Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: F. J. Owens (1985): Paramagnetic Resonance of Radicals in Decomposed Solid N-Methyl-N. 2,4,6 Tetranitroanililne (Tetryl), Molecular Crystals and Liquid Crystals, 126:2-4, 379-389

To link to this article: http://dx.doi.org/10.1080/00268948508084800

Mol. Cryst. Liq. Cryst., 1985, Vol. 126, pp. 379–389
0026-8941/85/1264-0379/$20.00/0

Printed in the United States of America

Paramagnetic Resonance of Radicals in Decomposed Solid N-Methyl-N 2,4,6 Tetranitroaniline (Tetryl)

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(*Received October 15, 1984*).

Electron paramagnetic resonance studies of uv decomposed solid N methyl N,2,4,6-tetranitroaniline (tetryl), $C_6(NO_2)_3$ H_2 (CH_3 NNO_2) measured dissolved in benzene show the presence of a six line spectrum which can be accounted for by an unpaired electron interacting equally with three hydrogen nuclei with an isotropic splitting of 10 Gauss and one nitrogen nuclei also with a splitting of 10.0 G. Studies of the radical in powders and single crystals show the g and A tensor are axial with diagonal components $A_{\parallel} = 27.0\ G.$, $A_{\perp} = 4.0\ G.$ and $g_{\perp} = 2.007$ and $g_{\parallel} = 2.003$. The spectrum is shown to be a nitroxide radical of tetryl, $C_6(NO_2)_3H_2$ (CH_3NO). The radical is stable at room temperature trapped in the solid lattice but in a solution of benzene loses the CH_3 forming another radical.

INTRODUCTION

Very little is known about the details of the initial chemical steps of the initiation of detonation of energetic organic molecules. It is generally agreed that the initial step is an endothermic rupture of the internal molecular bonds of the molecules. The necessary exothermicity is believed to result from the secondary interactions of the initial fragments produced which may be radicals. Indeed, it was shown some years ago that when a number of organic explosives are heated to temperatures close to that which would induce explosion EPR spectrum were detected in the materials indicating that radical species may have been produced.[1] However, no identification of the radicals was made in these studies.[2] A significant advancement in the understanding of the initiation of explosion in condensed materials would result if some of the early produced radicals which play a role in the process were identified. The importance of this has been recently recognized and a number of papers have been published which address the issue of the identification of radical species in condensed explosives.[3] One of the difficulties, however, is that by producing the radicals by high temperature above the melting point the spectra are obtained in the liquid phase. Such spectra do not always allow identification because of the absence of sufficient character. If, on the other hand, the radicals could be trapped in a single crystal, considerably more paramagnetic resonance data can be obtained such as the principle components of the hyperfine tensor which can provide more information to enable identification. One way to achieve this is to produce the radicals in single crystals by uv irradiation and compare these with radicals produced in the melt by heat.

This work reports a study of radicals produced in the solid phase of N-methyl -N,2,4,6 tetranitroaniline (tetryl) by uv light using electron paramagnetic resonance. The radicals responsible for the EPR spectrum are assigned. The possible role of the radicals in the explosion process is discussed.

EXPERIMENTAL

Electron paramagnetic resonance measurements were carried out using a Varian E-9 spectrometer operating at 9.2 GHz. Studies of the effect of temperature on spectra were made using a Varian 4540 temperature controller which regulated the temperature to ± 1 degree centigrade. Ultra-violet light irradiations of finely powdered samples were made at room temperature using a Hanovia high pressure mercury light of 140 peak wattage and a maximium wavelength of 250 nm. All samples were recrystalized a number of times from benzene solutions and dried before irradiation. Solution spectra were recorded by first irradiating powders and then dissolving then in benzene. Single crystals were grown by slow evaporation of tetryl dissolved in benzene. The crystals grew in the form of rectangular platelets with the large facet being the (011) plane and the long edge the [001] direction as previously described.[4]

