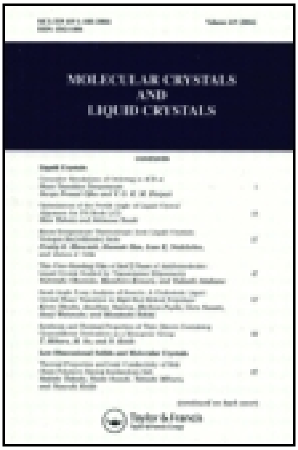

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ESR Study of 1,3-Phenylenebis(5-tert-Butyl-3-Phenyl-2-Phenylnitrene)

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ESR Study of 1,3-Phenylenebis(5-*tert*-Butyl-3-Phenyl-2-Phenylnitrene)

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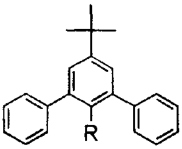
1,3-Phenylenebis(5-*tert*-butyl-3-phenyl-2-phenylnitrene) (***m*-4**) was generated by photolysis of the corresponding precursor diazide ***m*-3** in 2-MTHF at 3 K with a high-pressure Xe lamp, and its ESR spectrum was measured. The observed ESR spectrum was analyzed by computer simulation based on the eigenfield / exact diagonalization hybrid method to give two sets of zfs parameters: $|D| = 0.323\ \mathrm{cm}^{-1}$ and $|E| = 0.016\ \mathrm{cm}^{-1}$; $|D| = 0.340\ \mathrm{cm}^{-1}$ and $|E| = 0.011\ \mathrm{cm}^{-1}$. The temperature dependence of ESR signal intensity of ***m*-4** in the temperature region of 3–70 K was a linear relationship in the intensity vs reciprocal temperature plot, indicating that ***m*-4** is in a quintet ground state.

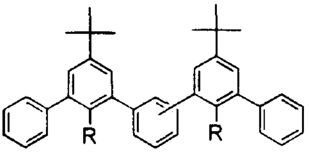
Keywords: nitrene; photolysis; ESR; quintet ground state

INTRODUCTION

Intramolecular ferromagnetic interaction between the unpaired electrons of open-shell organic molecules has attracted considerable interest for the development of high-spin organic molecules[1]. The basic principle leading to high-spin molecules is topological symmetry[2], and a wide variety of couplers have been investigated for synthesis of spin-ordering systems[3]. Among those, 1,3-phenylene has been shown to be one of the most useful in studies of 1,3-phenylene connected polycarbenes[4] and poly(triarylmethyl radical)s (Rajca polymer)[5]. However, these polycarbenes and polyradicals have a fundamental disadvantage that failure of generation of carbene or radical centers and their decomposition give an interruption of the ferromagnetic coupling leading to a significant reduction in their spin quantum number S. By using poly(1,3-phenylene)-based polyradicals or polynitrenes, we can avoid such a structural disadvantage. As a first step of our approach to poly(1,3-phenylene)-based polymer ferromagnets[6], we have generated 1,3- (***m*-4**) and 1,4-phenylenebis(5-*tert*-butyl-3-phenyl-2-phenylnitrenes) (***p*-4**) and investigated their ESR spectra. Although a variety of polynitrenes have been reported[7], 1,3-phenylene coupled dinitrenes have not been investigated so far. Herein we report the results.



1 R = N_3
2 R = $\underset{\bullet}{N}\bullet$



***m*, *p*-3** R = N_3
***m*, *p*-4** R = $\underset{\bullet}{N}\bullet$

EXPERIMENTS

Azide precursors **1** and *m*- and *p*-**3** were synthesized via diazonium salt from the corresponding aryl amines which were prepared in our previous report[8]. Also, 1,4-bis(2-amino-5-*tert*-butylbiphenyl)benzene, the corresponding precursor of *p*-**3**, was obtained by a similar procedure. Their structures were confirmed with ^{1}H and ^{13}C NMR and FT-IR spectra and elementary analysis.

