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# Hyperfine Couplings of *N*-Alkoxy-*N*-polynitrophenylaminyl Radicals Determined by ENDOR and TRIPLE Resonance Spectroscopy

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**Lead tetraacetate one-electron oxidation of nine different *N*-alkoxy-2,6-dinitroanilines substituted with trifluoromethyl, methyl and nitro groups in position 4 yielded aminyl radicals for which hyperfine couplings were measured by ENDOR and TRIPLE resonance spectroscopy. The optimum temperature range for proton ENDOR and general TRIPLE resonance measurements of aminyl radicals was 210–250 K and for nitrogen ENDOR 260 K in toluene. Further lowering for the temperature rapidly decreased the EPR intensity. The concentration of the sample and the amount of oxidant were optimized for obtaining ENDOR spectra. The relative signs of the hyperfine couplings of nitrogens, fluorines and protons were determined in the basis of general TRIPLE resonance experiments. The oxidation of *N*-methoxy-*N*-2,6-dinitrophenylamine and *N*-ethoxy-*N*-2,6-dinitrophenylamine with lead tetraacetate produced first the aminyl radical of the respective 2,6-dinitro compound at low temperature (below 260 K) and very soon afterwards the aminyl radical of the respective 2,4,6-trinitro compound, by a route in which hydrogen has to be removed from the system. Rotational correlation times were estimated for *N*-methoxy- and *N*-ethoxy-*N*-2,4,6-trinitrophenylaminyl radicals. Nitroxyl radicals were detected only under conditions where oxygen was present in the solvent.**

KEY WORDS EPR; ENDOR; TRIPLE; aminyl radicals

## INTRODUCTION

Aminyl radicals have structures which could permit stabilization by the capto-dative effect where, for example, the alkoxy group acts as a donor and the nitrophenyl group as an acceptor.[1–4] Aminyl radicals are formed by oxidation reactions, and the neutral radical can be prepared in several ways via hydrogen elimination reactions.[1,5–13] In this study, radicals were prepared with lead tetraacetate. In addition to aminyl formation, nitroanilines may undergo certain side-reactions in the oxidation process. The most prominent reaction is nitro group substitution. When 2,6-dinitrophenyl and lead tetraacetate are used as reactants, there is a tendency for the 2,6-dinitrophenyl to accept an additional nitro group in position 4.[2] Since no other nitrogen-containing compound is present, and there are no other reagents to produce it, the extra nitro group must come from the 2,6-dinitrophenyl itself.[2] In addition, $^{14}N$–$^{15}N$ exchange at an aromatic nitro group during nitration with acetyl nitrate has been detected in polynitrophenols.[14]

Isotropic hyperfine coupling constants (hfcs) of aminyl radicals have been determined earlier by simulation calculations on EPR spectra.[1–4] The main aim of this study was, through performing ENDOR experiments, to be able to measure the hfcs more precisely and assign them unambiguously, in addition to separating superposed radicals. The purpose was also to examine in position 4 the nitration reaction with use of a 2,6-dinitro compound and the product, 2,4,6-trinitro compound, and the neutral radicals prepared from each of them. Despite the small $g_N$-value of nitrogen, we were able to measure the small nitrogen hfcs of nitro groups from the high-field feature. Detection by ENDOR of $^{14}N$ in nitro groups attached to an aryl has been successful in only a few cases.[15–17] Hfcs of fluorine have been measured by ENDOR routinely, despite the smaller anisotropy and non-quadrupolar nature of $^{19}F$

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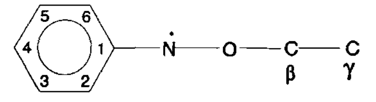
nuclei.[18–24] This is the first study in which aminyl radicals have been measured by ENDOR and TRIPLE resonance spectroscopy.



## EXPERIMENTAL

### Spectra

EPR, ENDOR and TRIPLE spectra were recorded on a Bruker ER 200 D-SRC spectrometer with a Varian E-12 magnet, a Bruker ER 033 M FF-lock and a Bruker ER4111VT variable-temperature unit (accuracy ±5 °C). *g*-Values were measured with a Varian E-9 EPR spectrometer connected to a TR 5211 microwave counter and a Varian gaussmeter, both interfaced with a personal computer.[25,26] In the ENDOR experiments, hfcs of nitrogen were recorded at temperatures 10–30 K higher than for proton and fluorine because the intensity improved dramatically. This is in accordance with earlier theory and findings.[27]

