da_\beta{}^H/dT$, were predicted; however, the experimental data necessary to test these predictions have never become available. Stone has suggested that there are several reasons why the calculated barriers "should not be taken too seriously."[43] In addition to the assumption of a *simple* barrier, both estimated values of V_0 are near the value of RT, ~0.6 kcal mole^{-1} at 298°K, a region where the approximate method of averaging is least accurate.

Subsequent to the work by Stone and Maki,[35] a number of workers[36,44–50] have argued for preferred orientation of alkyl groups in radicals in solution on the basis of eq 3. Of particular note is the work of Fessenden[36] who evaluated eq 3 for a series of radicals, $R\dot{C}H_2$, where R is an alkyl substituent. Exact solution was possible because the reduced moment of inertia was small enough to permit utilization of existing mathematical tables. The experimental values[44] of $a_\beta{}^H$ for the isobutyl radical over the temperature range −50 to −140° were in reasonable agreement with a calculated function assuming a barrier of 295 cal mole^{-1}. The temperature dependence for the propyl radical using a barrier of a 412 cal mole^{-1} was in excellent agreement with the experimental data. The equilibrium conformations were **1b** and **2b** (Figure 5), respectively.

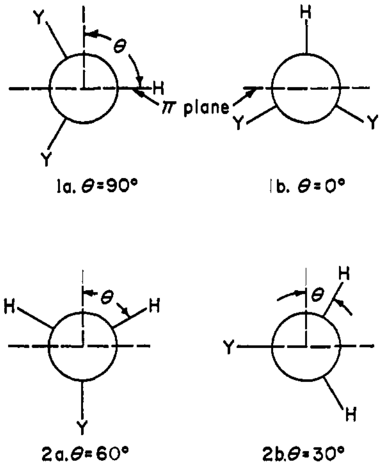

Figure 5. Equilibrium conformations of alkyl groups.

The 9-ethyl- and 9-isopropylxanthyl radicals studied by Sevilla and Vincow[50] are distinguished by the extent to which $a_\beta{}^H$ values approach the expected limits (see Table III) for conformations **1a** and **2a** (Figure 5), respectively. V_0 for the ethylxanthyl radial has been estimated as 6 kcal mole^{-1}.[51] An even larger barrier is indicated for the isopropyl radical.

Table III. **R** Values for Nitroalkane Anion[41] and Alkylxanthyl[51,52] Radicals

Radical	a_N, gauss	a_β, gauss	**R**[a]
$[CH_3NO_2]^-$	25.8	11.4	
$[CH_3CH_2NO_2]^-$	25.5	9.75	0.85
$[C_2H_5CH_2NO_2]^-$	24.8	9.98	0.87
$[CH_3CHNO_2CH_3]^-$	25.2	4.60	0.40
$[CH_3CHNO_2CH_2CH_3]^-$	24.7	3.19	0.28
9-Methylxanthyl		12.18	
9-Ethylxanthyl		6.22[b]	0.51
9-Isopropylxanthyl		0.86[c]	0.07

[a] Ratio of β-proton coupling constant to methyl proton coupling constant in parent radical. [b] Value for 110°. [c] Value for −10°.

In order to simplify the comparison of β-proton coupling constants within a series of related radicals such as the nitroalkane anions, it is convenient to define the quantity **R** in eq 4. $a_\beta{}^H$ is the coupling constant for the β protons of the alkyl substituent, and

$$\mathbf{R} = \frac{a_\beta{}^H}{a^H{}_{CH_3}} \qquad (4)$$

$a^H{}_{CH_3}$ is the coupling constant for the β protons of the corresponding methyl-substituted radical. The methyl group is usually regarded as freely rotating, *i.e.*, V_0 ~ 0;[52] eq 5 is valid even with a barrier provided that transitions between potential minima are rapid.[43]

$$a^H{}_{CH_3} = \rho_i{}^\pi\left(B_0 + \frac{B}{2}\right) \qquad (5)$$

With the definition of **R** in eq 4 it is not necessary to explicitly evaluate $\rho_C{}^\pi$ in eq 2 or $\rho_N{}^\pi$ in eq 3 as long as

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(37) D. Pooley and D. H. Whiffen, *Mol. Phys.*, 4, 81 (1961).

