An Electron Spin Resonance Study of the Anion Radicals of 1-Nitro-2,4,6-triphenylbenzene

M. J. Feighan[1] **and M. T. Jones**[2]

Contribution from the Department of Chemistry, Saint Louis University,
St. Louis, Missouri 63103, and the Department of Chemistry,
University of Missouri, St. Louis, Missouri 63121. *Received February 14, 1970*

Abstract: Two radicals are produced upon the reduction of 1-nitro-2,4,6-triphenylbenzene (NO_2TPB). One radical (A) is short lived ($\tau_{1/2} \sim 12$ sec) and displays a nitrogen hyperfine splitting of 12.56 G. The other (B), which is quite stable, displays an anomalously small nitrogen hyperfine splitting of approximatey 6.7 G. Studies of the electrochemical behavior of NO_2TPB, of the electrolytically and chemically generated free radicals, and of the chemical behavior of radical B have led to the conclusion that radicals A and B are conformers and both are anion radicals of NO_2TPB. The small nitrogen hyperfine splitting observed for radical B is explained as being the result of a weak interaction between the oxygen atoms of the nitro group and the ortho phenyl rings.

The steric influences of substituents on various chemical and physical properties of aromatic nitro compounds have been studied extensively over the past several decades.[3–9] The properties of nitrobenzene systems are very sensitive to groups which enhance resonance by extending the conjugation and to those which induce steric inhibition causing the nitro group to decouple from the ring. With the development of electron spin resonance spectroscopy, experimental studies of nitrobenzene systems were extended to the study of the anion radicals.[10] Several factors contributed to the interest in these compounds. It was found that the aromatic nitro compounds could accept an electron with ease, and the radicals formed appeared to be reasonably stable.[11] Furthermore, the anions were expected to be more highly conjugated than the neutral molecules due to an additional electron in the π system. This increased conjugation implied a greater tendency toward planarity in the radical; therefore, steric inhibition was expected to have more pronounced effects in the anion.

Generally, alkyl substituents were introduced as blocking groups into the nitrobenzene compounds because their effects were predominantly steric rather than electronic. The anion radicals of these compounds were then generated and examined for evidence of steric effects on hyperfine coupling constants. It was found that one alkyl group substituted ortho to the nitro group had little effect on the nitrogen coupling constant.[12] However, two ortho substituents cause a large increase in the nitrogen coupling constant compared to the anion radical of nitrobenzene. Similar behavior was anticipated for the anion radical of 1-nitro-2,4,6-triphenylbenzene (NO_2TPB). As reported in an earlier communication, the chemical reduction of NO_2TPB with sodium or potassium yielded a radical with a nitrogen coupling constant of only 6.7 G.[13] The anomalously small nitrogen splitting led to a multiple spectroscopic study of NO_2TPB, its reduction products, and related compounds. The electron spin resonance studies are described in this paper.

Experimental Procedures

A. **Reagents.** 1-Nitro-2,4,6-triphenylbenzene (NO_2TPB) was prepared by nitration of symmetric triphenylbenzene following the procedure of Vorlander, *et al.*[14] After several recrystallizations from absolute ethanol, the melting point of the product was 142–143°, which is in agreement with the reported value.[14] The three nitrobiphenyl isomers (Aldrich Co.) were purified by recrystallization from absolute ethanol.

The method recommended by Coetzee, *et al.*,[15] was used for the purification of acetonitrile (MeCN) and all necessary precautions were taken to keep the solvent "dry" during use. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were refluxed over sodium–potassium alloy for several days and then distilled from a fresh portion of the metal alloy. The THF and DME were stored on the vacuum line over sodium metal. Upon distillation from the storage container to the reaction vessel, the solvents were again degassed by the use of freeze–pump–thaw methods before the reaction vessel was sealed off from the vacuum line.

B. **Equipment.** Electron spin resonance measurements were made with a Varian V-4502 X-band spectrometer with 100-kHz field modulation, equipped with a multipurpose dual cavity, a Mark II Fieldial magnetic field regulator, a 12-in. electromagnet, and a variable-temperature control unit. The spectra were recorded with a Hewlett-Packard *X–Y* recorder. All reported coupling constants are the average of several upfield and downfield sweeps and also represent the average of high- and low-field splitting. Scan rates were calibrated using the accurately known hyperfine splitting of the tetracyanoethylene (TCNE) anion radical (1.574 G).[16] Coupling constants are reported in gauss and have an estimated accuracy of ±0.02 G.

The half-wave reduction potentials were obtained by cyclic voltammetry and have an estimated reproducibility of ±5 mV. The reduction potentials reported were determined on the first scan after applying the voltage.

A Perkin-Elmer Model 457 and a Cary 14 were employed for infrared and ultraviolet measurements, respectively.

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[1] Abstracted from the Ph.D. dissertation of M. J. Feighan, Saint Louis University, 1969.

[2] To whom correspondence would be addressed at the University of Missouri, St. Louis.

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[8] B. M. Wepster, *Recl. Trav. Chim., Pays-Bas*, **76**, 335 (1957).

[9] B. M. Wepster, *Progr. Stereochem.*, **2**, 99 (1958).

