Nitroxide Radicals. V.[1]

N,N′-Di-*t*-butyl-*m*-phenylenebinitroxide, a Stable Triplet

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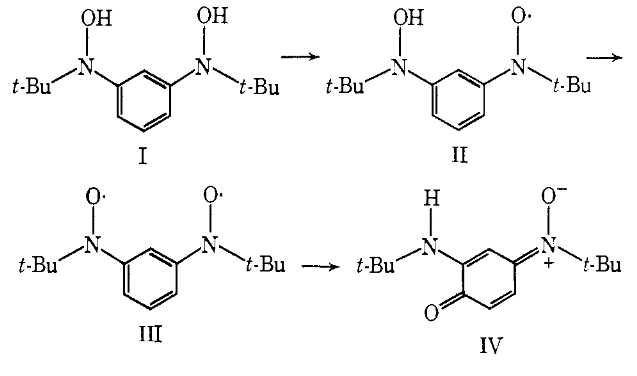
Abstract: The crystalline triplet N,N′-di-*t*-butyl-*m*-phenylenebinitroxide has been isolated and shown to decompose spontaneously in solution to an isomeric aminoquinone imine N-oxide by an intermolecular process. In a frozen toluene glass it has $D = 368$ and $E \approx 40$ MHz, but in other glasses two conformations are observed, one of which has D larger than that obtained in toluene. An approximate value of $J = 12$ kcal mole^{-1} has been measured.

Stable biradicals and in particular binitroxides[3] in which the scalar electron spin–spin interaction is sufficiently small to allow their esr spectra to be measured in dilute solution are now well known. Examples in which this interaction is very large, however, are less common[4] and binitroxides of this type have not previously been reported. We have now isolated the crystalline triplet (III) and examined its chemical and spectroscopic properties.

Treatment of the di-Grignard reagent of *m*-dibromobenzene with nitroso-*t*-butane (2 mol) followed by hydrolysis yielded the dihydroxylamine I, oxidation of which with silver oxide (0.5 mol) gave the mononitroxide II, $a_N = 33.6$, $a_{o\text{-H}} = a_{p\text{-H}} = 5.28$, and $a_{m\text{-H}} = 2.33$ MHz, which was stable indefinitely in dilute solution. Further oxidation of the mononitroxide II or oxidation of the dihydroxylamine I with an excess of silver oxide and removal of solvent at room temperature left a red oil which on crystallization, with rapid cooling, deposited orange-red crystals. Concentrated solutions of the oil or of the crystals at room temperature gave no nmr spectrum (60 MHz) and an esr spectrum consisting of a broad line superimposed on which was a weak spectrum of the monoradical II. The width of the esr line increased with decreasing temperature suggesting that the product was a biradical in which the zero-field splitting was large.[5] After a few hours the esr spectrum began to fade and an nmr spectrum slowly emerged showing signals from two *t*-butyl groups at τ 8.61 (NH-*t*-Bu) and 8.26 (C=N$^+$(O$^-$)-*t*-Bu) and from three olefinic protons. In the absence of solvent the oil eventually solidified to a deep-red crystalline solid, elemental analysis and infrared (N–H and C=N$^+$(O$^-$) absorption) and ultraviolet ($\lambda_{\max}$ 396 and 510 mμ) measurements on which confirmed that it was the aminoquinone imine N-oxide (IV). Crystalline samples of the triplet underwent a spontaneous topochemical change to this product overnight.



Measurements of the rate of formation of the aminoquinone imine N-oxide in toluene indicated that the rate of isomerization was concentration dependent (Figure 1) and hence that an intramolecular C–O coupling reaction was not involved. The reaction was slightly slower in more polar solvents such as ethanol and was further characterized in all solvents by an inhibition period which was concentration dependent but was not due to the presence of either the mononitroxide II, dissolved oxygen, hydroperoxides, or peroxides. Although the kinetic data were not consistent with a bimolecular process, it is evident that like *t*-butylphenylnitroxide[6] the triplet decomposes by an intermolecular route.

