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2,2′-(1,3-Phenylene)bis(4-*t*-butyl-6-phenylphenylnitrene): An ESR Study of a Quintet Dinitrene Coupled with 1,3-Phenylene

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4-*t*-Butyl-2,6-diphenylphenylnitrene and 2,2′-(1,3-phenylene)bis(4-*t*-butyl-6-phenylphenylnitrene) were generated by the phyolysis of the corresponding mono- and diazides and studied by ESR spectroscopy.

A wide variety of polyradicals and polycarbenes have been investigated for the synthesis of spin-ordering systems,[1] and it has been shown that the selection of couplers connecting the spin sites is particularly important for realizing high-spin states. In this work, we studied mononitrene **1c**, dinitrene **2c**, and tetranitrene **3c** by ESR as a part of work towards ferromagnetic poly(1,3-phenylene)-based polynitrenes and polyradicals (Chart 1).[2] Although a variety of polynitrenes have so far been studied,[3] poly(1,3-phenylene)-based polynitrenes have not been reported. We herein report on the ESR spectra of **1c** and **2c**.

Photolysis of 1b. Upon a few minutes photolysis of **1b** in 2-MTHF at 3 K with a high-pressure Xe lamp (500 W), a typical mononitrene ESR spectrum was observed at 676 mT, along with radical impurity at 337 mT. In the temperature range of 3–80 K, the mononitrene was stable and showed no detectable decomposition. An analysis of the nitrene ESR spectrum by computer simulation based on the eigenfield/exact diagonalization hybrid method gave $S = 1$ (triplet spin state), $g = 2.003$, the zfs parameters, $|D| = 0.934$ cm^{-1} and $|E| = 0$ cm^{-1} (ΔH = 5.2 mT).[4] The magnitude of 0.934 cm^{-1} for $|D|$ and $|E| = 0$ cm^{-1} are similar to those for phenylnitrene ($|D| = 0.99$ cm^{-1} and $|E| \simeq 0$ cm^{-1}).[5]

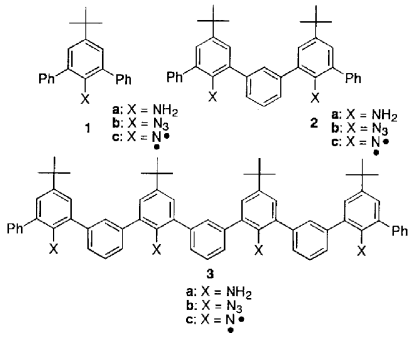

Chart 1.

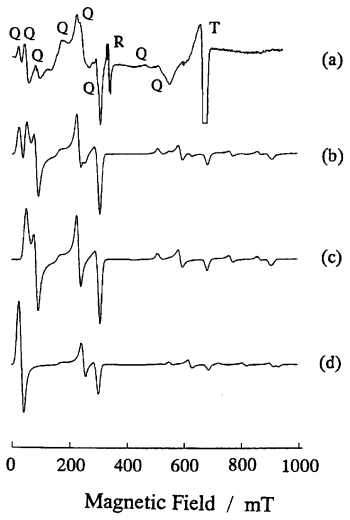

Fig. 1. ESR spectra recorded at 20 K after photolysis of **3b** in 2-MTHF glass matrix at 3 K. (a) The observed spectrum. Q, N, and R refer to quintet, mononitrene, and radical, respectively. (b) The spectrum reconstructed by superimposing Figs. 1(c) and 1(d) in a 2 : 1 ratio. (c) Spectrum simulated using $|D| = 0.323$ cm^{-1} and $|E| = 0.016$ cm^{-1}. (d) Spectrum simulated using $|D| = 0.340$ cm^{-1} and $|E| = 0.011$ cm^{-1}.