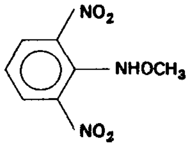
### Compounds

Amines were prepared by known methods.[4,28,29] High-vacuum samples were pumped to $10^{-6}$ mmHg using liquid nitrogen in the freeze–pump–thaw cycles. Oxidation with lead tetraacetate, which was placed in separate glass tubes in a high vacuum cuvette, was carried out after pumping at low temperature and occurred to varying extents depending on the condition of the lead tetraacetate, which has the desired effect only when properly prepared. After recrystallization from acetic acid, the lead tetraacetate must be dried at room temperature. At first the colour is grey, but in the course of time it turns brownish owing to some decomposition. The best results were obtained when the colour of the lead tetraacetate was light brown. Some amines (e.g. *N*-methoxy-*N*-2,4,6-trinitrophenylamine) react rapidly with oxygen to yield the corresponding nitroxide. To prevent this reaction, the reactants and solvent were mixed at low temperature (200 K). The lifetime of the aminyl radical was then longer.

## RESULTS AND DISCUSSION

Systematic EPR studies of substituent effects, assuming a kind of additivity relationship for the substituents, has produced fairly reliable information about hfcs of aminyl radicals.[1–4] ENDOR spectroscopy should provide additional information about the reliability of the previous simulations of EPR spectra, about hfcs and the influence of different donors and acceptors on the density distribution of unpaired electrons.

In this study we prepared and measured aminyl radicals generated from amines, with the molecular structures shown.



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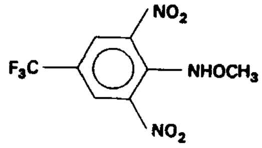

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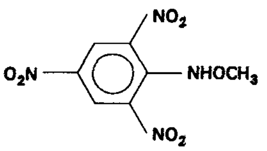

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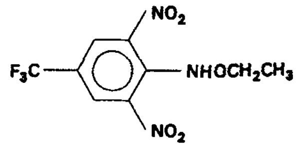

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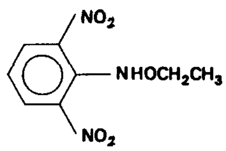

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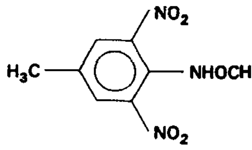

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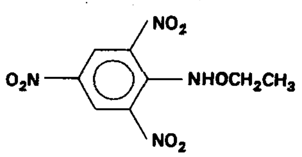

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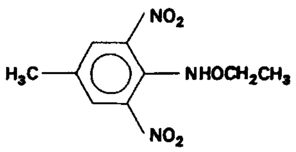

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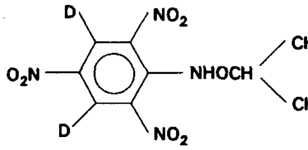

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### Oxidation reactions of *N*-alkoxy-*N*-2,6-dinitrophenylamines and *N*-alkoxy-*N*-2,4,6-trinitrophenylamines to give aminyl radicals

**Compounds 1 and 3, 4-unsubstituted (proton at position 4) and Compounds 2, 4 and 5, 4-nitro groups.** *N*-Methoxy-*N*-dinitrophenylamine (**1**) is rapidly substituted with an additional nitro group at the *para*-position 4 and the EPR spectrum of the *N*-methoxy-*N*-2,4,6-trinitrophenylaminyl radical (**2**˙, a neutral radical) is usually measured instead of **1**˙. Thus, in EPR, Stanciuc *et al.*[2] recorded the hfcs of **2**˙ from both **1** and **2** when these were oxidized with lead tetraacetate. In our ENDOR spectra, by contrast, the hfcs differed for the samples prepared from **1** and **2**, as can be seen from Table 1, even though the EPR spectrum of **1**˙ seemed to be heavily superposed by radical **2**˙.

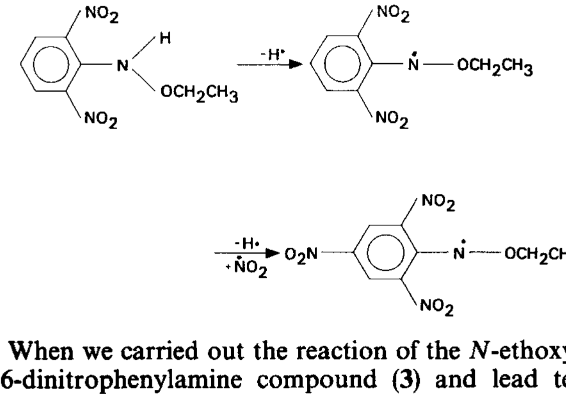
The reason why the EPR spectra of species **2**˙ from **1** and **2** were the same, whereas the ENDOR spectra of **1**˙ and **2**˙ were slightly different, may be that the EPR transition of the dinitro compound is more easily saturated by the microwave field than that of the trinitro compound. The samples we prepared from the trinitro compound gave a strong EPR signal immediately. The

