ORGANIC
LETTERS

1999
Vol. 1, No. 5
741−743

Triplet State of Würster's Blue-Based Di(cation radical)

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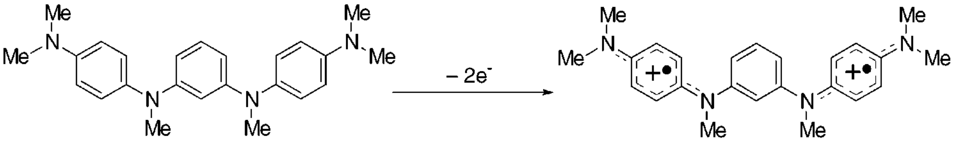
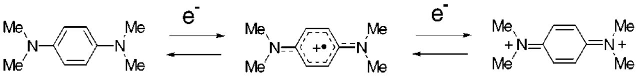
Received June 10, 1999

ABSTRACT



***N*,*N*′-bis[4-(dimethylamino)phenyl]-*N*,*N*′-dimethyl-1,3-benzenediamine was prepared in order to investigate the corresponding Würster blue-based di(cation radical). The generated diradical was found to be a ground-state triplet, and moreover, the observed ESR spectrum had no definite fine structure, suggesting a mixture of some conformers.**



1 $\quad$ **1^+** $\quad$ **1^{2+}**

Würster's blue cation radical (**1^+**), which is generated by one-electron oxidation of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD; **1**) is one of the famous chemically and thermally stable radicals and has long been investigated from different angles.[1] Its stability is ascribed to the electron delocalization in its semiquinone structure. Despite its stability, however, the use of this radical as a spin-containing unit for high-spin molecules[2] has not been reported so far.[3] This is probably because the coupling reaction between aryl

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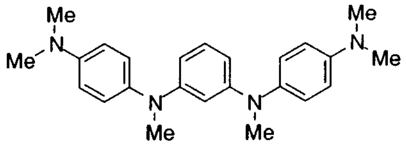
(3) Only one example was found; see: Nakamura, Y.; Iwamura, H. *Bull. Chem. Soc. Jpn*. **1993**, *66*, 3724.

10.1021/ol990727w CCC: $18.00

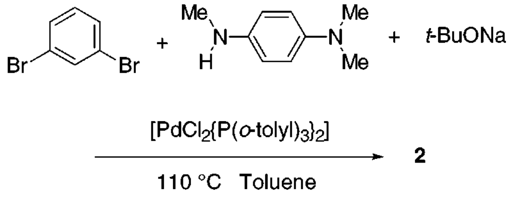
bromide and *N*-methylarylamine has not proceeded in the usual copper-catalyzed reaction. However, the recent progress in the Pd-catalyzed C−N coupling reaction made the synthesis of this kind of molecule possible.[4] In this paper, we report the synthesis of *N*,*N*′-bis[4-(dimethylamino)-phenyl]-*N*,*N*′-dimethyl-1,3-benzenediamine (**2**), which is expected to be easily converted into a triplet di(cation radical), and also the electronic structures of the generated di(cation radical).



2

The synthesis of **2** is carried out by following the procedure shown in Scheme 1 .[5] The product is isolated by column chromatography (SiO_2; EtOAc−hexane, 2:1) in 36% yield. Analytical data confirm the proposed structure.[6] It is noted that the usual copper-catalyzed reaction showed no reaction in each case for the starting materials.

Scheme 1



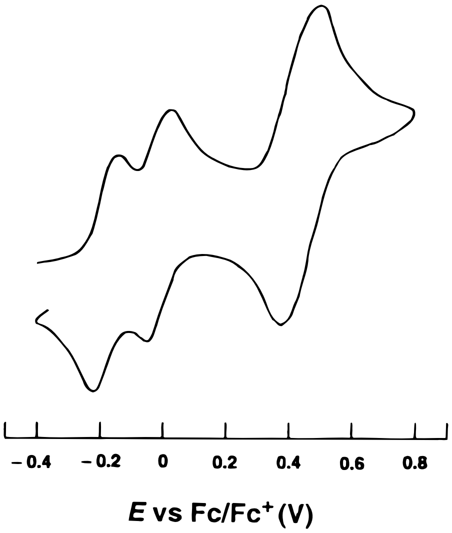


Figure 1. Cyclic voltammogram of **2** in MeCN at 25 °C, at a scan rate of 100 mV/s.

