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A Spectroscopic Study of Alkylnitrobenzene Anion Radicals

By Yasuto NAKAI

Central Research Laboratory, Sumitomo Chemical Co., Ltd., Takatsuki, Osaka

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A series of alkylnitrobenzene anion radicals has been studied by both electron spin resonance and infrared spectroscopy. It has been shown that there is a relationship between the magnitude of the nitrogen hyperfine splitting constant and the steric effect of the bulky alkyl group adjacent to the nitro group. In addition to the physical deformation factors, the effects of solvents, counter-ions, and temperature variation have been discussed. In the infrared spectra, the differences between anion radicals and neutral molecules have been found to be small, except for the change in the absorption intensity of the nitro-group stretching vibration.

The facility with which aromatic nitro compounds can accept an electron and the stability of the resulting radical anions have been reported on in a number of recent studies. A previous study has also been made of nitrobiphenyl anion radicals in the presence of alkali metal cations by means of electron spin resonance spectroscopy.[1] In this study the unique behavior of the nitro group in conjugate hydrocarbon systems with single-ring structures will be investigated.

The steric influences of substituents, chiefly alkyl groups, on such properties of aromatic nitro compounds as the ultraviolet spectrum, the infrared spectrum, the dipole moment, the molecular refraction, the basicity, and the reaction rate have been reported. In connection with these investigations, the question naturally arises whether the steric influence can also be detected for anion radicals, because there is an expected tendency towards coplanarity due to the additional pi-electron in the case of anion radical systems.

The structural nature of the negatively-charged molecules has been discussed mostly in electron spin resonance studies, whereas little information gained from other spectroscopic studies, particularly from infrared spectroscopy, has so far been made available.

Experimental

Solvents were dehydrated thoroughly and then redistilled in vacuo to remove the molecular oxygen. Each alkali metal was purified by repeated distillations in vacuo. Since the same procedure could not be applied to alkaline earth metals, each granular alkaline earth metal was cut or ground in order to obtain fresh surfaces; each metal was washed with carbon tetrachloride, dried in vacuo, and then amalgamated in order to facilitate the reducing activity.

For the study of the anion radicals by infrared spectroscopy, a special vacuum-tight rock-salt cell 0.1 mm. thick was connected to a glass system in which the anion radicals were produced (a detailed account of the latter has been given elesewhere[2]). The connection was made with polyethylene tubing which could withstand atmospheric pressure and was yet soft enough so that the sample solution could be forced into the optical cell by simply pressing the tubing. When the maximum resolution was required, a Model 521 Perkin-Elmer grating spectrophotometer at the Institute for Chemical Research of Kyoto University was used.

The ESR spectrometer employed was a high-resolution apparatus (JES-3B type) of the Japan Electron Optics Lab. Co., Ltd. The magnetic field was modulated at a frequency of 100 kc./sec. and at a modulation width of 0.1 gauss.

Results and Discussion

Analysis of Infrared Spectra.—The infrared spectra in the range from 800 to 2000 cm^{-1} contain distinct absorption bands corresponding to the symmetric stretching vibration and the asymmetric vibration of the nitro group, with frequencies at about 1350 and 1530 cm^{-1} respectively.[3] The frequencies at the maxima of these bands were carefully determined for each neutral compound, using nitrobenzene as a standard. The frequency of the asymmetric stretching vibration is practically the same for all the compounds investigated, as Table I shows. In other words, the variation in the values observed seems to be independent of the size of the alkyl groups adjacent to the nitro group. On the other hand, the frequencies of the symmetric stretching vibrations of the nitro group vary appreciably.

The spectra for the anion radical solution in dioxane in the presence of the potassium cation were measured for *o*-isopropyl-, *o*-*t*-butyl-, 2, 4, 6-trimethyl-, and 2, 4, 6-tri-*t*-butylnitrobenzenes. In each case the same solution was remeasured after the anion radical had been oxidized, by exposure to air, in order to reform the original neutral species.