**Table 1. Hfcs of aminyl radicals determined by ENDOR in toluene (in MHz; error ±0.05 MHz)**

| | | Position | | | | | |
|---|---|---|---|---|---|---|---|
| Reactant | $T$ (K) | 2,6$^a$ | 3,5($m$) | 4 | N$^\bullet$ | $\beta$ | $\gamma$ |
| **1** | 240 | 2.0$^b$ | −4.28 | ±14.90 (H) | 28.16 | −7.37 | |
| **2** | 210 | 2.24$^c$ | −4.43 | 3.36$^c$ (N) | 26.90$^c$ | −9.86 | |
| **3** | 230 | 2.28$^d$ | −4.16 | ±14.05 (H) | 28.25$^d$ | −7.44 | 0.31 |
| **4** | 245 | 2.21 | −4.45 | 3.29$^c$ (N) | 26.63$^c$ | −8.58 | 0.45 |
| **5** | 240 | 2.37 | −0.68 (D) | 3.35 (N) | 26.66$^c$ | −7.29 | 0.47 |
| **6** | 250 | 2.40 | −4.40 | −15.39 ($CF_3$) | 27.77 | −9.69 | |
| **7** | 240 | 2.06 | −4.34 | −15.24 ($CF_3$) | 27.83 | −8.46 | 0.39 |
| **8** | 230 | 2.85 | −4.14 | −16.27 ($CH_3$) | 28.37 | −8.19 | |
| **9** | 230 | 2.54 | −4.15 | −15.99 ($CH_3$) | 28.51 | −7.22 | 0.34 |

[a] Measured at 250 K.
[b] Uncertainty of ±0.3.
[c] From EPR iteration/simulation.
[d] Measured at 260 K.

weaker signal intensity for the samples prepared from the dinitro compound showed that a parallel chemical reaction was taking place in the sample. Thus the easier saturation of the dinitro compound allowed ENDOR transitions belonging to this species to be picked up, even though the trinitro compound was dominating the EPR spectrum. For the first time we were able to record the EPR and ENDOR spectra of the dinitro compound in this system. This could be confirmed straightforwardly by the proton ENDOR signal of position 4. From this we postulate that, in oxidation with lead tetraacetate, as with silver oxide,[4] the radical **1**$^\bullet$ appears first. Disregarding the large structural change at the *para*-position 4, where on substitution, the proton coupling of 14.9 MHz changes to the nitrogen coupling of 3.36 MHz, the main difference in the ENDOR spectra of **1**$^\bullet$ and **2**$^\bullet$ appears in the hfc of protons at $\beta$-positions, which changes from −7.37 to −9.86 MHz. The proton hfc of the *meta*-position changes from −4.28 to −4.43 MHz. Since the radical **1**$^\bullet$ had only a very short lifetime, the ENDOR spectrum at 250 K showed the hfc of the proton at the *para*-position for only about 20 min. The chemical reaction occurring at position 4 was detected from the decay of the *para*-proton signal and, after the ENDOR experiment, from the EPR spectrum. The following equation indicates the possible course of the chemical reactions. There is also a possibility of a reversible reaction between two neutral dinitroamine molecules where a mononitro and a trinitro compound are formed. It is not excluded that this kind of reaction occurs with two dinitroaminyl radicals.



When we carried out the reaction of the *N*-ethoxy-*N*-2,6-dinitrophenylamine compound (**3**) and lead tetraacetate at lower temperature, 200–260 K, we were able to record the EPR spectrum of the 2,6-dinitro radical **3**$^\bullet$. This is shown in Fig. 1, together with the EPR spectrum simulated from ENDOR defined hfcs. In the ENDOR spectrum of **3**$^\bullet$ we found a situation more or less analogous to that for **1**$^\bullet$. When the sample of **3**$^\bullet$ was kept at lower temperature until the following day, the EPR spectrum of **4**$^\bullet$ was measured in the sample, because of the nitro group ($NO_2$) substitution. The rate of the reaction was clearly slower for **3**$^\bullet$ than for **1**$^\bullet$. At temperatures above 260 K the reaction occurred so fast that the first stage (2.6-dinitro radical) was no longer distinguishable after a few minutes.