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(39) I. Miyagawa and K. Itoh, *J. Chem. Phys.*, **36**, 2157 (1962).

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(42) Since the reduced moments of inertia were too large for exact solution of the appropriate Schrodinger equation by standard methods, two classes of limiting solutions were used by Stone and Maki.[35]

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(51) M. D. Sevilla, private communication.

(52) The barrier for the methyl group in nitromethane has been estimated as **6** cal mole^{-1}.

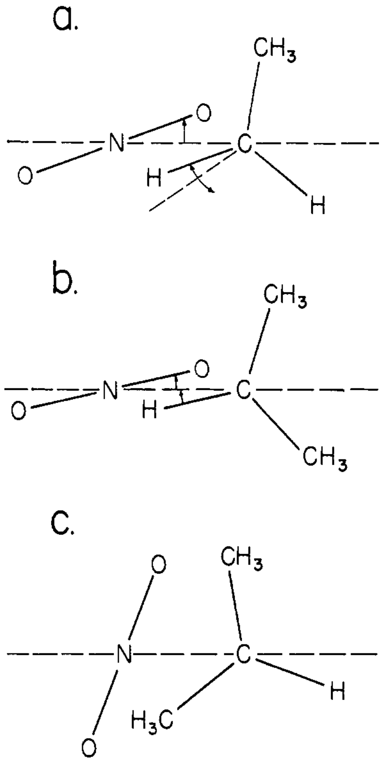

Figure 6. Representation of conformations of adjacent nitro and alkyl groups.

they remain essentially constant within the series. Furthermore, if one assumes $B_0 \ll B$, there is no need to select a value for B. Under these assumptions the values of **R** for conformations **1a**, **1b**, **2a**, and **2b** in Figure 5 are 0, 2, 0.5, and 1.5, respectively, under conditions of infinite barrier. The relation between **R** and $\langle \cos^2 \theta \rangle$ is as given in eq 6. To facilitate comparison of **R** values for radicals in Table I, values of **R** for the nitroalkane anion radicals[41] and alkylxanthyls[50,51] are presented in Table III.

$$\mathbf{R} = 2\langle \cos^2 \theta \rangle \qquad (6)$$

A substantial body of esr data for rigid radicals is available[38,44,45,53,54] to support the validity of eq 2. Nevertheless, we felt that it was appropriate to examine several nitroaromatic anion radicals where the β protons are essentially fixed in relation to the benzene ring.

The 4- and 5-nitroindan anion radicals are in this category. The experimental **R** values for the methylene protons in the *para* position (position 4, Table I) in the 5-nitroindan anion radical are 1.35 and 1.36. **R** for the *ortho* (position 2, Table I) methylene protons of 4-nitroindan anion radicals are 1.56 and 1.53. Since conformation **2b** (Figure 5) describes both of these methylene groups, the theoretical **R** value is 1.50. One might choose to argue that the reduced value of **R** for the *para*-position methylene groups, 1.36 in 4-nitroindan anion radical, is evidence for some torsional motion of the methylene group, *i.e.*, axial-equatorial inversion. In the same context the closer coincidence of experimental **R** values in the 5-nitroindan with 1.50 would be regarded as evidence for a more rigid structure as a consequent of the adjacent nitro group. These detailed assertions may not be fully warranted and should surely be viewed with caution. However, we do regard the data for the nitroindan radicals as reasonable evidence for the validity of eq 2.[55]