Differences between the reduced and unreduced states were evidenced in the infrared spectra by the enhanced absoprtion associated with the asymmetric vibrations, but there was no shift in the frequency within the resolution of the instrument. If the decrease in the frequency of the symmetric stretching vibration is directly related to the coplanarity of the nitro group with the aromatic ring, as has been suggested by Wepster et al.,[4] the present results might predict that the configurations of the neutral molecule and its anion radical are similar. This matter will be discussed in the next section.

The Steric Effect of Alkyl Groups.—The sterically induced decoupling of the nitro group

TABLE I. THE STRETCHING FREQUENCY OF NITRO GROUP IN THE IR SPECTRA

Compoud (in CCl_4)	Asymmetric frequency cm^{-1}	(Difference from nitrobenzene)	Symmetric frequency cm^{-1}	(Difference from nitrobenzene)
Nitrobenzene	1529	0	1346	0
Nitromesitylene	1524	−5	1363	17
2,4,6-Triethylnitrobenzene	1524	−5	1366	20
2,4,6-Triisopropylnitrobenzene	1524	−5	1372	26
2,4,6-Tri-*t*-butylnitrobenzene	1530	1	1375	29

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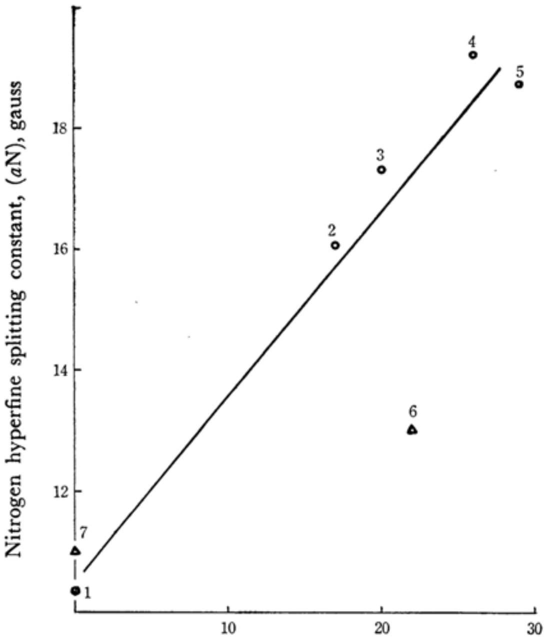
[1] Y. Nakai, K. Kawamura, K. Ishizu, Y. Deguchi and H. Takaki, This Bulletin, to be published.

[2] Y. Deguchi, *J. Chem. Phys.*, **32**, 1584 (1960).

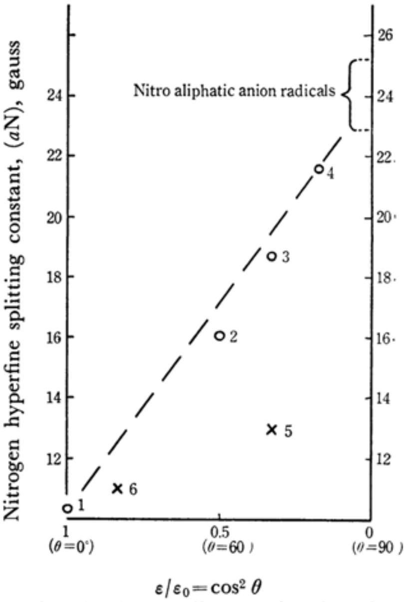
[3] J. F. Brown, *J. Am. Chem. Soc.*, **77**, 6341 (1955).

[4] A. Van Veen, P. E. Verkade and B. M. Wepster, *Rec. Trav. Chem.*, **76**, 801 (1957).



Difference in symmetric stretching vibration frequency between nitrobenzene and alkylnitrobenzene, cm^{-1}

Fig. 1. A relation between the observables for the nitro group as measured by ESR and IR.
1) Nitrobenzene
2) Nitromesitylene
3) 2, 4, 6-Triethylnitrobenzene
4) 2, 4, 6-Triisopropylnitrobenzene
5) 2, 4, 6-Tri-*t*-butylnitrobenzene
6) *o*-*t*-Butylnitobenzene
7) *o*-Methylnitrobenzene



Ratio of extinction coefficients for the ultraviolet absorption between alkylnitrobenzenes and nitrobenzene at 250 mμ.*