Although the EPR spectrum of the *N*-isoproxy-*N*-2,4, 6-trinitro-3,5-[$^2H_2$]phenylaminyl radical, **5**$^\bullet$, appeared to be unresolved owing to the smaller hfc of deuterium, the ENDOR and general TRIPLE resonance spectra could both be measured. The hfc of the aminyl nitrogen was not found, however, and its value is based on an EPR simulation. This is characteristic of all the trinitro compounds, as can be seen from Table 1, where the hfcs are collected. The absence of the ENDOR feature of the aminyl nitrogen might be due to the large anisotropy of the nitrogen hfc in trinitro compounds.

The nitrogen hfc of the two nitro groups of *m*-dinitrobenzene is 13.1 MHz.[14] After the alkoxyaminyl group has been attached to the *ortho*-position (between) to the two nitro groups of *m*-dinitrobenzene, the hfc decreases from 13.1 MHz for the unsubstituted *m*-dinitrobenzene to 2.0–2.9 MHz for **1**$^\bullet$ or **3**$^\bullet$. Comparison of the hfcs of *m*-dinitrobenzene and *N*-alkoxy-*N*-2,6-dinitrophenylaminyl radicals **1**$^\bullet$ and **3**$^\bullet$ showed the spin

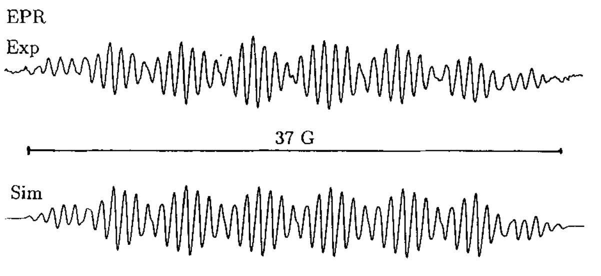


Figure 1. EPR (above) and simulated (below) spectra of *N*-ethoxy-*N*-2,6-dinitrophenylaminyl radical (**3**$^\bullet$) generated by oxidation with lead tetraacetate at 250 K.

density of the nitro group nitrogen to be reduced by a factor of 0.15–0.22 in the aminyl radicals. In these aminyl radicals, where the alkoxy group functioned as a donor group, the hfc of the aminyl nitrogen varied by only 1.9 MHz due to different substituents in position 4. Therefore, the aminyl nitrogen itself has the most prominent effect on the polynitrophenyl ring, which also can be seen from the large hfc.

Comparison of the EPR spectra of 2,6-dinitrophenylaminyl and 2,4,6-trinitrophenylaminyl radicals suggests that, in the case of the dinitro compound, a substitution reaction is occurring by which an extra nitro group is introduced into position 4. Although no exact explanation has been offered,[2] the extra group could come from another, decomposing 2,6-dinitro-substituted molecule.

**Compounds 6 and 7, 4-trifluoromethyl groups.** The ENDOR and general TRIPLE resonance spectra of the *N*-ethoxy-*N*-2,6-dinitro-4-trifluoromethylphenylaminyl radical (**7**$^\bullet$) are a good example of spectra from which it was possible to measure the hfcs of all magnetic nuclei in the molecule from one spectrum (Fig. 2). Using a general TRIPLE resonance experiment, we were able to determine the relative signs of hfcs of protons and those of nitrogens and fluorine. If we assume a positive coupling for the aminyl nitrogen, the sign of nitrogen in the nitro group will also be positive. Fluorine in the trifluoromethyl group in *para*-position 4 is then of negative sign; the *meta*-protons in positions 3 and 5 and the methylene protons ($\beta$-position) in the ethoxyl group are of negative sign, while the methyl protons ($\gamma$-position) in the ethoxyl group are of positive sign. This reasoning could be carried out at once when all the features of all the magnetic nuclei were measured from one TRIPLE resonance spectrum compared with one ENDOR spectrum with the same parameter set. The unpaired electron distribution in these aminyl radicals thus extends from the trifluoromethyl group in position 4, over the aminyl nitrogen and oxyl oxygen, to the methylene carbon as a kind of conjugation. Hfcs of the rest of the molecule seem to arise by spin polarization.