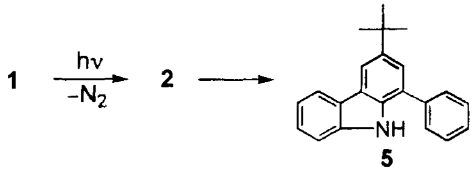
Photolysis of the azide precursors was carried out in 2-MTHF at 3 K by using a high-pressure Xe lamp (500 W). ESR measurements were carried out in the temperature region of 3–70 K. Photolysis of **1** at room temperature was carried out in benzene.

RESULTS AND DISCUSSION

Photolysis of 1

The generation, ESR spectrum, and stability of mononitrene **2** at cryogenic temperature were first investigated. A few minutes photoirradiation gave a typical mononitrene ESR spectrum at 676 mT, along with radical impurities at

337 mT. In the temperature region of 3–70 K, the mononitrene was thermally stable. Analysis of the nitrene ESR spectrum was carried out by computer simulation based on the eigenfield / exact diagonalization hybrid method[9]. The following spin Hamiltonian parameters were used: $S = 1$ (triplet spin state), $g = 2.003$, the zfs parameters, $|D| = 0.934$ cm^{-1} and $|E| = 0$ cm^{-1}, and the line width (ΔH) = 5.2 mT. Photolysis of **1** in benzene for 1.5 h with a Xe lamp (500 W) at room temperature gave 4-*tert*-butyl-2-phenylcarbazole (**5**) in 42 % yield. The structure was determined by IR, ^{1}H NMR, mass spectra, and elemental analysis.



Photolysis of *m*-3

Dinitrene ***m*-4** was generated by photolysis of diazide ***m*-3**. Since ***m*-3** showed λ_{max} at 245 nm (ε 66300 dm^3 mol^{-1} cm^{-1}) (in CH_2Cl_2), the selected light with the wavelength of 310±30 nm from a Xe lamp (500 W) was used in photolysis of ***m*-3**. Photoirradiation was carried out for ca. 1.5 h. The observed ESR spectrum is shown in FIGURE 1(a). The dominant peaks appear at 24, 44, 83, 183, 227, 310, and 555 mT. The peak at 340 mT (R) is due to radical impurities and the peak at 677 mT (N) to the mononitrene. The observed spectrum was analyzed by computer simulation in the same manner as for mononitrene **2**, showing that there are two conformers for ***m*-4** in 2-MTHF at cryogenic temperature. The spin Hamiltonian parameters for those are $S = 2$ (quintet spin state), $g = 2.003$, $|D| = 0.323$ cm^{-1}, and $|E| = 0.016$ cm^{-1} ($\Delta H = 6.0$ mT) (FIGURE 1(c)), and $S = 2$ (quintet spin state), $g = 2.003$, $|D| = 0.340$ cm^{-1}, and $|E| = 0.011$ cm^{-1} ($\Delta H = 6.0$ mT) (FIGURE 1(d)), respectively. When the former and latter spectra are superimposed in the ratio of 2 : 1, the spectrum shown in FIGURE 1(b) is obtained. FIGURE 1(e) shows the angular dependence of the resonance fields for the Euler angles used to obtain