[10] See, for example, E. G. Janzen and J. L. Gerlock, *J. Amer. Chem. Soc.*, **89**, 4902 (1967), and references contained therein.

[11] Y. Nakai, *Bull. Chem. Soc. Jap.*, **39**, 1372 (1966).

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

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[14] D. Vorlander, E. Fischer, and H. Wille, *Chem. Ber.*, **62**, 2836 (1929).

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Generation of Radicals. The anion radicals were produced by both chemical reduction and electrolytic techniques. The chemical reductions were accomplished using standard high-vacuum techniques with one significant modification. The metal mirrors were not produced by the usual technique of distillation of pure metal inserted directly into the reaction vessel. Instead the metal was produced by thermal decomposition of sodium or potassium azide in the reaction vessel while pumping on the vessel. This technique presents a number of advantages. The azides are convenient to store and to introduce into the reaction vessel. They are much safer to work with as they are nonreactive when handled in the atmosphere. One minor problem arose during the decomposition. Small particles of undecomposed azide are sometimes carried into other portions of the reaction vessel. A small plug of glass wool inserted between the area in which the azide was decomposed and the rest of the reaction vessel was found to be sufficient to catch these particles. The metal was then distilled through this plug and once or twice more in the usual manner to produce the metal mirror.

The solvents used in the chemical reductions were THF and DME. Sample concentrations were 10^{-3}–10^{-4} *M*. Several other metal reducing agents were tried with NO_2TPB but except for barium the others were ineffective.[17] Radical formation was also observed from NO_2TPB when the anion radicals of naphthalene and anthracene were employed as reducing agents.

In the *intra muros* electrolytic technique,[18] a potential several tenths of a volt more negative than the peak value measured from the voltammogram was used for the controlled potential in the radical formation. Prior to electrolysis the solutions were degassed for at least 30 min. Unless otherwise stated, the solvent was acetonitrile and all solutions were 0.1 *M* in tetraethylammonium bromide and 2×10^{-3} *M* in nitro compound.

Experimental Results

A. Electrolytic Generation of Radicals. Electrolysis of the phenyl-substituted nitrobenzene compounds at their respective $E_{1/2}$ potentials produced colored solutions with the nitrogen coupling constants listed in Table I. Only one radical species was observed for each compound even when the potential was increased to as large a value as −2.3 V, with the exception of NO_2TPB, which will be discussed below. The anion radicals observed are consistent with one-electron reduction products as given in the literature for the nitrobiphenyls in other solvents systems.[19]

Table I. Electrolytic Reduction of Phenyl-Substituted Nitrobenzene Series[a]

Compound	$-E_{1/2}$, V	a_N, G	Radical color
Nitrobenzene	1.16	10.27	Golden orange
2-Nitrobiphenyl	1.23	9.84	Flesh pink
3-Nitrobiphenyl	1.15	9.91	Yellow-orange
4-Nitrobiphenyl	1.12	9.31	Lavender
NO_2TPB	1.31	12.56 (A) 6.74 (B)	Blue Yellow-purple

[a] Solvent, MeCN; 0.1 *M* TEABr; 10^{-3} *M* nitro compound.

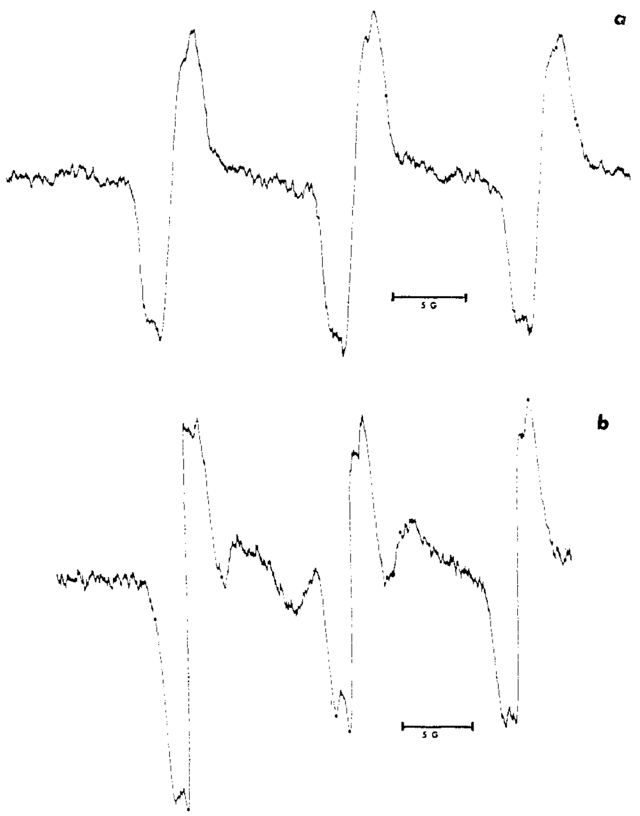

Figure 1. Esr spectra produced by electrolytic reduction of NO_2TPB: (a) radical A, (b) superimposed spectra of radicals A and B.