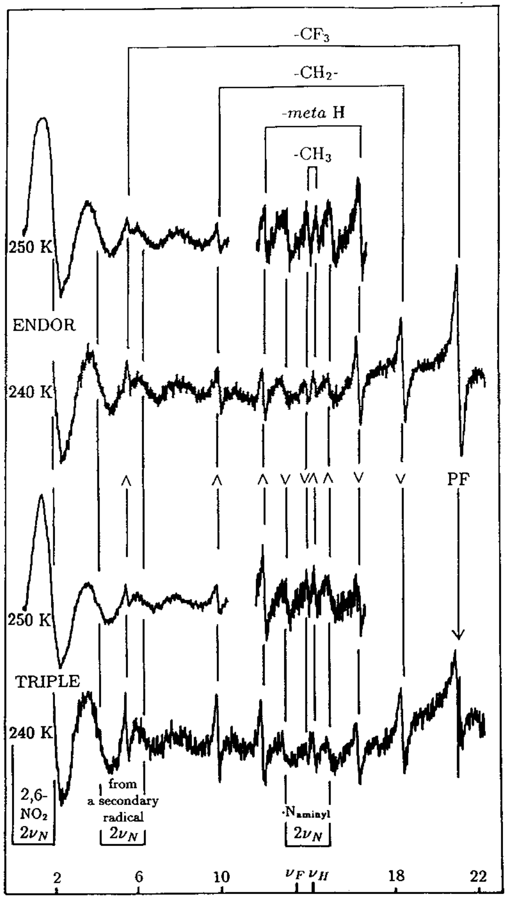


**Figure 2.** ENDOR (above) and general TRIPLE resonance (below) spectra of *N*-ethoxy-*N*-2,6-dinitro-(*p*-trifluoromethyl) phenylaminyl radical (**7**$^\bullet$) in toluene at 240 and at 250 K.

ENDOR and general TRIPLE resonance spectra of the *N*-methoxy-*N*-2,6-dinitro-4-trifluoromethylphenylaminyl radical (**6**$^\bullet$) were recorded in a similar way to those of the ethoxy compound, **7**$^\bullet$, and the hfcs are collected in Table 1. Measurement of the *g*-value for **7**$^\bullet$ gave a value of 2.0043. This may be compared with the value of 2.003602 ± 0.000008 for DPPH, and the values of 2.002717 for pyrene (in DME/K)[30] and 2.002723 for naphthalene (in DME/K) standards.

In the ENDOR spectra of 4-substituted 2,6-dinitro compounds, **6**$^\bullet$, **7**$^\bullet$, **8**$^\bullet$ and **9**$^\bullet$, an extra nitrogen line pair of the secondary radical was seen protruding from the baseline as in Fig. 2. The origin of this additional line pair is not known. The nitrogen dioxide radical has been examined by EPR, and nitrogen hfcs from 10.7 to 27.5 G have been measured in different olefinic liquid solvents.[31] The ENDOR measurements showed a hyperfine coupling of 3.7 G (*ca.* 10.4 MHz) for the nitrogen of the unknown radical. We assume the reaction of the 2,6-dinitro compound to give the 2,4,6-trinitro compound to be a homolytic nitration by $NO_2$, but the elucidation of the mechanism was not a purpose of this study. This could be carried out by the spin trapping technique and subsequent isolation and characterization of the principal diamagnetic compounds formed during the process.

**Compounds 8 and 9, 4-methyl groups.** Owing to their *para*-substituent, the *N*-methoxy-*N*-2,6-dinitro-4-methylphenylaminyl radical **8**$^\bullet$ and the *N*-ethoxy-*N*-2,6-dinitro-4-methylphenyl-aminyl radical **9**$^\bullet$ were easily saturated by microwave irradiation, and the ENDOR and general TRIPLE resonance spectra could be measured. The aminyl nitrogen of these compounds has the largest spin density in this series. Comparison of the hfcs of the fluorine of the trifluoromethyl in **6**$^\bullet$ and **7**$^\bullet$ and the hfcs of the proton of the methyl in **8**$^\bullet$ and **9**$^\bullet$ showed almost similar spin densities. Systematically, the protons have slightly higher spin densities than the fluorines. Unpaired electronic distribution in these aminyl radicals is clearly an interesting problem for which further theoretical calculations are needed.

## Aminyl radicals and the substituent effect

In this series of measurements we kept the donor part as a methoxyl, an ethoxyl or an isopropoxyl group and varied the substituent at *para*-position 4. Thus a coherent set of compounds was investigated and less than

20% variation in the hfcs was detected. According to the hfcs in Table 1, the spin density distribution is surprisingly constant for different substituents. The largest variation was in the $\beta$-position of the alkoxy group. The variation of hfcs of nitrogen in nitro groups at 2,6-positions is, relatively, the next largest. The limited variation provides a good basis for theoretical calculations of the electronic structure of *N*-alkoxyaminyl radicals.