Fig. 2. A relation between the observables for the nitro group as measured by ESR and UV.
1) Nitrobenzene
2) Nitromesitylene
3) 2, 4, 6-tri-*t*-Butylnitrobenzene
4) 2, 3, 5, 6-Tetramethylnitrobenzene**
5) *o*-*t*-Butylnitrobenzene
6) *o*-Methylnitrobenzene
* Data from Ref. 14.
** Data from Ref. 15.

pi-electron system from the aromatic pi-electron system has been postulated solely on the basis of an interpretation of the electron spin resonance spectra.[5] On the basis of the observed changes in the nitrogen hyperfine splitting constants, a simple model involving hindered rotation in nitro aromatic anion radicals may be suggested. In this model the nitro group is twisted around the C–N bond.

Since the amount of twisting is likely to be similar in the anion radicals and in the neutral molecules, we have anticipated and found a linear relation between the nitrogen hyperfine splitting constants, a_N, and the shift of the symmetric stretching vibration frequency, as is shown in Fig. 1.

The decrease in the C–N bond order was also deduced from the ultraviolet absorption at 250 mμ by the equation of Braude[6] :

$$\varepsilon/\varepsilon_0 = \cos^2\theta \qquad (1)$$

where ε and ε_0 are the molar extinction coefficients for alkylnitrobenzene and nitrobenzene respectively, and where θ is the angle of twist of the nitrogroup out of the plane of the benzene ring. The ratio versus a_N is again plotted in Fig. 2.

The fact that the value of a_N extrapolated to $\theta=90°$ falls in the range of a_N values characteristic of aliphatic nitro anion radicals confirms the expectation of the absence of conjugation between the nitro group and any groups to which it is bonded. In other words, the unpaired electron appears to be completely localized on the nitro group in this case.

For monoalkylnitrobenzenes, however, neither the infrared nor the ultraviolet spectroscopic data conform to the proportionality behavior shown in Figs. 1 and 2. For example, the nitrogen hyperfine splitting constant for *o*-*t*-butylnitrobenzene anion is 13.0 gauss, while the steric deformation predicted by Eq. 1 is 65 degrees, a value which cannot be predicted from Fig. 2. The cause of this deviation may be as follows. The resonance interaction of the nitro group with the benzene

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[5] D. H. Geske, J. L. Ragle, M. A. Bambenek and A. L. Balch, *J. Am. Chem. Soc.*, **86**, 987 (1964).
[6] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3754.

Table II. Calculated nitrogen hyperfine splitting constants

	o-*t*-Butyl-nitrobenzene	Nitromesitylene	2, 4, 6-Triethyl-nitrobenzene	2, 4, 6-Tri-*t*-butyl-nitrobenzene
$\beta_{C-N}=1$ ($\theta=0°$)				
ρ_N	0.3121	0.2519	0.2249	0.3121
ρ_O	0.1846	0.1028	0.1085	0.1846
a_N (Eq. 3)	13.1	17.4	14.5	17.7
a_N (Eq. 4)	15.3	12.3	11.0	15.2
$\beta_{C-N}=0.7$ ($\theta=45°34'$)				
ρ_N	0.3769	0.3501	0.3607	
ρ_O	0.2081	0.1934	0.2026	
a_N (Eq. 3)	22.4	20.8	21.2	
a_N (Eq. 4)	18.5	17.2	17.7	
$\beta_{C-N}=0.5$ ($\theta=60°$)				
ρ_N		0.405		0.3817
ρ_O		0.214		0.2087
a_N (Eq. 3)		24.8		22.8
a_N (Eq. 4)		19.8		18.7
a_B(Experimental)	13.0	16.1	17.3	18.7

ring is believed to be such as to constrain the nitrogen and the two oxygens to lie on the same plane, or such as to minimize the out-of-plane deflection, even in the presence of an alkyl group on one side, by bending the two groups away from each other, particularly in the case of the anion radicals. In those cases where the nitro group has alkyl groups on both sides, such bending is prevented, regardless of whether it is the neutral molecule or the radical anion. Thus, the changes in the observables in optical spectroscopy may be directly related to the extent of twisting. Any shift in the nitro-group absorption bands in the infrared spectra would reflect the twisting in the case of the monoalkylnitrobenzenes, but in the case of anion radicals, the shift may reflect both twisting and bending. Since the infrared spectra have not shed light on structural differences between the neutral molecule and the radical anion, as has been described in the last section, electron spin resonance spectra still seem to be a valuable source of infromation on the extent of intramolecular rotation for radical anions.[7]