Application of a voltage of −1.4 V to solutions of NO_2TPB initially yielded a light blue solution which displayed a spectrum of three lines of equal intensity with a splitting constant, attributed to nitrogen, of 12.56 G (Figure 1a). In subsequent discussion, this will be referred to as radical A. After a few minutes of electrolysis, a second spectrum was observed to be superimposed upon the first (Figure 1b). The signal amplitude of the second spectrum (radical B) continued to increase relative to that of radical A as the electrolysis was continued. The nitrogen splitting for radical B was 6.74 G. The color of the solution, initially light blue, turned greenish blue when radical B appeared and finally purple when a high concentration of radical B was attained.

No proton hyperfine structure was observed for either radical under these conditions. However, when small percentages of water were added, the three nitrogen lines of radical A were split into triplets with a 1:2:1 ratio (Figure 2). This hyperfine coupling (1.1 G) is attributed to the meta protons of the central ring. This is in agreement with the values generally observed for meta protons in nitrobenzene systems.[12] No proton hyperfine structure was detected for the B radical.

B. Chemical Reduction. Chemical reduction of NO_2TPB by sodium or potassium in THF or DME yields a solution which is light yellow when dilute and purple when concentrated. It has a spectrum (Figure 3) identical with that observed for radical B which was produced by electrolytic reduction. Table II lists the nitrogen coupling constants (a_N) for this radical prepared in different solvents and with different metals. The size of a_N depends on the concentration of the metal ion and the radical species; therefore, a range of splitting constants is given for a_N. These results represent ten or more different radical reactions of each metal and solvent combination using concentrations of NO_2TPB in the range of 10^{-3}–10^{-4} *M*. A variation of a_N with metal ion concentration is characteristic of ion pairing, and it is noteworthy that the range of a_N is greater for radicals produced by sodium reduction. This reflects

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(17) The metals used were silver amalgam, cadmium amalgam, calcium, zinc, aluminum, and barium.

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

(19) Y. Nakai, K. Kawamura, K. Ishizu, Y. Deguchi, and H. Takari, *Bull. Chem. Soc. Jap.*, 39, 847 (1966).

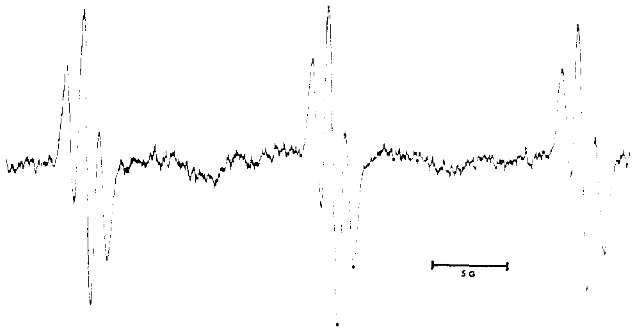

Figure 2. Esr spectrum produced by electrolytic reduction of NO_2TPB in acetonitrile–5% water.

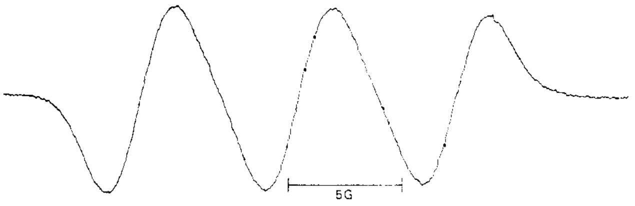

Figure 3. Esr spectrum produced by reduction of NO_2TPB by sodium in THF.

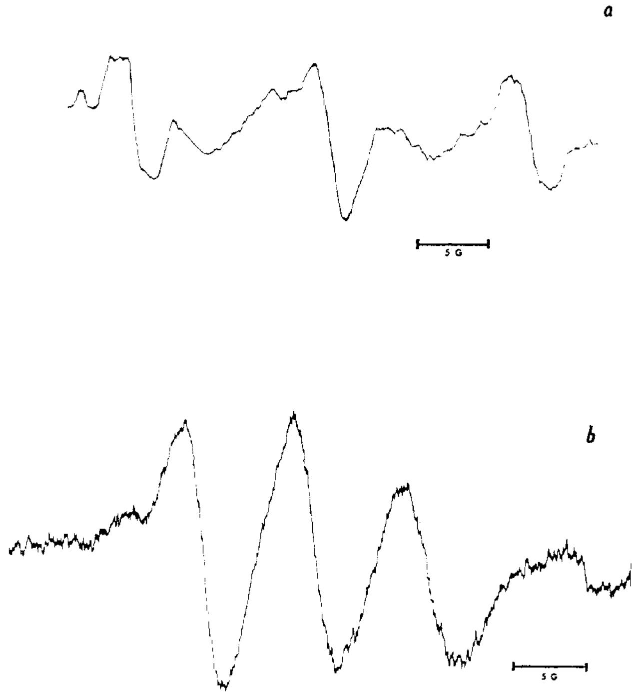

Figure 4. Esr spectra produced by reduction of NO_2TPB with anthracenide: (a) superimposed spectra of radicals A and B immediately after reaction, (b) spectrum several minutes after reaction.

the greater degree of ion pairing found with sodium in comparison to potassium. For large-scale reactions carried out in a nitrogen atmosphere, there was still greater variation with metal concentration. Presumably, this was because of the presence of small amounts of water and other impurities in the solvent which led to increased metal ion concentrations. The a_N observed was as large as 7.0 G.