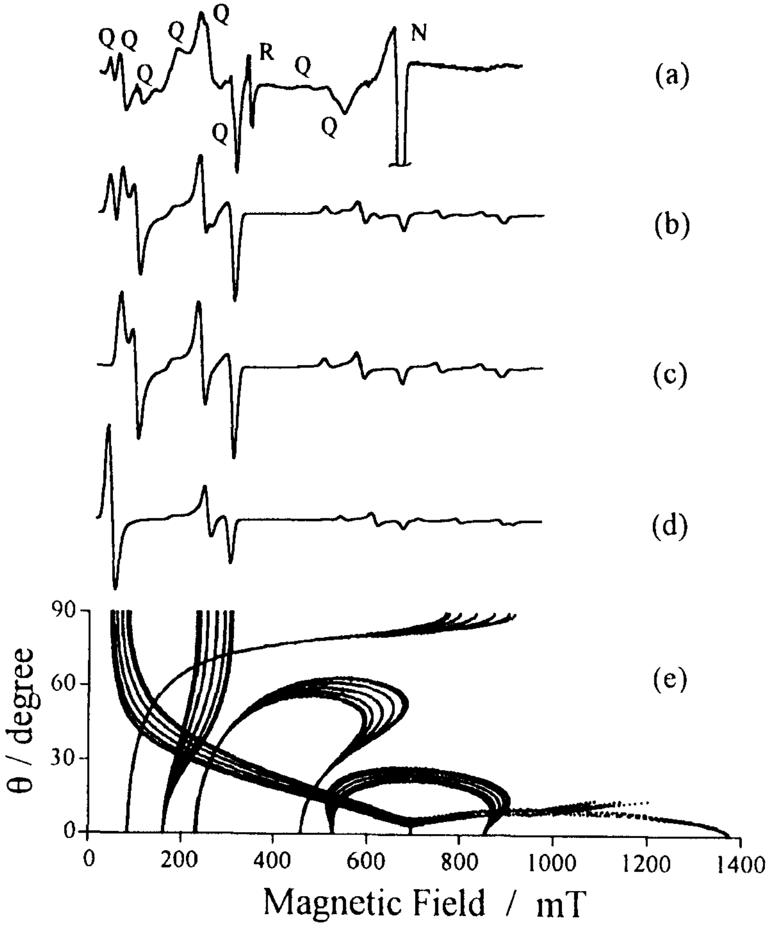


FIGURE 1. ESR spectra after photolysis of ***m*-3** in 2-MeTHF glass matrix at 20 K. (a) The observed spectrum. Q : Quintet; N : mononitrene triplet; R : radical. (b) The spectrum reconstructed by superimposing the spectra shown in Figures 1(c) and 1(d) in a 2 : 1 ratio. (c) The simulated spectrum reconstructed using $|D|$ = 0.323 cm^{-1}, $|E|$ = 0.016 cm^{-1}. (d) The simulated spectrum reconstructed using $|D|$ = 0.340 cm^{-1}, $|E|$ = 0.011 cm^{-1}. (e) The angular dependence of the resonance fields for the Euler angles θ used to obtain the simulated spectrum in Figure 1(c).

the simulated spectrum in FIGURE 1(c). This simulated ESR spectrum fits satisfactorily with the observed one at 0–310 mT, but the agreement is less satisfactory at 310–1000 mT. In the high field region, the resonance field for each allowed transition is more sensitive to a slight change in the fine-structure parameter D compared with those in the low-field region. Therefore, further accurate agreement between the observed and simulated spectra is difficult.

The temperature dependence of the ESR signal intensity for ***m*-4** was measured. The peak at 310 mT in FIGURE 1(a) was followed. The intensity vs reciprocal temperature plot showed a linear relationship (FIGURE 2), indicating that dinitrene ***m*-4** is in the quintet ground state. Interestingly, this dinitrene was thermally stable up to the temperature at which 2-MTHF began to melt (~80 K).

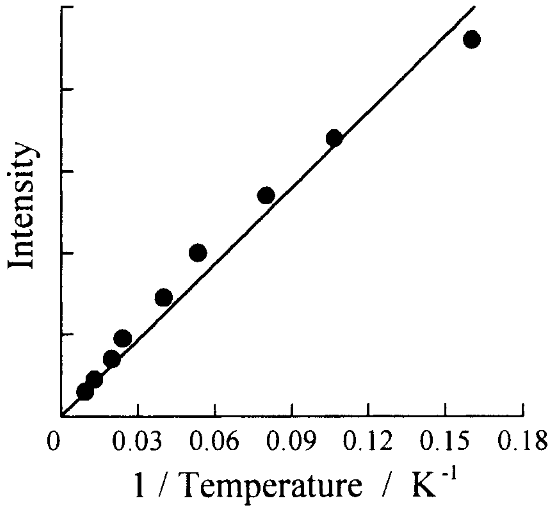
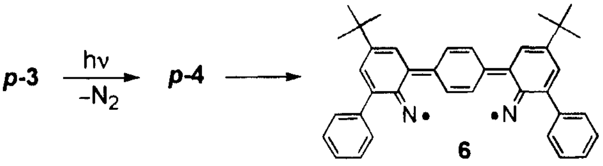


FIGURE 2. ESR signal intensity vs reciprocal temperature plot of ***m*-2**. The peak at 310 mT in Figure 1(a) was followed.