Turning now to consideration of data for the *p*-alkylnitrobenzene anion radicals, it is important to note the comment of Carrington and Todd[48] who suggested, on the basis of the data of Ayscough, Sargent, and Wilson[13] (Table I), that the preferred orientation of the ethyl group in 4-ethylnitrobenzene anion radical corresponds to **2a** (Figure 5). Data for this anion radical in four solvent media are included in Table I. The **R** values (extreme right column, Table I) range from 0.74 to 0.80. If one accepts the Stone–Maki model,[35] the corresponding range of V_0 is 0.9 to 0.55 kcal mole^{-1} with **2a** (Figure 5) as the equilibrium conformation.[56]

R values calculated for the *p*-isopropylnitrobenzene anion radical from the data in this work and from the data of Kolker and Waters[14] (Table I) are 0.44 and 0.47, respectively. Within the Stone–Maki model this corresponds to a barrier, V_0, of 1.0 kcal mole^{-1} and **1a** (Figure 5) as the equilibrium conformation. The observed temperature coefficient, 1.39×10^{-3} gauss deg^{-1}, may be compared with a calculated value of 3.8×10^{-3} gauss deg^{-1}. There are several possible explanations for the discrepancy between observed and calculated temperature coefficients. One possibility is that the approximate solution[35] is inadequate. A more likely alternative is that the real barrier is more complex than the simple sinusoidal barrier assumed in the calculation.[35] In fact, there could even be a shallow potential minimum at $\theta = 0°$. We conclude that it is not possible to specify in detail the nature of the potential barrier.

With the strong indication at hand that the *p*-alkyl substituents undergo anisotropic averaging, it is appropriate to examine data for the *o*-alkylnitrobenzene anion radicals. It should be clear at the outset that the *ortho*-substituted radicals no longer possess twofold symmetry; thus, there is no reason to suppose that the potential barrier experienced by the β protons and the nitro group has twofold symmetry.

Observation of a coupling constant for three equivalent methyl protons in the *o*-methylnitrobenzene anion radical provides no information about the barrier to rotation. It does establish that transitions between potential minima are rapid[57] (*cf.* eq 5). Janzen and Gerlock[58] find line-width effects in the esr spectrum of 2-trifluoromethylnitrobenzene anion indicating hindered rotation of the trifluoromethyl group. While it is possible that 2-*t*-butylnitrobenzene anion is similar in a dynamic sense, the question cannot be settled on the basis of the esr spectrum.

We feel that it is significant to note that **R** for the *o*-ethylnitrobenzene anion, 0.56, is substantially smaller than **R** for the *para* substituent, 0.74–0.80, which is in turn smaller than **R** for the nitroethane anion radical,

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[54] L. M. Stock and H. Suzuki, *J. Am. Chem. Soc.*, **87**, 3909 (1965).

[55] E. G. Janzen and J. L. Gerlock, *J. Org. Chem.*, **32**, 820 (1967), find no splittings for the bridgehead protons in 2-nitrotriptycene anion radicals. This observation is consistent with eq 2 since $\theta = 90°$.

[56] Figure 3 in ref 35 was used for this estimate. The reduced moments of inertia for nitroaromatic and nitroaliphatic anion radicals are sufficiently comparable that this procedure is valid.

[57] We assume that eq 3 is applicable.

[58] E. G. Janzen and J. L. Gerlock, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 1966, Abstract 158-V.

0.85 (Table III). It should be recalled that **R** for **2a** (Figure 5) at the limit of large barrier is 0.50. While it is tempting to utilize the Stone–Maki model to estimate $V_0 \sim 4$ kcal mole^{-1} it is also clear from the absence of C_{2v} symmetry (*vide infra*) that the approximation of a simple twofold barrier is *not* applicable; thus a barrier cannot be evaluated quantitatively. The schematic representation of conformation in Figure 6a is consistent with both alkyl proton and nitrogen coupling constants.