Table II. Chemical Reduction of NO_2TPB

Metal	Solvent	a_N, G[a]	Range
Na	DME	6.70	6.57–6.83
Na	THF	6.61	6.53–6.64
K	DME	6.72	6.70–6.78
K	THF	6.70	6.66–6.72
Na	MeTHF	7.71	
Na–K alloy	THF	7.13	

[a] The observed coupling constant depends on the concentration of the metal ion; therefore, these values vary with the amount of time in contact with the metal and the initial concentration of the sample. The range is greatest for the Na radical owing to more extensive ion pairing. These values are based on ten or more different radicals in each case.

In the chemical reduction, as in electrolytic generation, no hyperfine structure was resolved. However, the line widths, ~2.90 G (Na) and ~2.69 G (K), are larger than usually found for nitrobenzene anions (~0.3–0.5 G) and most likely result from unresolved splitting.

Radical A was not unambiguously observed when metal reduction techniques were used, but in a few instances early in the reaction a distorted spectrum was recorded for very dilute concentrations of radical species. Nevertheless, it is believed that radical A was formed in *all* chemical reactions as in the electrolytic generation but, because the radical could not be examined in the esr spectrometer until sufficient concentrations had built up (*i.e.*, after a rather long period of time), radical A was usually not observed. This belief is strengthened by the observation of radical A and its subsequent conversion to B when anthracene negative ion was used as the reducing agent as described below.

C. Reduction with Anthracene Anion Radical. The anthracenide anion was prepared by sodium reduction in THF under vacuum. When sufficient concentration of the anthracenide radical was present the metal was sealed off from the reaction vessel, and the anthracenide was allowed to react with NO_2TPB which was behind a breakseal in the reaction vessel. A "brilliant" purple color was observed when the compounds reacted and the sample was examined immediately in the esr cavity. A slightly distorted spectrum of radical A was initially recorded (Figure 4a). The sample was left in the cavity and repetitious scanning showed the spectrum of A decreasing and that of B increasing in signal amplitude. Within 5–10 min the spectrum was predominantly that of radical B with minor distortions due to radical A (Figure 4b). The a_N observed for radical A was ~14 G and for radical B, ~7.6 G.

D. Effect of Sodium Tetraphenylboron upon Radical B. To establish whether radical B was an anion subject to ion pairing effects, sodium tetraphenylboron was added to a DME solution of the radical. Before the addition of sodium tetraphenylboron, a_N was 6.67 G. After the addition of excess sodium ion, *via* a breakseal, a_N had increased to 7.73 G. These observations are consistent with the equilibrium reaction

$$\mathrm{Na^+ + R_B\cdot^- \rightleftarrows (NaR_B)\cdot}$$

in which the equilibrium is shifted to the right by an increase in sodium ion concentration. The ion-paired radical yields a larger nitrogen hyperfine splitting than does the free ion. These results leave little doubt that radical B is an anion.

Table III. Temperature Dependence o a_N for NO$_2$TPB and 4-Nitrobiphenyl

NO$_2$TBP Na, DME		NO$_2$TPB Na, THF		NO$_2$TPB K, DME		NO$_2$TPB K, THF		4-NO$_2$Bip Na, DME	
Temp, °C	a_N, G	Temp, °C	a_N, G	Temp, °C	a_N, G	Temp, °C	a_N, G	Temp, °C	a_N, G
23	6.69	21	6.61	18	6.70	17	6.72	23	10.32
−14	6.63	4	6.57	7	6.68	11	6.71	0	10.25
−36	6.61	−13	6.54	−6	6.66	5	6.70	−20	10.19
−55	6.61	−30	6.53	−22	6.61	−16	6.68	−40	10.10
−63	6.65	−51	6.52	−38	6.60	−47	6.63	−60	10.04
		−68	6.51	−56	6.59	−65	6.63		

E. Temperature Dependence of a_N. The results of the variable-temperature study of radical B of NO$_2$TPB are given in Table III. Since no data are reported in the literature for the chemical reduction of *p*-nitrobiphenyl, a variable-temperature study was conducted on the anion radical of this compound also. In comparison, temperature variation is seen to have a greater effect on a_N for *p*-nitrobiphenyl than for the B radical of NO$_2$TPB. However, in both cases a_N decreases as the temperature is lowered. These trends are consistent with the results observed by Ling and Gendell with the nitrobenzene anion radical[20] and further support the idea that radical B is an anion.

Attempts were made to measure the variations in a_N for radical A when this species was generated in concentrated solutions of the neutral NO$_2$TPB, by allowing the solution to come into contact with the metal. Owing to the superimposed spectra, accurate measurements were not possible; however, a decrease of 1 G was estimated for a_N as the temperature was lowered from room temperature to −60°. This change is greater than the variation in a_N for radical B by a factor of 10.

F. Lifetimes of Radicals A and B. The half-life of the electrolytically generated radical A, based on the decay of its esr signal amplitude from the time of turning off the electrolysis, is approximately 12 sec. On the other hand, radical B proved to be extremely stable.[21] After the electrolysis was discontinued, the signal amplitude for radical B increased slightly even beyond the time that all of radical A had decayed. The following three factors are most likely responsible for these observations. (1) Radical A was converted into radical B. (2) The overlap of the spectra was eliminated by the decay of radical A, thus giving the true signal amplitude of radical B.[22] (3) Diffusion of radical B out of the esr cavity would reduce the rate of electron transfer between the radical and its parent and the rate of spin–spin exchange between radicals. This, in turn, would produce a narrowing of the spectral line width and an increase in signal amplitude. This effect would be expected to continue past the time that all of radical A had decayed.