Esr Measurements. The binitroxide III in a frozen toluene glass gave the spectrum shown in Figure 2a, which is typical of a triplet state[7] for which the zero-field tensor is not axially symmetric, that is, $E \neq 0$. Spectrum 2a is not identical with the theoretical reconstructions given in ref 7 because the ratio of the line width to the zero-field splitting is much larger for the nitroxide triplet. In fact, its electron resonance spectrum is much closer to those of dimer ion-pair triplet states.[8] The intensity of the half-field transition is lower than those of the $\Delta m = \pm 1$ lines because D is small compared with the Zeeman splitting. A further consequence of the small value of D is that the position of the half-field line cannot be used to determine the magnitude of $(D^2 + 3E^2)^{1/2}$ with any precision. Fortunately, because the zero-field splitting is small compared with the microwave quantum, both D and E are readily obtained from the $\Delta m = \pm 1$ spectrum.[7] For example, the separation between the extreme pair of

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[2] (a) University of Aberdeen; (b) author to whom all inquiries should be addressed; (c) University of Southampton.

[3] (a) R. Briere, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, 3290 (1965); (b) E. G. Rozantsev, V. A. Golubev, M. B. Neiman, and Yu. V. Kokhanov, *Bull. Acad. Sci. USSR*, 559 (1965).

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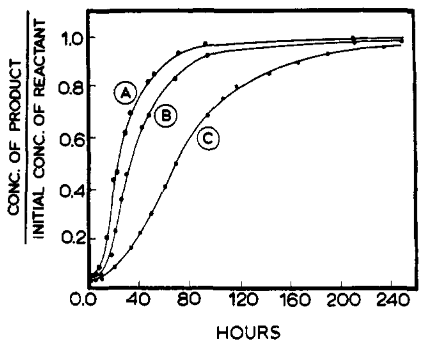

Figure 1. Rate of formation of the aminoquinone imine N-oxide in (a) 0.076 *M*, (b) 0.154 *M*, and (c) 0.222 *M* solutions of the triplet III.

lines in the spectrum is $2D$ while the separation between the inner pair is $D - 3E$. The remaining pair is separated by $D + 3E$, but because of overlapping lines this distance cannot be measured accurately. The value of D and an estimate of E obtained from such measurements are 368 and 40 MHz, respectively. A particularly interesting feature of spectrum 2a is the appearance of hyperfine splitting on one pair of the $\Delta m = \pm 1$ transitions. Under certain conditions five equally spaced lines with intensities 1:2:3:2:1, caused by interaction with both nitrogens, can be clearly distinguished. The observation of hyperfine structure from both nitrogen nuclei shows that the electron–electron coupling, either scalar or dipolar, is much greater than the anisotropic hyperfine interaction.[3a] The magnitude of this component of the hyperfine tensor, which is twice the line separation,[3a] is approximately 62 MHz.

The interpretation of these results is straightforward, and it was surprising to find a completely different electron resonance spectrum on changing the solvent from toluene to ethanol. The spectrum obtained from the ethanol glass is shown in Figure 2b, and careful examination reveals that it is, in fact, the sum of two spectra, one of which is identical with that observed in toluene while the other has a much larger zero-field splitting tensor. The separation between the outer pair of peaks in spectrum 2b may be identified with $2D$ for the second triplet-state species. Measurement of E is not straightforward and E was estimated in the following way. The spectra shown in Figure 2a and 2b were obtained in digital form by measuring the intensity of the spectrum at 200 equally spaced points. Varying amounts of spectrum 2a were then subtracted from spectrum 2b and the resulting spectrum was replotted. The second peak in spectrum 2b is associated entirely with the triplet state observed in the toluene matrix, and so when this peak was no longer observed after subtraction the resulting spectrum must be that of the second triplet state. The form of the spectrum is similar to that in Figure 2a, and from it we were able to measure the separation $D - 3E$. This procedure gave a value of E of about 30 MHz. The positions of the peaks corresponding to the separations $2D$, $D - 3E$, and $D + 3E$ for both triplet states are shown in Figure 2. It is tempting to attribute the new spectrum to a hydrogen-bonded species, but this interpretation would be incorrect because both spectra are observed in such nonpolar solvents as *o*-terphenyl. Indeed spectra corresponding to two triplet-state species are observed in most solvents. The results may be summarized by saying that the triplet state III, in solid solutions, can adopt two conformations, one with D = 368 MHz and $E \sim$ 40 MHz, and the other with a larger zero-field splitting of 512 MHz and $E \sim$ 30 MHz. The occurrence of only one conformation in the toluene glass is, presumably, the result of the ability of the cavity in the glass to stabilize this particular conformation. In other solvents the surrounding molecules seem to accept both conformations.