Photolysis of **1b** at 20 °C for 1.5 h with a high-pressure Xe lamp gave 1-phenyl-3-*t*-butylcarbazole (**4**) in 42% yield. The formation of **4** can be easily explained by the well-known cyclization of arylnitrene to give carbazoles.[6]

Photolysis of 2b. Dinitrene **2c** was generated by the photolysis of diazide **2b**. Since **2b** had λ_{max} at 245 nm (in CH_2Cl_2), the selected light with a wavelength of 310 ± 30 nm from a high-pressure Xe lamp was used for the photolysis of **2b**. Upon photolysis for ca.1.5 h at 3 K, an ESR spectrum shown in Fig. 1(a) was observed. Dominant peaks appeared at 24, 44, 83, 183, 227, 310, and 555 mT, while the peak due to mononitrene appears at 677 mT and the peak due to radical impurities at 340 mT. Simulation of the spectrum indicated the presence of two major conformers. The spin Hamiltonian parameters for those isomers 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) (Fig. 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) (Fig. 1(d)), respectively. When the former and latter spectra are superimposed in a ratio of 2:1 (Fig. 1(b)), satisfactry agreement with the experimental is observed. However, at 310–1000 mT the agreement is less satisfactory because in the high-field region the resonance field for each allowed transition is more sensitive to a slight change in the fine-structure parameter $|D|$ than in the low-field region.

The temperature dependence of the intensity in the ESR signals of **2c** was studied by monitoring the peak height at 310 mT in Fig. 1(a). As shown in Fig. 2, a linear relationship of the ESR signal intensity vs $1/T$ was observed, showing whether **2c** is in a quintet ground state or a weak exchange coupled spin system

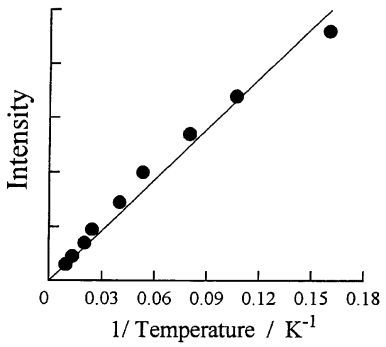

Fig. 2. ESR signal intensity vs 1/T plots for **2c**. For the plots the peak at 310 mT in Fig. 1(a) was used.

in which the quintet, triplet and singlet spin states are nearly degenerate. However, the possibility of the latter case can be reasonably ruled out because 1,3-phenylene is a suitable spin coupler with a well known large exchaneg interaction.[7,8] Therefore, we can safely conclude that **2c** is in a quintet ground state. Dinitrene **2c** was thermally stable up to the melting point of 2-MTHF (ca. 80 K).

Photolysis of Tetraazide 3b. The photolysis of **3b** in 2-MTHF was carried out at 3 K in the same manner as for **2b**. The observed spectrum is similar to that of **2c**, indicating that the dominant species observed is a quintet. This result suggests that the irradiation of **3b** with a Xe lamp does not induce complete decomposition of all four azide groups, or that the nonet species is unstable even at such a low temperature to decompose to a quintet species. Irradiation was also carried out with a 351 nm line of a CW Ar ion laser, but this gave almost the same results as described above.

In conclusion, **1c** and **2c** were generated by the photolysis of **1b** and **2b** and studied by ESR spectroscopy. ESR spectrtoscopic analyses showd that **2c** is in a quintet ground state. On the other hand, the photolysis of **3b** did not show any detectable formation of **3c**.

Experimental

4-*t*-Butyl-2,6-diphenylphenyl Azide (1b). To a solution of **1a**[10] (3.01 g, 10.0 mmol) in EtOH (70)–H_2O (70)–H_2SO_4 (10 cm^3) was added dropwise a solution of $NaNO_2$ (1.38 g, 20.0 mmol) in H_2O (10 cm^3) at 0 °C; the mixture was stirred at 0 °C for 1 h. After a solution of NaN_3 (1.43 g, 22 mmol) in H_2O (11 cm^3) was added, the mixture was stirred at 0 °C for 1 h and poured into ice–water. Extraction with CH_2Cl_2, drying, evaporation, and chromatography (silica gel, 1:3 benzene-hexane) gave **1b** in 80% yield. Colorless needles (EtOH); mp 58–60 °C; IR (KBr) 2130 cm^{-1} (N_3); UV-vis (CH_2Cl_2) 243 nm (ε 33300); ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 9H), 7.32 (s, 2H), 7.40 (t, J = 7.3 Hz, 2H), 7.47 (t, J = 7.3 Hz, 4H), 7.52 (d, J = 7.3 Hz, 4H). Found: C, 80.61; H, 6.34; N, 12.97%. Calcd for $C_{22}H_{21}N_3$: C, 80.70; H, 6.47; N, 12.83%.