G. Oxidation of Radical B. As an aid in identifying radical B, it was of interest to establish the identity of its one-electron oxidation product. Two different oxidants were used; molecular oxygen and tetracyanoquinodimethane (TCNQ). The various species present were monitored by their electronic spectra. Neutral NO$_2$TPB has a single absorption peak at 244 µm. Radical B in THF shows a strong peak in the visible region, ~375 µm, and a weak peak at ~520 µm. These latter values were measured in parallel with the esr spectrum.

Consider the following experiment. A reaction vessel was prepared so that both the esr and the electronic spectra could be monitored. Neutral NO$_2$TPB was allowed to react with a sodium metal mirror. As the radical concentration increased, the intensity of the peaks at 375 and 520 µm increased and the neutral peak at 244 µm decreased. The reaction was allowed to continue until the intensity of the peak at 244 µm had decreased to approximately 50% of its original value. The sample tube was then opened to the air. The brownish purple of the radical immediately turned yellow. The visible and uv regions were scanned after a few minutes of exposure to the air. The peaks at 375 and 520 µm had disappeared and the peak at 244 µm had increased to ~85% of its initial value. No other peaks could be observed in the visible or uv range. No esr signal was detected after exposure to the air.

This experiment strongly suggests that the result of oxidation of radical B by molecular oxygen is neutral NO$_2$TPB. It leaves open one question, however. Did the oxidation of radical B to neutral NO$_2$TPB involve just the transfer of an electron from radical B to the molecular oxygen, or was there also a transfer of oxygen to radical B? The reason for the latter concern is that it is conceivable that radical B is the anion radical of 1-nitroso-2,4,6-triphenylbenzene (NOTPB) and that the reaction with oxygen can be represented as

$$(\mathrm{NOTPB})^- + \mathrm{O_2} \longrightarrow \mathrm{NO_2TPB} + {}^1\!/_2\mathrm{O_2}^{2-}$$

This latter question appears to be answered by the results of the experiment in which TCNQ was allowed to react with radical B. In this experiment, TCNQ, which was stored behind a breakseal, was introduced under high vacuum into a THF solution of radical B. Again the esr and electronic spectra were monitored. This time the esr spectrum obtained was that of the TCNQ anion radical.[16] The behavior of the electronic spectrum was identical with that observed when oxygen was used. This latter experiment supports the conclusion that radical B and the neutral NO$_2$TPB are related to each other by the absence or presence of a single electron.[23]

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(20) C. Ling and J. Gendell, *J. Chem. Phys.*, **47**, 3475 (1967); see also M. T. Jones and D. E. Zeller, *ibid.*, **48**, 3341 (1968).

(21) This observation was not unexpected, since radical B, produced by chemical reduction, is stable for periods of months as long as the radical is not in direct contact with the metal. Continued contact with the metal yields decay products which are not paramagnetic.

(22) As can be observed from Figure 1, there is a spectral line of radical A fairly free from overlap with the spectrum of radical B. However, the reverse is not true. Thus, changes in concentration of radical A lead to changes in signal amplitude for spectral lines due predominately to radical B.

(23) One other possibility remains, *i.e.*, that radical B is the trianion of NO$_2$TPB Calculations of the expected esr spectrum are not in agreement with such an assignment. It should be recognized, however, that such calculations are subject to considerable uncertainty.

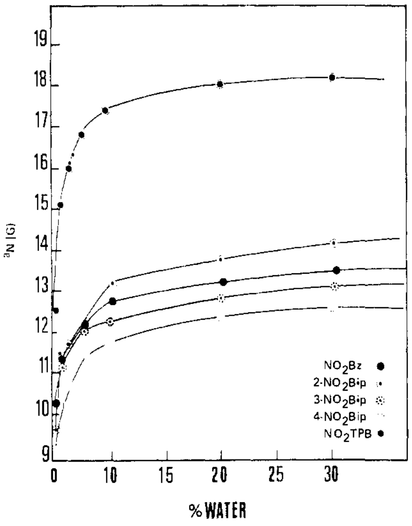

Figure 5. Dependence of the nitrogen hyperfine splitting on solvent composition (water–acetonitrile system).

H. Effect of Protic Solvent. The addition of water to acetonitrite solutions of the electrolytically generated anion radicals results in increased nitrogen hyperfine splittings. The results for the various compounds are shown in Figure 5 and Table IV (also see ref 24). As is obvious, a_N increased by 43% with the addition of 20% water for radical A.

Table IV. Nitrogen Coupling Constants[a] as a Function of Solvent Concentration. MeCN–H_2O System

Water, %	NO_2Bz	2-NO_2-Bip	3-NO_2-Bip	4-NO_2-Bip	NO_2TBP
0	10.27[b]	9.83	9.91	9.31	12.56 6.74
1	11.23	11.32	11.10	10.16	15.20 7.56
2		11.81	11.43	10.70	16.08
5	12.21	12.10	12.05	11.37	16.95
10	12.81[c]	13.15	12.49	11.85	17.51
20	13.17[d]	13.79	12.89	12.29	18.02
30	13.41	14.17	13.05	12.61	18.23

[a] Coupling constant in gauss. [b] 10.48 G, ref 24. [c] 12.78 G, ref 24. [d] 13.20 G, ref 24.