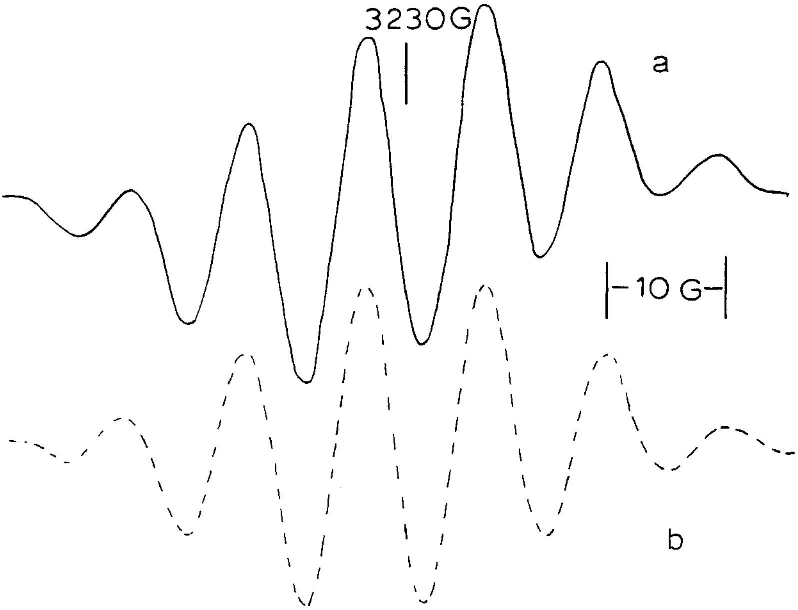


FIGURE 1 (a) EPR spectrum of irradiated powders of tetryl dissolved in benzene and recorded at room temperature. (b) Computer simulation of solution spectrum assuming an unpaired electron has an isotropic hyperfine interaction with one nitrogen nucleus of 10.0 *G*. and three hydrogen nuclei also of 10.0 *G*.

RESULTS AND ANALYSIS

Powders of tetryl were irradiated at room temperature and then dissolved in benzene and the EPR spectrum recorded. The spectrum obtained in benzene at room temperature is shown in Figure 1(a). It consists of 6 lines, each separated from each other by 10.0 Gauss. The *g* value at the center of the spectrum is 2.0058. The relative intensity of the six lines is .19, .67, 1, .67, .19. When the modulation and the power were reduced, no further structure could be observed on the individual resonance. It was possible to simulate this spectrum on a computer by assuming a radical having one unpaired electron interacting with one nitrogen nucleus ($I = 1$) and three hydrogen nuclei and assuming that the isotropic hyperfine interaction with the nitrogen and hydrogen nuclei were both 10.0 *G*. Figure 1(b) shows the computer generated spectrum assuming a Gaussian shaped line of 4.9 Gauss width. The simulated spectrum is in excellent agreement with the experimental spectrum. Over a period of 24 hours the six line spectrum in benzene at room temperature converted to a three line spectrum shown in Figure 2. This spectrum consists of three lines of equal intensity with a splitting between the lines of 10.0 *G*. No further splitting could be observed on each of the three lines at low power and low modulation. This spectrum is clearly due to an unpaired electron having a hyperfine interaction with one nitrogen nucleus.

In order to obtain further information about the spectrum, the EPR of fixed but randomly oriented radicals were recorded by recording the spectrum in frozen benzene. When a molecule or radical is fixed with respect to the direction of the dc magnetic field, the anisotropic dipolar hyperfine interactions are no longer averaged to zero as in the liquid phase and the separation of the resonances from each other are dependent on the orientation of the symmetry axis of the molecule with respect to the direction of the dc magnetic field. The spectrum recorded in frozen benzene therefore consists of a superposition of spectra (weighted by the function governing the probability for a given orientation) arising from all possible ori-