2,2″-Diazido-5,5″-di-*t*-butyl-3,3″-diphenyl-1,1′ : 3′,1″-terphenyl (2b). This compound was prepared from **3a**[10] in a similar manner to that mentioned above. Yield 48%; colorless prisms (ether–EtOH); mp 142–144 °C; IR (KBr) 2100 cm^{-1} (N_3); UV-vis (CH_2Cl_2) 245 nm (ε 66300); ^{1}H NMR ($CDCl_3$) δ 1.36 (s, *t*-Bu, 18H), 7.34 (d, J = 2.4 Hz, ArH, 2H), 7.40 (d, J = 2.4 Hz, ArH, 2H), 7.42 (t, J = 7.3 Hz, ArH, 2H), 7.47 (t, J = 7.3 Hz, ArH, 4H), 7.53–7.56 (m, ArH, 7H), 7.67 (s, 1H). Found: C, 79.02; H, 6.32; N, 14.43%. Calcd for $C_{38}H_{36}N_6$: C, 79.14; H, 6.29; N, 14.57%.

2,2″,2‴,2⁗,2⁗′-Tetraazido-5,5″,5‴,5⁗,5⁗′-tetra-*t*-butyl-3,3⁗′-diphenyl-1,1′ : 3′,1″ : 3″,1‴ : 3‴,1⁗ : 3⁗,1⁗′ : 3⁗′,1⁗″ : 3⁗″,1⁗‴-septiphenyl (3b). This compound was prepared from **3a**[10] in a similar manner to that mentioned above. Yield 14%; colorless prisms (CH_2Cl_2–EtOH); mp 159–160 °C; IR (KBr) 2100 cm^{-1} (N_3); UV-vis (CH_2Cl_2) 246 nm (ε 140000); ^{1}H NMR ($CDCl_3$) δ 1.356 (s, *t*-Bu, 18H), 1.362 (s, *t*-Bu, 18H), 7.33 (d, J = 2.4 Hz, ArH, 2H), 7.39 (d, J = 2.4 Hz, ArH, 2H), 7.40–7.42 (m, ArH, 6H), 7.47 (t, J = 7.3 Hz, ArH, 4H), 7.53–7.57 (m, ArH, 13H), 7.69 (s, ArH, 2H), 7.70 (s, ArH, 1H). Found: C, 77.82; H, 6.14; N, 15.44%. Calcd for $C_{70}H_{66}N_{12}$: C, 78.18; H, 6.19; N, 15.63%.

ESR Measurements of Nitrenes. The photolysis of azide precursors was carried out in the cavity of an ESR instrument at 3 K. ESR spectra were recorded with a JEOL TE300 spectrometer.

Photolysis of 1b. A solution of **1b** (490 mg, 1.50 mmol) in benzene (15 cm^3) in a Pyrex tube was degassed and the tube was sealed off. Photolysis was carried out at 20 °C for 1.5 h with a high-pressure Xe lamp (500 W). After the mixture was evaporated, the residue was chromatographed on silica gel with 1:2 CH_2Cl_2–hexane to give 1-phenyl-3-*t*-butylcarbazole in (**4**) 42% yield.

4: colorless prisms (MeOH); mp 105–107 °C; IR (KBr) 3433 cm^{-1} (NH); HR-FABMS m/z for $C_{22}H_{21}N$ 299.1674. Found, 299.1688; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, *t*-Bu, 9H), 7.21–7.25 (m, ArH, 1H), 7.38–7.39 (m, ArH, 2H), 7.44 (t, J = 7.8 Hz, ArH, 1H), 7.51 (d, J = 2.0 Hz, ArH, 1H), 7.56 (t, J = 7.8 Hz, ArH, 2H), 7.71 (d, J = 7.8 Hz, ArH, 2H), 8.08 (d, J = 2.0 Hz, ArH, 1H), 8.12 (d, J = 7.8 Hz, ArH, 1H), 8.21 (br s, ArH, 1H); Found: C, 88.00; H, 6.97; N, 4.25%. Calcd for $C_{22}H_{21}N$: C, 88.25; H, 7.07; N, 4.68%.

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8 For example, the J/k_B's of 1,3-phenylenebis(phenylmethylene)[7] and 1,3-phenylenebis(*t*-butylaminoxyl)[9] are reported to > 300 K, respectively.

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