By comparison with the range of **R** values for *p*-isopropylnitrobenzene anion, 0.44–0.47, the value of 0.36 for *o*-isopropylnitrobenzene anion is also considerably reduced. This value of **R** corresponds to $V_0 =$ 1.3 kcal mole^{-1} for conformation **1a** (Figure 5); since the barrier is not strictly twofold, this value can only be regarded as indicative. The schematic representation in Figure 6b combines data for both nitrogen and proton coupling constants. A substantially larger nitrogen coupling constant would be expected if the two isopropyl methyl groups were *cis* to the nitro group (Figure 6c) rather than *trans* (Figure 6b). Therefore, we can infer that the spatial requirements of the two methyl groups cause the preferred orientation to be that shown in Figure 6b.

The question of the conformation of the neutral parent molecules, the 2-alkylnitrobenzenes, has been examined on the basis of spectrophotometric data.[59] The twist angles for the nitro group inferred for the various substituents were 2-methyl, 34°; 2-ethyl, 40°; 2-isopropyl, 47°; and 2-*t*-butyl, 65°. The abrupt increase in the twist angle for the *t*-butyl derivative was ascribed to the fact that all the other groups have at least one β-hydrogen atom which permits a favorable orientation such as Figure 6b.

Electrochemistry. Esr data provide an understanding of the structure of the anion radical. By contrast standard electrode potentials as approximated by half-wave potentials are dependent on the free-energy difference between the neutral molecule and the anion. The change in half-wave potential attributable to steric effects, ΔE_s,[5] for the *o*-alkylnitrobenzene as computed from data in Table I are 0.06, 0.05, 0.09, and 0.16 v,[60] for methyl, ethyl, isopropyl, and *t*-butyl, respectively. The abrupt effect of the *t*-butyl groups on ΔE_s parallels the change of a_N with alkyl substitution.

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[60] Since $E_{1/2}$ for 4-*t*-butylnitrobenzene is not available, a value of 1.19 v *vs.* sce was assumed in the calculation of ΔE_s.

Absorption and Emission Spectra of 1,2,4,5-Tetracyanobenzene–Naphthalene Complex Crystal

Suehiro Iwata, Jiro Tanaka, and Saburo Nagakura

Contribution from the Institute for Solid State Physics, University of Tokyo, Azabu-shinryudo-cho, Minato-ku, Tokyo. *Received December 30, 1966*

Abstract: The electronic absorption and emission spectra of the charge-transfer complex of 1,2,4,5-tetracyanobenzene with naphthalene were studied by measuring them under various conditions, and by carrying out a theoretical study on the basis of configuration interaction among the ground, locally excited, and charge-transfer configurations. By combining the theoretical results with the polarized absorption measurements of the single crystal, it is concluded that the longest wavelength band at 24,600 cm^{-1} may be ascribed to the first charge-transfer transition, and that the second charge-transfer band appears at 31,500 cm^{-1} overlapping with local excitation bands. The fluorescence spectrum of the crystal at liquid N_2 temperature, which commences at 23,200 cm^{-1} and shows vibrational structure, nicely satisfies the well-known mirror image relation to the first charge-transfer band. On the other hand, the fluorescence spectrum of the crystal at room temperature is structureless and is shifted to lower frequencies compared with that at liquid N_2 temperature. The phosphorescence spectrum of the complex observed at liquid He temperature shows well-resolved vibrational structure which is satisfactorily coincident with that of the phosphorescence spectrum of naphthalene itself. This means that the phosphorescent state of the complex may be regarded as the locally (within naphthalene) excited triplet state.

The electronic spectra of charge-transfer (abbreviated hereafter to CT) complexes in crystalline state are interesting research subjects in connection with the CT theory developed by Mulliken.[1] The experimental evidence for the existence of the CT absorption can be obtained from the directions of the transition moments of the bands determined by polarized absorption measurements of single crystals, and the study of absorption and emission spectra of CT complexes may give valuable information about the interaction between the CT and locally excited structures and about electron- and energy-transfer phenomena in CT complex crystals. So far, however, the measurements of polarized absorption spectra have been carried out with rather few CT complex crystals, although many studies have been done with electronic spectra of solutions.[2,3] The most

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