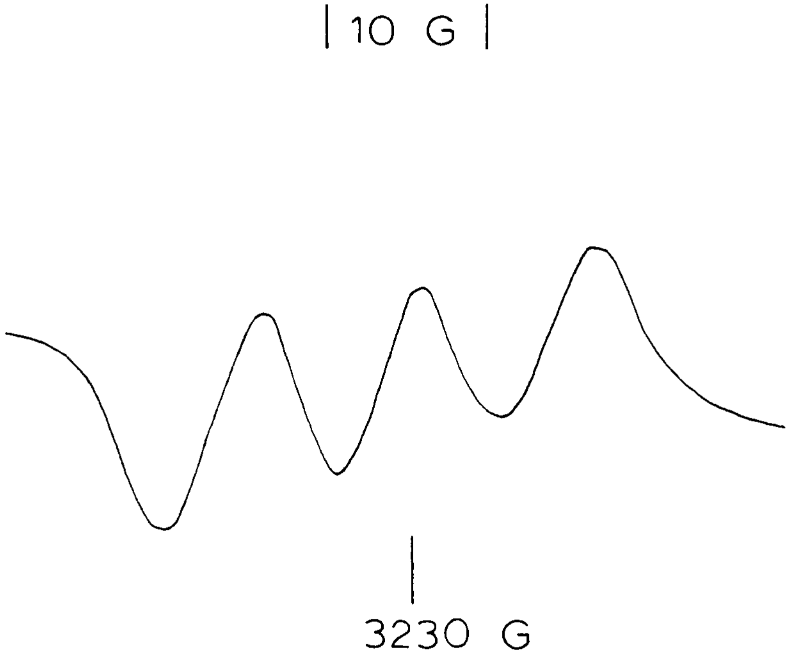


FIGURE 2 Spectrum obtained of irradiated tetryl dissolved in benzene after conversion of 6 line spectrum to three line spectrum.

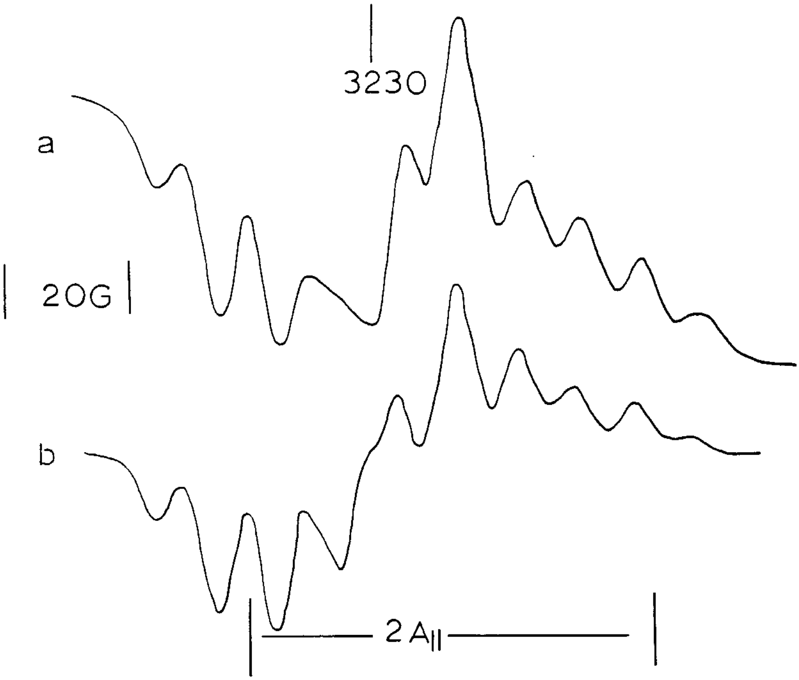


FIGURE 3 (a) EPR spectrum of irradiated tetryl before conversion to three line spectrum dissolved in benzene and recorded below the freezing point of benzene. (b) EPR spectrum directly from irradiated fine powders of tetryl.

entations of the axis of the radical with respect to the dc magnetic field. Figure 3(a) shows the spectrum recorded in the frozen benzene before the conversion to the three line spectrum. This spectrum is then the powder spectrum of the 6 line spectrum. This powder spectrum is consistent with an unpaired electron on a radical having an isotropic hyperfine interaction with 3 hydrogen nuclei and an axially symmetric anisotropic hyperfine interaction with one nitrogen nuclei. The outer lines of the spectrum in Figure 3 are separated from each other by 10.0 *G*. and are due to the hydrogen splittings. The parallel and perpendicular components of the g and the A tensor can be obtained from the powder spectrum as indicated in Figure 3(a). The g_{11} is 2.0038, and A_{11} is 27.5 *G*. There is sufficient resolution of structure at the center of the spectrum to determine $g_\perp$ and $A_\perp$ but these can be obtained indirectly from the liquid phase spectrum. Since 10.0 *G*. is the nitrogen isotropic hyperfine splitting determined from the liquid spectrum, for axial symmetry $A_\perp$ can be calculated from the measured A_{11} and the trace of the hyperfine tensor given by,

$$A_{iso} = \frac{A_{11} + 2A_{\perp}}{3} \tag{1}$$

Assuming the signs of all the tensor components are the same, $A_{\perp}$ is obtained to be 1.5 G.