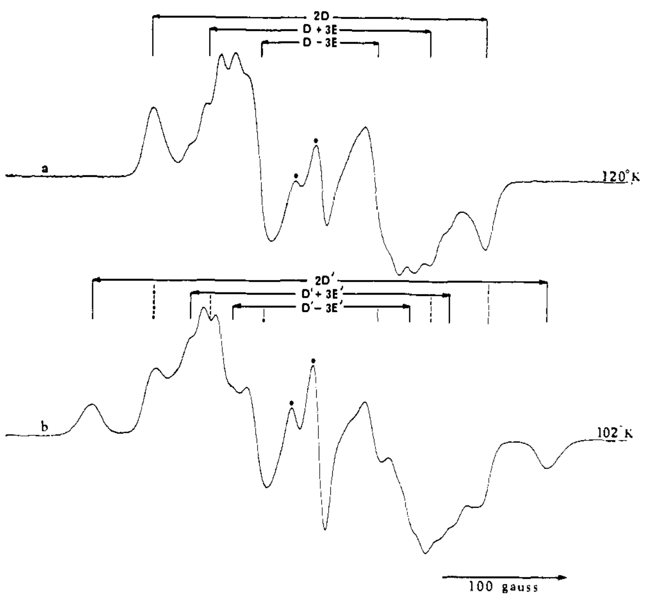

Figure 2. Esr spectra of the triplet III in (a) toluene and (b) ethanol. The squares (■) mark lines due to the monoradical.

In principle it should be possible to use the experimental values of D to determine the nature of the two conformers. The determination would involve the calculation of D for various configurations of the molecule using an appropriate self-consistent field wave function and the values of certain multicenter integrals.[9] In practice such a task is extremely difficult, especially for molecules containing heteroatoms, and so we prefer to adopt a simpler procedure, which permits us to calculate D for many conformers. The zero-field splitting tensor is given by

$$D = \frac{1}{2}g^2\beta^2\langle\psi(1,2)|\mathfrak{D}_{\mathrm{op}}|\psi(1,2)\rangle \tag{1}$$

where $\mathfrak{D}_{\mathrm{op}}$ is the dipole–dipole operator and $\psi(1,2)$ is the wave function

$$\psi(1,2) = \frac{1}{\sqrt{2}}\{\varphi_i(1)\varphi_j(2) - \varphi_j(1)\varphi_i(2)\} \tag{2}$$

in which φ_i and φ_j are the molecular orbitals containing the unpaired electrons. Provided three-center and higher integrals are neglected, eq 1 can be written as

$$D = \frac{1}{2}g^2\beta^2\sum_{p<q}[C_{ip}C_{jq} - C_{iq}C_{jp}]^2\langle pp|qq\rangle \tag{3}$$

where, for example, C_{ip} is the coefficient of the $2p_z$ atomic orbital of atom p in φ_i; in fact, we shall take the C_{ip} to be the Hückel coefficients. The two-center

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[9] M. Godfrey, C. W. Kern, and M. Karplus, *J. Chem. Phys.*, **44**, 4459 (1966).

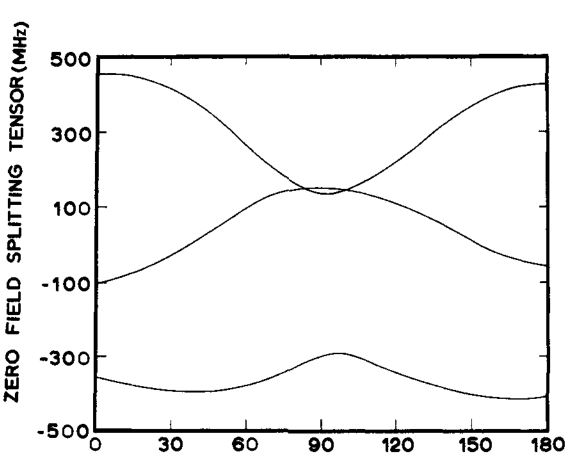


Figure 3. The variation of the principal components of the zero-field splitting tensor as a function of the deviation from planarity.

integrals corresponding to different components of the zero-field splitting tensor were calculated with the operators

$$\mathfrak{D}_{zz} = \frac{r_{pq}^2 - 3z_{pq}^2}{r_{pq}^5} \tag{4}$$

$$\mathfrak{D}_{xz} = -\frac{3x_{pq}z_{pq}}{r_{pq}^5}$$

etc., where r_{pq} is the separation between the electrons on atoms p and q. The tensor components were evaluated within a molecular axis system in which z is perpendicular to the benzene ring, x is parallel to a line joining the two nitrogen atoms, and y is orthogonal to the other two axes. The electron distribution within a $2p_z$ orbital was then represented by two half-charges located above and below the plane containing the atom. This approximation has been used previously[10–13] and has been shown[13] to be quite good if the separation between the half-charges is 1.4 Å even when the internuclear distances are as small as 1.6 Å. Indeed, a similar procedure[14] has been found to yield zero-field splittings within 20% of the experimental results which were as large as 3000 MHz. We therefore expect the calculations for the nitroxide triplet III, with its much smaller value of D, to be sufficiently reliable to predict the trend in D as the molecular geometry is varied.