The Computation of Hyperfine Splitting Constants.—Spin density (ρ) calculations based on the simple Hückel LCAO approximations have been carried out for a variety of parameters in the C–N bond integral expressed in the equation:

$$\beta_{NC} = \beta^0_{NC} \cos\theta \tag{2}$$

The nitrogen hyperfine splitting constants computed

Fig. 3. The ESR spectrum of 2, 4, 6-triethylnitrobenzene anion radical.

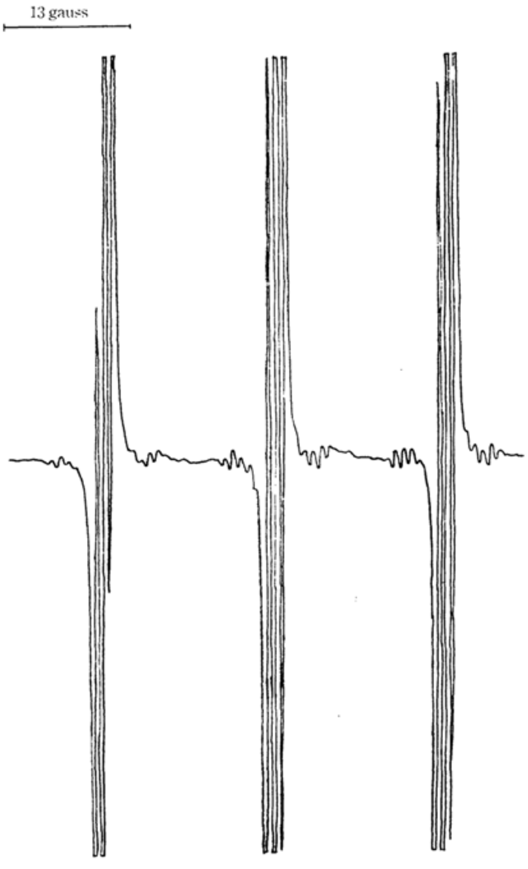

Fig. 4(a). The ESR spectrum of 2, 4, 6-tri-*t*-butylnitrobenzene anion radical.

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[7] K. Ishizu, This Bulletin, **37**, 1093 (1964).

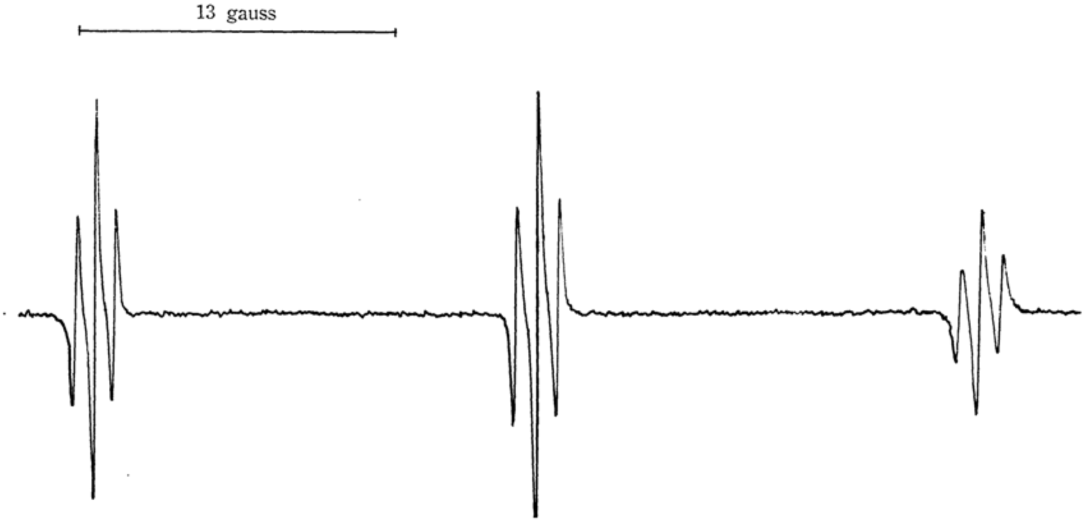

Fig. 4(b). The ESR spectrum of 2,4,6-tri-*t*-butylnitrobenzene anion radical.