Figure 3(b) shows that the spectrum obtained directly from the irradiated powders of tetryl is the same as that obtained in the frozen benzene indicating that the radical trapped in the lattice is the same as that observed in the benzene solution.

In order to further verify the spin Hamiltonian parameters obtained from the liquid and frozen benzene, the spectrum was examined in a single crystal of tetryl. The crystals grow in well-formed rectangular platelets in which the large facet is known to be (011) plane and the long edge the [100] direction.[4] The unit cell of the lattice is monoclinic with four molecules per unit cell each having a different orientation with respect to the axis of the cell. This means that if the radical is associated with the tetryl molecule at a given orientation of the dc magnetic field there will be four different spectra each with different nitrogen hyperfine splittings because of the dependence of the nitrogen hyperfine splittings on the orientation of the dc magnetic field with respect to the radical. Because the nitrogen splitting at a given orientation will not be equal to the hydrogen splitting the spectrum of each radical may consist of up to 12 lines. Thus, at any orientation of the dc magnetic field in the crystal the spectrum will consist of 4 sets of 12 lines and there will be considerable overlap of the different lines. Because of this it was not possible to measure the dependence of the magnetic field value of each line on the orientation of the magnetic field with respect to the crystal axis, nevertheless it was possible to obtain sufficient data to verify the spin Hamiltonian parameters obtained from the benzene data. Figure 4 shows the EPR spectrum for two different orientations of the dc magnetic field in the (011) planes of the lattice. Figure 5 shows the angular variation of the outer lines of the spectrum with respect to the [100] direction in the (011) plane. The spectrum in the crystal will be described by the spin Hamiltonian,

$$\beta\, H \cdot g \cdot S + S \cdot A_n \cdot I_n + a_h \sum_{i=1}^{3} s \cdot I_{h_i} \tag{2}$$

where H is the magnetic field, g the g tensor, S the electron spin, A_n

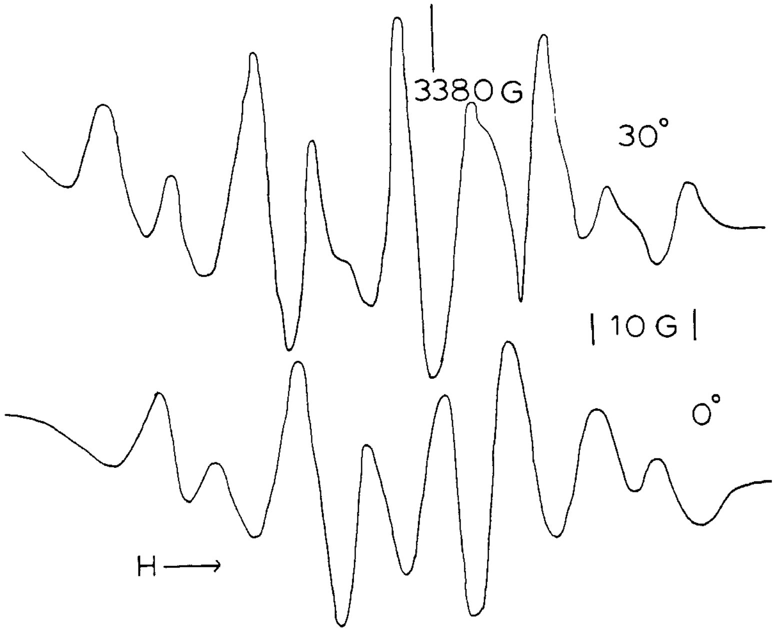


FIGURE 4 EPR spectrum in single crystal of tetryl for the dc H field in the (011) plane parallel to [100] and 30 degrees from [100].