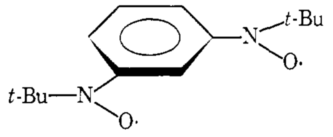
The conformational changes are presumably related to the deviation from planarity of the nitroxide groups, and we have therefore calculated the principal components of the total tensor for various angles of the group to the ring. The Hückel coefficients were calculated by setting all carbon Coulomb integrals equal to α and all carbon–carbon resonance integrals equal to β. The Coulomb integrals for the heteroatoms were given the values

$$\alpha_O = \alpha\ 1.5\beta$$
$$\alpha_N = \alpha + 1.7\beta \tag{5}$$

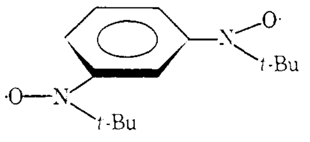
with the resonance integrals

$$\beta_{NO} = 1.6\beta$$
$$\beta_{CN} = 1.2\beta \cos\theta \tag{6}$$

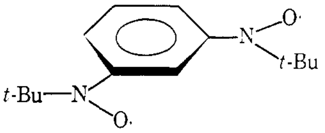
where θ is angle between the $2p_z$ orbital on the nitrogen atom and that on the adjacent carbon atom. These are all reasonable values and have been found to predict proton coupling constants in conjugated nitroxide radicals.[15] The bond lengths were taken from the "Handbook of Chemistry and Physics."[16] There are an infinite number of ways of varying θ_1 and θ_2 for the two groups independently, and so we have assumed that $|\theta_1|$ always equals $|\theta_2|$. The most plausible deviation would then seem to be one in which one group moves out of the paper while the other moves into it. Figure 3 shows just how the principal components of the zero-field splitting tensor vary as a function of θ in this case. $\theta = 0$ corresponds to conformation IIIa, whereas $\theta = 180°$ is conformer IIIb. The figure shows that unless the nitroxide groups are nearly orthogonal to the benzene ring the zero-field splitting does not possess the near-axial symmetry found experimentally. Calculations employing other possible conformers, such as IIIc, or any retaining twofold symmetry produced curves similar to those shown in Figure 3. Although the magnitude of the tensor may be in error, the calculation is unlikely to yield the wrong symmetry. Both triplets, observed in the various matrices, must correspond to conformations in which the nitroxide groups are inclined at angles close to 90° to the benzene ring. The possibility of *cis–trans* isomerism therefore arises, but unfortunately the zero-field splitting calculations are insensitive to whether the nitroxide groups are *cis* or *trans* to one another. According to Figure 3 the larger value for D of 512 MHz and an E value of 30 MHz correspond to an inclination of about 75° to the ring (note well: D is 1.5 times the largest component of the zero-field splitting tensor). Although it is not possible to decide between conformations IIIa, IIIb, or IIIc with θ equal to 75°, the smaller value for D of 368 MHz cannot be explained by the calculations for the smallest theoretical value is 444 MHz corresponding to the *trans* orthogonal configuration. This discrepancy may be due to the nitroxide groups adopting an aliphatic character in such nonplanar configurations.



IIIa



IIIb



IIIc

However, the calculations do show that the biradical is markedly nonplanar which might be caused by the steric effects of the *t*-butyl groups. It is possible to see

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whether this is the case by using the proton coupling constants of the monoradical II to estimate the deviation from planarity in this molecule. The McLachlan spin densities were calculated as a function of the twist of the nitroxide group and the coupling constant obtained from the McConnell relationship with Q = 63.1 MHz. The theoretical values correspond to an angle of 46°. Steric reasons cannot therefore be invoked to explain the nonplanarity of the triplet state. The actual conformation adopted by the triplet will be the result of a subtle combination of electron repulsion which would produce an orthogonal conformation and electron delocalization which would favor a planar molecule. It would seem that electron repulsion dominates.