The EPR spectra of aminyl radicals with different substituents and number of magnetic nuclei look different even though no large variation in the hfc (spin density) of a particular position is observed. The hfcs specified by ENDOR appear to be an accurate basis for analysing spin density distribution and for further insight into spin polarization mechanisms. We illustrate how precise ENDOR determined hfcs are by showing, in Fig. 3, the measured EPR spectrum of 7$^\bullet$ together with the simulated EPR spectrum where only non-optimized (ENDOR) parameters were used.

**Rotational correlation time.** In the experimental spectra of aminyl radicals, a slightly slower tumbling can be seen as for the nitroxide free radical spectra. Because of the large hfc of aminyl nitrogen, near 10 G (27 MHz), the sections of nitrogen quantum numbers 1, 0 and $-1$ are so well separated that it was easy to pick up several absorptions due to each quantum number. This can be seen from experimental EPR spectrum of 4$^\bullet$, shown in Fig. 4. From these intensities $h(1)$, $h(0)$ and $h(-1)$, we calculated the rotational correlation time. Rotational frequencies were much greater than magnetic anisotropies in these isotropic solutions at not so low temperatures (255–240 K), so the fast motion region values were expected.

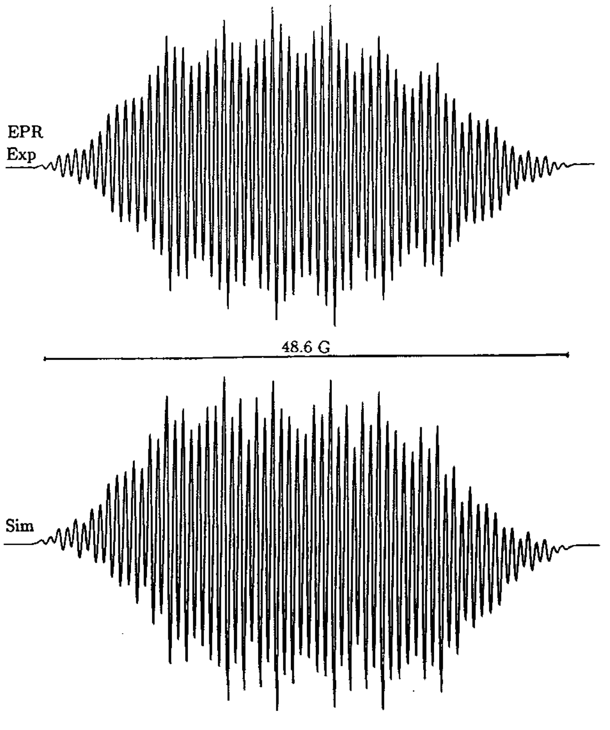


**Figure 3.** Experimental EPR spectrum of *N*-ethoxy-*N*-2,6-dinitro-(*p*-trifluoromethyl)phenylaminyl radical (7$^\bullet$) and the simulated EPR spectrum with non-optimized ENDOR values. Spectra were recorded at 250 K on oxidation with lead tetraacetate.

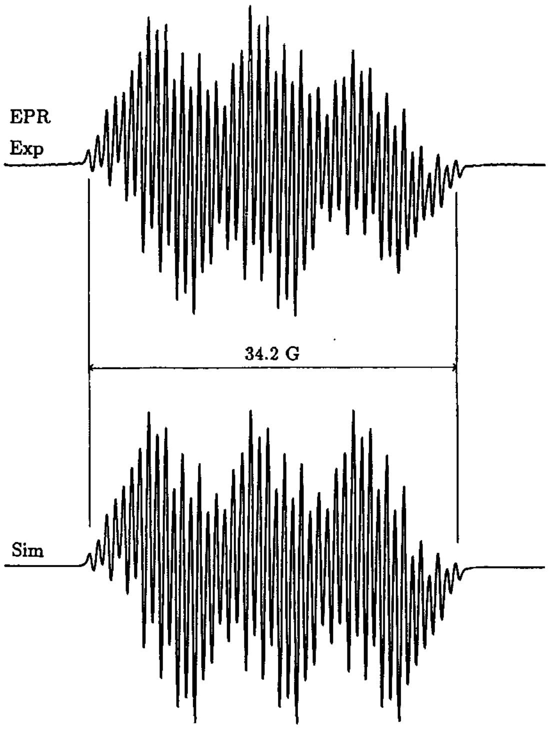


**Figure 4.** EPR and simulated spectra of *N*-ethoxy-*N*-2,4,6-trinitrophenylaminyl radical (4$^\bullet$) showing enhancement of rotational correlation time.