Unfortunately, it was not possible to study radical B over such a wide range. Both radicals A and B decomposed rapidly in the presence of water, and it was only possible to observe radical B in solutions containing 2% or less water. Within this range, however, the relative changes in a_N were much smaller for radical B than for radical A.

I. Polarographic and Cyclic Data. When tetraethylammonium bromide (TEABr) and tetraethylammonium perchlorate (TEAP) were used as electrolytes, NO_2TPB exhibited two reduction waves with half-wave potentials at −1.31 and −1.68 V. The first wave appeared to be a reversible one-electron reduction. To estimate the number of electrons involved in each reduction step, the diffusion currents (i_d) were measured. For the polarogram of NO_2TPB it was difficult to accurately measure i_d because a maximum occurred in the region between the two reduction peaks. However, as a close approximation, i_d for the second wave was twice as large as for the first wave, indicating a two-electron process at the more negative potential.

Kitagawa, *et al.*, have shown that the presence of metal ions has a significant effect on the peak potentials and coupling constants.[25] Since one of the major differences in the two reduction methods used in this study was the presence of the metal cations in the chemical method, it was of interest to examine the effect of using a sodium salt as the supporting electrolyte. When 0.1 *M* sodium perchlorate was employed, the first peak was slightly shifted while the second peak was shifted markedly to a more anodic potential so that it coincided with the first peak. Moreover, measurements of i_d showed that this peak was three times the diffusion current of the first reduction peak in the normal polarogram when run under the same experimental conditions. This would indicate a three-electron step for the sodium perchlorate case. These results agree with the observation of Kitagawa. However, no radical color was observed, nor was a radical detected by *in situ* electrolysis in the esr cavity under conditions identical with those used when radicals were observed with tetraalkylammonium salts.

Discussion

A. Radical A. Sufficient evidence has been obtained from this study to safely assign radical A as an anion radical of NO_2TPB. This identification is based on the electrolytic generation of this radical at a potential which yields a one-electron reversible wave by cyclic voltammetry and polarography. Radical A is always formed at least simultaneously with, if not preceding, the formation of radical B. Finally, the resolution of the hyperfine structure attributed to the meta protons of the central ring when small percentages of water were added to the solvent increases the creditability of this assignment.[26]

Geske and coworkers[12,27] have shown that the introduction of substituent groups into the ortho positions of nitrobenzene causes an increase in a_N. These changes are attributed to the twisting of the nitro group away from coplanarity with the ring, with a consequent localization of charge on the nitro group. A nitrogen coupling constant of 12.56 G for radical A is smaller than anticipated when compared to the alkyl analogs such

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(24) P. Ludwig, T. Layloff, and R. N. Adams, *J. Amer. Chem. Soc.*, **86**, 4568 (1964).

(25) T. Kitagawa, T. Layloff, and R. N. Adams, *Anal. Chem.*, **36**, 925 (1964).

(26) It has been suggested that radical A might be the anion radical of the isomer of NO_2TPB obtained when the nitro group is substituted in the para position of one of the substituent phenyl rings. Thus, the radical would be a substituted 4-nitrobiphenyl anion. This possibility appears unlikely for several reasons. (1) The concentration of the material to be reduced is ~2 × 10^{-3} *M*. Even a 10% contamination with the substituted 4-nitrobiphenyl would only yield a solution approximately 2 × 10^{-4} *M*. In general, this would be too low a concentration of starting material for an esr electrolytic reduction experiment. (2) All extended reductions (chemical or electrochemical) yield only radical B and not a mixture of radical A and B as one might expect if both radicals A and B were derived from different isomers of NO_2TPB. There is no reason to expect the anion radical of a substituted 4-nitrobiphenyl to be less stable than those of the other nitrobiphenyl anion radicals studied. (3) The values of the hyperfine splittings for radical A are not those that one would expect from a substituted 4-nitrobiphenyl anion radical. Calculations of the expected hyperfine splittings for such a radical suggest that one should observe a nitrogen hyperfine splitting of ~9 G and two sets of two equivalent protons with hyperfine splitting of ~1 and ~3 G, arising from the meta and ortho protons of the central ring, respectively.

(27) D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125 (1967).

as nitromesitylene (a_N = 17.8 G) or tri-*tert*-butylnitrobenzene (a_N = 18.8 G).[12] The nitro group may indeed be slightly more coplanar with the central ring than it is in hindered alkyl compounds since some of the steric strain can be relieved by the twisting of the ortho phenyl substituents. Acting in opposition will be the tendency for resonance interaction with the central ring. An estimate of the electron-withdrawing nature of the phenyl substituents can be made by considering the decrease in a_N for the para and ortho nitrobiphenyl compounds compared to nitrobenzene. These differences, 0.96 G for the para and 0.88 G for the two ortho substituents, when added to the observed value of 12.56 G for NO_2TPB yield a nitrogen coupling constant of 14.4 G. This is still 3–4 G smaller than the expected range and probably is indicative of more coplanarity than in the alkyl-substituted compounds.[28]

B. Radical B. The assignment of the identity of radical B has not proven to be as straightforward as that for radical A. Two distinct possibilities exist. (1) Radicals A and B are conformational isomers. (2) Radical B is the anion radical of 1-nitroso-2,4,6-triphenylbenzene.