Most aliphatic nitroxide biradicals are characterized by quite small values of the triplet–singlet separation,[17] J, whereas a conjugated triplet state such as III would be expected to have a large value of J. Since the solution spectrum contains a single line, we have attempted to measure J for the two conformers from the temperature dependence of the signal intensity of their solid-state spectra. The solvent used in this determination was *o*-terphenyl because both conformers are observed in this solvent and *o*-terphenyl has a long glass range. The intensity I was fitted to the theoretical expression

$$I = \frac{C}{T}\frac{3e^{J/RT}}{1 + 3e^{J/RT}} \qquad (7)$$

where C is a constant depending, among other things, on the spectrometer. In both cases J was positive, showing that the triplet is the ground state. Unfortunately, both values of J are large, 12 kcal mole^{-1}, which prevents us determining them with any accuracy.

Experimental Section

N,N′-Di-*t*-butyl-*m*-phenylenedihydroxylamine (I). To a cold solution of the di-Grignard reagent of *m*-dibromobenzene, prepared from *m*-dibromobenzene (20 g) and magnesium (4.5 g) in tetrahydrofuran (200 ml), nitroso-*t*-butane (12.0 g) in tetrahydrofuran (50 ml) was added with stirring. The tetrahydrofuran was then evaporated *in vacuo* and water (200 ml) added. The aqueous suspension was extracted with ether (six 100-ml portions), and the ethereal fractions were combined and dried ($MgSO_4$). Removal of the ether left a red solid which was thoroughly washed with petroleum ether (bp 60–80°). Crystallization of the resulting almost colorless solid from ethanol gave the product (8.0 g, 38%) as colorless needles: mp 206–208°; λ_{max} (in ethanol) 243 mμ (log ϵ 3.95); ν_{max} 3250–3200 cm^{-1} (OH). The product gave a bright red color with alkaline 2,3,5-triphenyltetrazolium chloride characteristic of hydroxylamines.[18]

Anal. Calcd for $C_{14}H_{24}N_2O_2$: C, 66.6; H, 9.5; N, 11.1. Found: C, 66.7; H, 9.4; N, 11.2.

Oxidation of the Dihydroxylamine I. The dihydroxylamine (0.2 g) in chloroform (50 ml) was shaken with silver oxide (0.6 g) for 30 min. Filtration and removal of chloroform at room temperature gave a red oil, rapid crystallization of which from petroleum ether (bp 40–60°) gave **the triplet III** as orange-red plates, mp 68–70°, whose ir spectrum showed no absorption in the 3500–3000 and 1650–1600-cm^{-1} regions and which had λ_{max} (in ethanol) 289 mμ (log ϵ 4.28).

Slow crystallization of the red oil from petroleum ether (bp 60–80°) gave after 24 hr 3-(*t*-butylamino)-N-*t*-butyl-1,4-benzoquinone imine N-oxide (0.156 g, 78%) as deep-red plates: mp 123–124°; λ_{max} (in ethanol) 394 mμ (log ϵ 4.26); ν_{max} 3380 (N-H) and 1625 cm^{-1}; τ 8.61 (9 H, singlet, NH-*t*-Bu), 8.26 (9 H, singlet, $=N^+(O^-)$-*t*-Bu), 4.60 (1 H, br singlet, NH), 3.77 (1 H, doublet, J = 10.02 Hz, 5-H), 3.21 (1 H, doublet, J_2 = 3.0 Hz, 2-H), and 2.3 (1 H, quartet, J_1 = 10.02 and J_2 = 3.0 Hz, 6-H).

Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 67.2; H, 8.8; N, 11.2. Found: C, 67.2; H, 9.0; N, 11.4.

Kinetic Measurements. The dihydroxylamine I (1 mol) was suspended in solvent (15 ml) and shaken with silver oxide (2.5 mol) for 90 min. The solution was filtered through anhydrous magnesium sulfate, diluted to 25 ml with solvent, and inserted in a thermostat at 35°. Samples (0.5 ml) were removed at intervals and diluted to 100 ml with solvent. A further dilution of 3–10 to 100 ml, depending on the initial concentration, was necessary before the concentration of the aminoquinone imine N-oxide IV could be conveniently measured from the intensity of its absorption at 396 mμ. The initial reading was taken 2 hr and the infinity reading 310 hr (from which the initial concentration of the triplet was calculated) after the commencement of shaking with silver oxide.

Addition of either the dihydroxylamine I (0.1 mol), *t*-butyl hydroperoxide (0.1 mol), or benzoyl peroxide (0.1 mol) after 3 hr failed to increase the inhibition time, and saturation of the solution with oxygen failed to reduce it.

Esr Measurements. The spectra were recorded using a Varian E-3 spectrometer in conjunction with a Varian (E-4557) variable-temperature unit, the sample temperature being measured with a copper–constantan thermocouple.

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