Different equations for the practical calculation of rotational correlation times directly from experimental spectra have been evaluated,[32,33] We used the following equation[33,34] for $\tau_c$:

$$\tau_c = 6.0 \times 10^{-10}\, \Delta H(0)\left[\sqrt{\frac{h(0)}{h(-1)}} + \sqrt{\frac{h(0)}{h(1)}} - 2\right]$$

where $\Delta H(0)$ is the average peak-to-peak linewidth from the simulated spectra and the $h(1, 0, -1)$ intensity values are from the experimental spectra. From the calculated rotational correlation time the effective contact volume, $V_{\mathrm{eff}}$, and the effective radius assuming a spherical form, $r$, were also calculated (Table 2). $V_{\mathrm{eff}}$ was calculated from the Debye–Einstein equation:

$$V_{\mathrm{eff}} = \tau_c \frac{kT}{\eta}$$

where $\eta$ is the dynamic viscosity of the solvent and the temperature $T$ was usually 255–240 K.

In this study, the concentration of each substance was only approximately the same (*ca.* $1 \times 10^{-3}$ M) and accordingly the radical concentration might vary because all the amine molecules are not oxidized to the aminyl radicals and only a small percentage of substance concentration was changing to the radical state. From the EPR intensity, receiver gain, modulation and microwave power we could conclude that the radical concentration was varying from $5 \times 10^{-5}$ to $1 \times 10^{-6}$ M. The *N*-ethoxy-*N*-2,4,6-trinitrophenylaminyl radical 4$^\bullet$ in toluene showed a lower correlation time, probably owing to the higher radical concentration in the sample.

**Table 2. Rotational correlation time and contact volume in toluene**

| Substance | $\sqrt{\frac{h(0)}{h(1)}}+\sqrt{\frac{h(0)}{h(-1)}}-2$ | $\Delta H(0)$ (G) | $\tau_c$ (s) | $V_{eff}$ (m$^3$) | $r^a$ (Å) |
|---|---|---|---|---|---|
| **4**$^{\cdot}$ | $1.03+1.25-2=0.28$ | 0.22 | $3.6\times10^{-11}$ | $1.3\times10^{-28}$ | 3.1 |
| **2**$^{\cdot}$ | $1.11+1.54-2=0.65$ | 0.25 | $9.8\times10^{-11}$ | $3.4\times10^{-28}$ | 4.2 |

[a] Tumbling radius calculated assuming a spherical molecule.

The variation of $\tau_c$ is almost the only experimental way to reach maximum ENDOR enhancement if the sample is otherwise properly prepared.

An estimate of other important parameters for ENDOR measurement can be made. The sum of diagonal elements of the squared dipolar hyperfine tensor, Tr($A'^2$), was not measured, but a crude estimate could be carried out on the basis that aminyl nitrogen would have a similar tensor structure as nitroxyl nitrogen. The isotropic hfc of aminyl nitrogen is one third less than that of the nitroxide nitrogen. Therefore, we conclude that a value near 1000 is correct for Tr($A'^2$). The spin–rotational relaxation constant $B_{SR}$ was estimated from $g$-values[35] to be $7 \times 10^{-6}$. With these values, according to the theory,[27,36] the optimum rotational correlation time, $\tau_c$, would be about $1 \times 10^{-10}$ s, which was exactly the value found from empirical experiments, by the trial-and-error method.

Generally, difficulties in measuring ENDOR spectra occurred owing to difficult saturation by microwave field. The concentration should be made low, but then the oxidation reaction would not work satisfactorily. The lower temperature diminished the EPR intensity owing to dimerization of neutral radicals. Therefore, the optimum region for ENDOR measurements was fairly narrow.

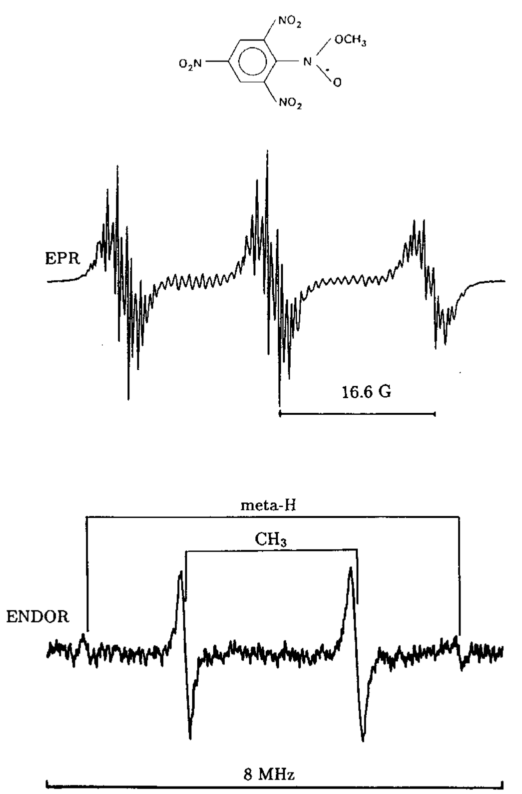


**Figure 5.** EPR (at 243 K) and ENDOR (at 200 K) spectra of nitroxide radical obtained by oxygen attaching to aminyl nitrogen of *N*-methoxy-*N*-2,4,6-trinitrophenylamine (**2**) in an argon-degassed (incomplete oxygen removal) sample.