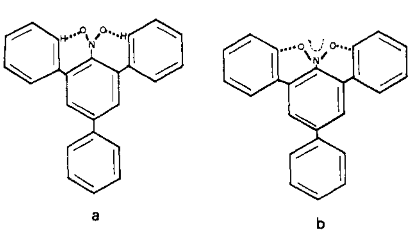
Of the two possibilities the first is best supported by the evidence. We have looked carefully for positive evidence to support the latter assignment and have found nothing which gives it substantial support. Radical B is produced under conditions which might lead to further reduction and the production of NOTPB.[29] But yet, this has never been a problem with nitrobenzene itself.[20] The only other evidence suggesting that radical B might be the anion radical of NOTPB can be derived from a comparison of the nitrogen hyperfine splittings for the anion radicals of nitrobenzene and nitrosobenzene. For two different solvent systems, a_N for the nitrosobenzene anion radical is smaller by 2.5–3.5 G than that observed for nitrobenzene (see Table V). It might also be pointed out that collective experience to date has shown that nitroso radicals are less stable than the corresponding nitro radicals. Of course, radical B could be the exception.

Table V. Comparison of the Nitrogen Hyperfine Splitting Constants for the Anion Radicals of Nitrosobenzene and Nitrobenzene

Anion radical of	$a_N{}^a$	$a_N{}^b$
Nitrosobenzene	7.97[c]	10.10[d]
Nitrobenzene	11.46[c]	12.5[e]

[a] Liquid NH_3, −78°. [b] EtOH, 23°. [c] D. H. Levy and R. J. Meyers, *J. Chem. Phys.*, **42**, 3731 (1965). [d] G. A. Russell and E. J. Geels, *J. Amer. Chem. Soc.*, **87**, 122 (1965). [e] Estimated from data given in ref 24.

The evidence supporting the assignment of radical B as an anion radical of NO_2TPB is as follows. Oxidation of radical B by both O_2 and TCNQ yields a product whose electronic spectrum is identical with that of NO_2TPB. The electronic spectra for nitrobenzene and nitrosobenzene are different.[9,30] We assume that likewise they are different for NO_2TPB and NOTPB.


a

b

Figure 6. Possible modes of intramolecular interaction for radical B.

If this assumption is correct then the only way that oxidation of NOTPB by TCNQ could yield NO_2TPB would be for the following reaction to take place.

$$\text{NOTPB} + Na_2O \longrightarrow NO_2\text{TPB} + 2\text{Na}$$

This reaction seems highly improbable when one considers the very limited solubility of ionic compounds such as Na_2O in ether-type solvents.

C. Structural Relationship between Radicals A and B. If, as the data suggest, radicals A and B are both anion radicals of NO_2TPB, how are they related to each other? Certainly radical A has the same conformation as the neutral NO_2TPB.

In previously reported McLachlan-type calculations of the spin density and the hyperfine constants for radical B, Jones and Feighan[13] found the best fit to the experimental results by assuming that there are weak interactions between the ortho phenyl rings and the oxygen atoms of the nitro group. These interactions could be one of two types: (a) weak hydrogen bonds between the nitro-group oxygen and the protons of the ortho phenyl rings; (b) orbital overlap between the p orbitals centered on the oxygen atoms of the nitro group and the π system of the ortho phenyl rings. If the oxygens are weakly bonded to the hydrogens of the ortho phenyl rings, a seven-membered ring structure (Figure 6a) would result which could be relieved of strain by various small angles of twist by the substituents involved. On the other hand, orbital overlap between the p orbitals of the oxygens and the π system of the ortho phenyl substituents would result in the usually more favored six-membered ring (Figure 6b). In both, the radical structure would be locked, and there is a path for the transfer of spin density away from the nitro group. This would account for the extensive delocalization of charge over the whole molecule, which is reflected in the small nitrogen coupling constant. Since the model used in the calculations is the same for either case of intramolecular association, it is not possible on the basis of calculations to rule out either possibility.

Another possibility exists for the structure of radical B, namely, that the nitro group undergoes a rehybridization, resulting in a somewhat decreased pyramidal shape.[31] In addition, this might or might not require weak interactions between the nitro-group oxygens and the ortho phenyl rings as before. How this latter possibility might be checked is an open question at the moment.

It has been suggested by one of the referees that a comparison of the optical spectrum of radicals A and B might be helpful in determining whether radicals of A and B are two completely different molecules or different conformers of NO_2TPB. We did not have ac-

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(28) Detailed MO calculations for radicals A and B and the anion radicals of the three isomers of nitrobiphenyl are underway to answer this question and will be published at a later date.

(29) For example, the following reaction could take place: $NO_2\text{TPB} + 3\text{Na} = \text{NOTPB}\cdot^- + \text{Na}^+ + Na_2O$.