the nitrogen hyperfine tensor, a_h the hydrogen isotropic hyperfine interaction and I the nuclear spin. For the case of an isotropic hydrogen hyperfine interaction and an axially symmetric nitrogen hyperfine and g tensor, the eigen values of the spin Hamiltonian have been shown to be correct to first order,[5]

$$E = g\beta H M_s + K M_s m_n + \sum_{i=1}^{3} a_i m_{h_i} M_s \qquad (3)$$

where

$$g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta \qquad (4)$$

and

$$K^2 = A_{\parallel}^2 g_{\parallel}^2 \cos^2\theta + A_{\perp}^2 g_{\perp}^2 \sin^2\theta \qquad (4)$$

where θ is the angle between the z principle axis and the dc magnetic field. The line at the highest magnetic field in Figure 4 whose angular

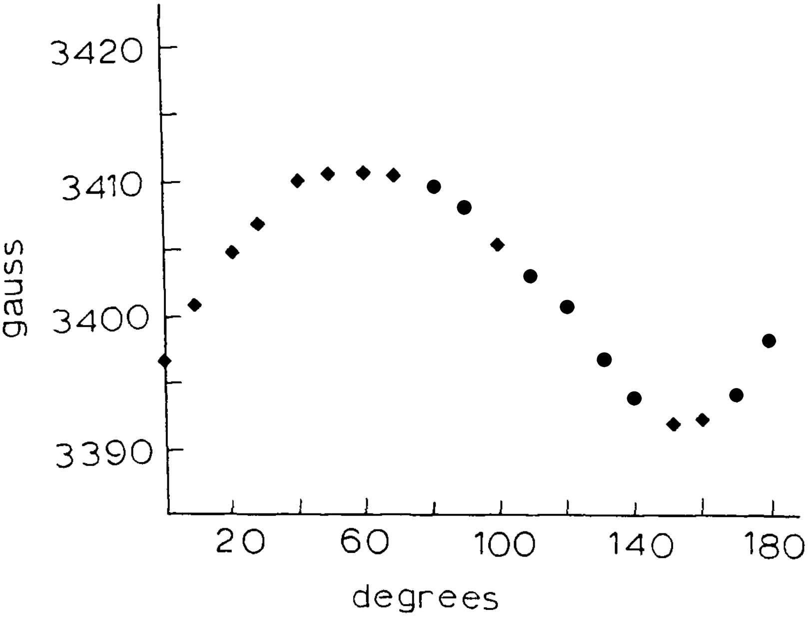


FIGURE 5 Dependence of the resonance field for the high field resonance in the (011) plane as a function of the angle the dc H field makes with respects to the [100] direction.

variation can be followed completely should correspond to a transition between spin states having nuclear spin quantum numbers $m_n = 1$, and $m_h = 3/2$. For this resonance it was possible to fit the angular variation in the (011) plane to equations 3, 4, and 5 by picking $g_{11} = 2.0071$, $g_\perp = 2.0026$, $A_{11} = 27.5$ G. and $A_\perp = 1.25$ G. and assuming the z axis lies in the plane of the facet 60 degrees from (100).

When the crystal was warmed above room temperature the spectrum totally disappeared with no conversion to the three line spectrum as observed in the benzene.

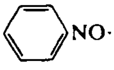
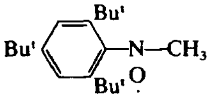
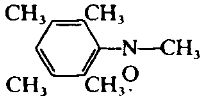
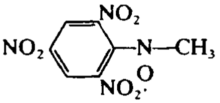
DISCUSSION

The EPR spectrum of uv irradiated solid tetryl which was dissolved in liquid benzene is consistent with an unpaired electron having an equal hyperfine interaction with 3 hydrogen nuclei of 10.0 G. and an isotropic interaction with one nitrogen nuclei also of 10.0 G. The principle components of the nitrogen hyperfine tensor are obtained from the powder pattern of the fixed radicals in the frozen benzene and are $A_{11} = 27.0\ G.$ and $A_{\perp} = 1.5\ G.$ In the frozen spectrum the hydrogen splitting is 10.0 $G.$ as in the liquid phase. Similar g and A tensor components are obtained from the spectrum obtained directly from the irradiated powders. Partial analysis of the data from irradiated single crystals confirms the spin Hamiltonian parameters obtained from the powder spectrum analysis. The high field line of the spectrum in the single crystal could be followed as a function of the orientation of the dc magnetic field and the fit of the data to the spin Hamiltonian yielded parameters quite close to those obtained from the powder spectrum. The g_{11} obtained from the single crystal data is slightly different then that obtained from the powder. This is not really surprising as tensor components obtained from powder patterns cannot be as accurate as those obtained from the single crystals because of the broadness of powder lines. It is also possible that there are some differences in the g components for the radicals in the different sites of the lattice an effect which would be lost in the powder spectrum.