## ENDOR spectra of nitroxyl radicals

When the samples were prepared without high vacuum only by degassing, we also detected the nitroxyl radical. The nitroxyl radical is reported in this connection because it appears with the aminyl radical if oxygen is present. The electron is highly localized in the N—O bond, and nitrogen lines can be seen. For example, from the sample of *N*-methoxy-*N*-2,6-dinitrophenylamine (**1**) oxidized with lead tetraacetate with incomplete degassing, we recorded the EPR spectrum of the respective nitroxide. The ENDOR spectrum of the nitroxyl radical generated from **1** was recorded at 200 K. Figure 5 shows the EPR and ENDOR spectra. The hfcs were as follows: for the nitroxyl nitrogen, 46.6 MHz from EPR spectrum; for the methoxyl methyl proton, 3.00 MHz; and for the *meta*-protons, 6.54 MHz. According to a general TRIPLE resonance experiment, the hfcs of the protons were of the same sign. The difference between the hfcs of nitrogen and aminyl nitrogen was about 20 MHz, large enough to make the identification of the nitroxyl and aminyl radicals easy and straightforward. 2,4,6-Tri-*tert*-butylnitrosobenzene has been used as a spin trap[37] and it has two trapping sites, the nitrogen and oxygen atoms of the nitroso group. The *N*-alkoxyanilino radicals are also distinguishable from the nitroxides by their different $g$-values and the nitrogen and *meta*-proton hfcs.[38]

The nitroxyl radical could also be detected in viscous solvents, from which molecular oxygen was not completely removed even by high vacuum. An extra example was for *N*-methoxy-*N*-2,4,6-trinitrophenylamine (**2**) in toluene–tetralin (50:50, v/v) at 260 K, where the nitroxyl radical was detected after incomplete degassing with freeze–pump–thaw cycles because of viscosity. The nitroxyl radical was also measured from *N*-ethoxy-*N*-2,6-dinitrophenylamine (**3**). It is worth noting that when oxygen is present, the nitroxyl radical appears first, and subsequently the aminyl radical is generated while the nitroxyl radical disappears. In high-vacuum samples where oxygen was completely removed before oxidation, we did not detect any traces of nitroxyl radicals.

## CONCLUSIONS

Nine *N*-alkoxy-*N*-polynitrophenylaminyl radicals were studied by ENDOR spectroscopy. For six of radicals, all hfcs of magnetic nuclei were found in the spectra. General TRIPLE resonance experiments gave the relative signs of the different nuclei: protons, nitrogens and fluorine. Detection of hfcs of nitrogen by ENDOR in nitro groups attached to benzene succeeded when the temperature was raised above 250 K. The EPR and ENDOR spectra of the highly reactive *N*-methoxy-*N*-2,6-dinitrophenylaminyl and *N*-ethoxy-*N*-2,6-dinitrophenylaminyl radicals were measured using lead tetraacetate as oxidant. We were able to show that oxidation with lead tetraacetate first gives the aminyl radical of the 2,6-dinitro compound and then the nitration reaction at *para*-position 4 produces the radical of the trinitro compound and the mixture of the two radicals. *N*-Alkoxy-*N*-polynitrophenylaminyl radicals seem to have fairly similar spin densities despite their different *para*-substituents. This basic set of hfcs will be used in future in comparison with hfcs of other aminyls where the donor alkoxy group is replaced by an acceptor group. A good foundation has thus been laid for theoretical calculations on aminyl radicals, which are in progress.

When oxygen is present, oxidation with lead tetraacetate produces the nitroxyl radical as the first radical. ENDOR spectra of this were measured.

In the case of the 2,6-dinitro compound, a substitution reaction occurred, in which an extra nitro group was introduced to the *para*-position 4. The extra nitro group must come from another, decomposing 2,6-dinitro-containing molecule. Proof of the presence of the nitrogen dioxide radical in the oxidation reaction medium must be sought by other means, e.g. by applying spin trapping methods or micellar techniques.

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