(30) J. H. Boyer, U. Toggweiler, and G. A. Stoner, *J. Amer. Chem. Soc.*, **79**, 1748 (1957).

(31) J. M. Gross and M. C. R. Symons, *J. Chem. Soc. A*, 451 (1966).

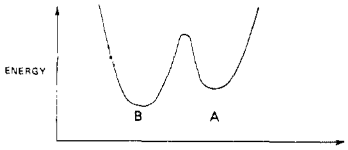

Figure 7. Potential energy surface for the relationship of radical A to radical B.

cess to an optical cell which would have allowed us to measure the optical spectrum during the electrolytic reduction of NO_2TPB and hence the spectrum of radical A. It would be of interest to know how the optical spectra of radicals A and B compare. However, it should be pointed out that the interpretation of such an experiment would be unambiguous only in the event that radicals A and B yield identical or very similar optical spectra. In the event that the optical spectra for radicals A and B differ, it would be uncertain as to whether they differ because radicals A and B possess different molecular structures or because of the postulated interactions between the nitro-group oxygens and ortho phenyl rings which would be expected to modify the optical spectrum.

D. Discussion of the Experimental Evidence in Terms of the Conformation Model. One would expect that the potential energy surface describing the relationship of radical A to radical B to be of the type shown in Figure 7. From our experimental results estimates of the height of the energy barrier between radical A and B and the minimum depth of the potential of radical B below radical A can be made. Under the assumption that the process of the conversion of radical A to radical B is similar to the hindered rotation problems studies by nmr,[32] one can make an estimate of the energy barrier between radical A and B using the following equation

$$\frac{1}{\tau} = A \exp(-\Delta E^*/kT)$$

where $\tau = 12$ sec, $A = 10^{14}$/sec, and $T = 300$°K; thus $\Delta E^* = 21$ kcal. The minimum depth of the potential energy well for radical B can be estimated from the Boltzman distribution function and the fact that at 300°K one observes only radical B. If the relative populations of radical A to radical B were greater than approximately 1:100, one would expect to observe both radical species at thermal equilibrium. Since one does not, their ratio must be less than 0.01 and the energy between the two states greater than $\sim$2.5–3.0 kcal.

The rate of interconversion between radicals A and B is rather slow and in the opinion of some might better be interpreted as more characteristic of a process involving some degree of bond breaking rather than a simple conformational change. In fact, this may be rather close to the truth. While many conformational changes occur with activation energies considerably lower than the 21 kcal observed here, it is true that rotations about bonds with character intermediate between double and single yield activation energies of this same order (for example, *N*,*N*-dimethylnitrosoamine).[33] In the case of the nitrosoamine, the partial double bond character of the nitrogen–nitrogen bond presents a rather large activation energy. The same type of situation may in fact prevail for radical A, wherein it takes a concerted change on the part of the nitro group and perhaps one or both of the phenyl rings ortho to it to accomplish the changes which result in the formation of radical B.

At this point it might be helpful to summarize what we believe the sequence of events to be from the point at which NO_2TPB is initially reduced until radical B is formed. First, we believe that there is probably only one type of conformer of the neutral NO_2TPB. Thus, its reduction always leads to a single radical species, namely radical A. The conformation which yields the lowest energy for the neutral NO_2TPB is not the conformation which yields the lowest energy for the anion radical. Thus radical A is converted into radical B by changes in the relative orientations of the nitro group and one or both of the phenyl rings ortho to the nitro group. The factor which results in the stabilization of radical B is that the rather large amount of electron density usually found on the nitro group of a "normal" nitrobenzene anion radical can partially leak off onto the ortho phenyl rings. Oxidation of radical B, of course, removes this large concentration of electron density from the nitro group and hence the necessity for electronic interaction between the nitro group and the ortho phenyl rings. Thus the neutral compound returns to the original structure of NO_2TPB. Much of what is said in this paragraph cannot be substantiated beyond doubt but is put forth as a "working" hypothesis. It does help explain the apparent different reactivities of radicals A and B toward water, namely, that the effect of water upon the relative intensities of the esr spectra of radicals A and B described earlier in the text arises because of a competition between two processes. One process results in the conversion of radical A to radical B. The other results in the destruction of radical A. The greater the concentration of water, the larger the rate of destruction of radical A and the smaller the amount of radical A converted to radical B. Thus, the observation reported earlier does not represent the difference in reactivity of radical A and B toward water but is a consequence of two simultaneous, competitive reactions.

Finally, it should be noted that the effects upon the nitrogen hyperfine splitting constant of radicals A and B of temperature variation, of ion pairing, and of the presence of water in the solvent are all consistent with the proposed structure for the radicals. One would not expect the nitrogen hyperfine splitting for radical B to be as sensitive as radical A to changes in these variables if there were already a fairly strong intramolecular interaction ($\sim$2.5–3.0 kcal) between the nitro group and the ortho phenyl rings.

Acknowledgments. The support of Saint Louis University through its purchase of the esr spectrometer is acknowledged, as is the partial support of this research by the NSF through Grants No. GP-7011 and GP-15619.

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(32) See, for example, J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 13.

(33) C. E. Looney, W. D. Phillips, and E. L. Reilly, *J. Amer. Chem. Soc.*, **79**, 6136 (1957).