Photolysis of *p*-3

To determine the intramolecular exchange interaction, dinitrene ***p*-4** was also generated from ***p*-3** in the same manner as for ***m*-3**. Dinitrene ***p*-4** is theoretically converted to a quinonoidal dinitrene **6** in the excited triplet state[7].



Photolysis of ***p*-3** was carried out in the same manner as for ***m*-2**. The observed ESR spectrum at 50 K was shown in FIGURE 3. The dominant peaks appear at 246, 262, 271, and 304 mT. The peaks at 339 (R) and 668 mT (N) are due to radical impurities and mononitrene, respectively. The temperature dependence of signal intensity was investigated for the four peaks indicated by arrows. In the temperature region below 15 K, the four peaks

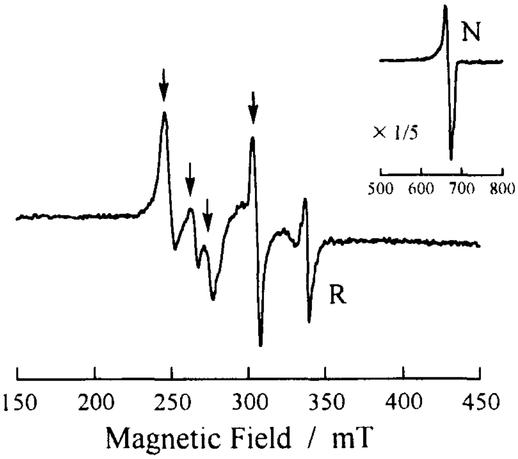
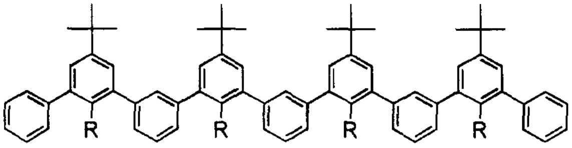


FIGURE 3. ESR spectrum after photolysis of ***p*-3** in 2-MTHF glass matrix at 50 K. N : Mononitrene triplet; R : radical.

disappeared completely, and in 15–40 K, their intensity of ESR signal increased with raising temperature. These ESR results indicate that the ground state is singlet. Although the ESR spectrum in FIGURE 3 was analyzed by computer simulation, assuming that it is a triplet spin state ($S = 1$), we could not obtain satisfactory agreement. Therefore, we could not confirm that the observed spectrum was due to the lowest excited triplet state of **6**.

Photolysis of Tetraazide 7

Furthermore, we prepared tetraazide 7 from the corresponding tetraamine compound[8], and its photolysis was carried out in the same manner as for ***m*-2**. The observed ESR spectrum is shown in FIGURE 4. It was similar to that of ***m*-2**, suggesting that photolysis of 7 was incomplete or tetranitrene **8** was unstable. Further investigation is in progress.



7 R = N_3
8 R = $\ddot{N}\cdot$

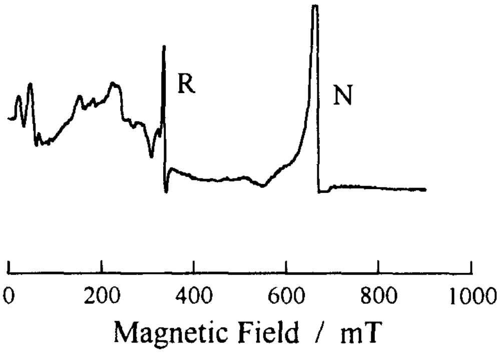


FIGURE 4. ESR spectrum after photolysis of 7 in 2-MTHF glass matrix at 20 K. N : Mononitrene triplet; R : radical.

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