The principle components of the nitrogen tensor are in accord with those expected for an unpaired electron localized on an NO group. For example, the nitrogen hyperfine tensor components of di-*t*-butyl nitroxide are $A_{\perp} = 6.3\ G.$ and $A_{11} = 32.0\ G.$ quite close to those observed here.[6] Generally for an unpaired electron localized on an NO group the nitrogen hyperfine tensor is axial and $A_{\perp}$ is small because the unpaired electron is localized mostly in a *P* type orbital made up of oxygen *p* and nitrogen *p* atomic orbitals oriented perpendicular to the N-O axis. Since there are nodes in the plane of the N-O axis the component of the hyperfine tensor parallel to the molecular axis will be small. In this case the perpendicular direction is parallel to the N-O axis but perpendicular to the *p* orbitals. The isotropic splitting of 10.0 $g.$ is also consistent with that for an NO group on a benzene ring. For example the average nitrogen isotropic hyperfine splitting in different solutions is 9.1 $G.$ for the $C_6H_5NO^{-7}$. The observation of the equal interactions with the three hydrogen nuclei indicates that the NO is formed on the CH_3NNO_2 group of the tetryl molecule. In other words the radical is assigned to $C_6(NO_2)_3H_2(CH_3)NO$. Further support for this assignment comes from the work of Terabe[8] who observed the EPR spectrum of the stable radical 2,4,6 tri-*t*-butylnitrosobenzene, having the structure shown in Table I. The stable spectrum observed in liquid benzene very much resembled the spectrum observed here when the irradiated tetryl was dissolved in benzene. Table I shows a comparison of the isotropic hyperfine split-

TABLE I

Isotropic hyperfine splitings of radicals previously reported and having similar structure to the radical produced in solid tetryl.

radical	A_N	A_H (Gauss)	A_H (ring)	ref.
	9.1**		2.4 (o,p)* 0.9 (m)	7
	13.3	12.33	.81	8
	13.7	12.17	.34	9
	10.0	10.0		this work

*o ortho, p para, m meta, ***Average of values in a number of solution.

tings and the g value of the spectrum observed here and 2,4,6 tri-*t*-butyl nitrosobenzene and 2,3,5,6 tetralmethylphenyl methyl nitroxide also observed by EPR dissolved in benzene.[9] In both of these radicals the unpaired electron was localized on the (NO)CH_3 group of the benzene ring and the nitrogen and hydrogen isotorpic hyperfine splitting were almost identical as observed here. The similarity of the data measured here and the parameters of the above two radicals as shown in Table I supports the assignment of the radical in tetryl.

The disappearance of the six line spectrum at room temperature in benzene and the growth of a three line spectrum having an isotropic hyperfine splitting of 10.0 G. with a nitrogen nucleus suggests that the CH_3 fragment is being removed from the (NO)CH_3 of the radical forming a new radical. The data are not sufficient to offer a definitive assignment of this spectrum. Possibilities are $C_6(NO_2)_3H_2NO^-$ or CH_3O —NO— $C_6(NO_2)_3H_2$. This latter could be formed from the nitroxide of tetryl by reaction with O_2 that may be present in the benzene. Both of these radicals could be expected to have an isotropic hyperfine splitting in the order of 10.0 *G*. as measured here.

The question of the role of the nitroxide radical in the chemistry of explosion is difficult to assess. It is clear that radicals should be expected to play a role in the process. It is interesting that nitroxide radicals have been detected in the thermal and photolytic decomposition of a number of organic explosives such as nitroamines and nitroaromatics.[3,4,10,11] This may suggest their role in the initiation process but further work is necessary to verify this possibility.

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