by the equations[8,9]:

$$a_N = 99.0\,\rho_N - 71.6\,\rho_O \quad (3)$$

$$a_N = Q_N\rho_N = 49\,\rho_N \quad (4)$$

are compared with the experimental values in Table II.

Analysis of the ESR Spectra.—An electron spin resonance spectrum always consists of three well-defined groups of lines corresponding to the interaction with a ^{14}N nucleus if a proper radical concentration is maintained, as is illustrated in Fig. 3. Without deuterium substitutions, the alkyl-proton splittings cannot be distinguished from the ring-proton splittings. The reliable computation of hyperfine components is prevented by linewidth alternations, and by the overlap of the spectral lines due to the presence of cation-paired and isolated radical anions.[10] Efforts to observe the hyperfine splitting of the tertiary-butyl group which has been observed for those derivatives of phenoxyl[11] have been fruitless. The hyperfine splitting of ^{13}C and ^{17}O nuclei are shown in Fig. 4.

The Effect of Metal Cations on the Spectra.—The nitrogen hyperfine splitting constant (a_N) increases with the reciprocal of the cationic radius (r) or with the electronic charge of the cation (z) in solution. A tight ion-pair formation may be directly predicted by a comparison with meta-substituted nitrobenzenes which follows the equation:[12]

$$a_N = \text{constant} \times z/(r + 0.6) \quad (5)$$

Equation 5 is consistent with the presence of a rather loose ion-pair (a solvent shared to a limited extent), in contrast to the results of the present investigation.

TABLE III VARIATION OF THE NITROGEN HYPERFINE SPLITTING CONSTANT OF 2,4,6-TRI-*t*-BUTYLNITROBENZENE

(A)*

Solvent	a_N
p-Dioxane	18.45
Tetrahydrofuran	18.44
1,2-Dimethoxyethane	18.66
Tetrahydropyran	18.74
N,N'-Dimethylformamide	18.76

(B)**

Cation	a_N
Lithium	19.11
Sodium	18.80
Potassium	18.66
Calcium	18.34
Strontium	18.95
Barium	18.44

* The cation was K^+ in all cases.

** The solvent was 1,2-dimethoxyethane in all cases.

Effect of Solvents.—The decrease in the hyperfine splitting constant with an increase in the dipole moments of the solvents (shown in Table III) suggests that an oriented ionic atmosphere

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

[9] A. Ishitani, K. Kuwata, H. Tsubomura and S. Nagakura, This Bulletin, **36**, 1357 (1963).

[10] H. Nishiguchi, Y. Nakai, K. Nakamura, K. Ishizu, Y. Deguchi and H. Takaki, *Mol. Phys.*, **9**, 153 (1965); *J. Chem. Phys.*, **40**, 241 (1964).

[11] K. Mukai, private communication.

[12] K. Nakamura, private communication.

of the solvent molecule may release the ion-pair, pulling the metal cation away from the anion radical as well as inducing a more unpaired electron spin on the bulky aromatic ring so as to decrease that on the nitro group. This result is to be contrasted with those with phenoxyls[11] or diphenyl nitric oxide,[13] which are supposed not to be present as ion-pairs in the solution.

The Effect of Temperature Variation.—The nitrogen hyperfine splitting constant increases once below room temperature to a maximum in the temperature range from 0 to −10°C, and then it decreases at a rate of about a hundredth of a gauss per degree.

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13) J. Pannell, *Mol. Phys.*, **7**, 317 (1964).

14) B. M. Wepster, "Progress in Stereochemistry," Vol. 2, Butterworths Scientific Publications, London (1958), p. 100.

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