Electrochemical oxidation of **2** by cyclic voltammetry (CV) shows three pairs of redox waves (Figure 1). The first two oxidation peaks are reversible and are assigned to one-electron-transfer processes with redox peak separations of 60 and 65 mV, respectively. The third redox wave has a peak-to-peak separation of 105 mV, which is larger than the theoretical value of 59 mV, and the peak current is almost twice as large as those of the first two oxidation peaks. These results indicate that this redox wave is an overlap of two redox single-electron waves with a very small redox potential difference, in contrast with the case for *N*,*N*′-bis[4-(diphenylamino)phenyl]-*N*,*N*′-diphenyl-1,3-diaminobenzene.[2l] These results show that oxidation states +1 to +4 of **2** have lifetimes longer than a few seconds in solution at 25 °C. The redox potentials of **2** are summarized in Table 1 together with those of the related compounds measured under the same conditions. As compared with the oxidation potentials of **1**, it is expected that two successive oxidation steps generate the di(cation radical) $\mathbf{2}^{2+}$ via one-electron removal of each peripheral *p*-phenylenediamine (PD) moiety and the third quasi-two-electron oxidation leads to bis(quinoid) species ($\mathbf{2}^{4+}$). The decrease of electron-donating ability by fusion of two PD units is attributed to the *m*-phenylene linker, as indicated by the first redox potential of *N*-phenyl-*N*,*N*′,*N*′-trimethyl-*p*-phenylenediamine (PTMPD; **3**).

Table 1. Redox Potentials of **2** (V) and Their Related Compounds[a]

compd	$E_1°′$	$E_2°′$	$E_3°′$
1	−0.29	0.29	
2	−0.19	−0.01	0.44[b]
3	−0.13	0.38	

[a] Conditions: 0.1 M *n*-Bu_4NClO_4 in MeCN, potential vs Fc/Fc^+, Pt electrode, 25 °C, scan rate 100 mV/s. [b] Quasi-two-electron oxidation.

Chemical oxidation of **2** (1 mM) with less than 1 equiv of thianthrenium perchlorate[7] in *n*-butyronitrile at −78 °C yields a bluish green solution, which shows an ESR spectrum with a poorly resolved six-line pattern resulting from some ^{14}N nuclei and ^{1}H nuclei of *N*-methyl groups[1c] at −150 °C. Although we failed to determine the hyperfine coupling

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(4) (a) Beller, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1316. (b) Hartwig, J. F. *Synlett* **1997**, 329. (c) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046. (d) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (e) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852.

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(6) Data for **2**: white solid; mp 135−136 °C; ^{1}H NMR ($CDCl_3$) δ 2.92 (12H, s), 3.18 (6H, s), 6.16 (2H, dd, J = 8.1 and 2.2 Hz), 6.25 (1H, t, J = 2.2 Hz), 6.72 (4H, d, J = 8.8 Hz), 6.95 (1H, t, J = 8.1 Hz), 7.05 (4H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 40.5, 41.1, 102.4, 105.9, 113.7, 126.2, 129.0, 139.2, 147.6, 150.8. Anal. Calcd for $C_{24}H_{30}N_4$: C, 76.97; H, 8.07; N, 14.96. Found: C, 77.04; H, 7.91; N, 14.70.

(7) Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

(8) The singlet−triplet energy gap, ΔE_{S-T}, is calculated to be 51.5 kcal/mol. However, no electron correlation is taken into consideration in the RHF calculations for the singlet state of $\mathbf{2}^{2+}$. Hence, the actual value of ΔE_{S-T} is expected to be smaller. See: Ito, A.; Miyajima, H.; Yoshizawa, K.; Tanaka, K.; Yamabe, T. *J. Org. Chem.* **1997**, *62*, 38.

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constants of $\mathbf{2}^{+}$, it is suggested that the unpaired spin is localized on only one of the two PD units because the same ESR spectrum is obtained from one-electron oxidation of **3**. Treatment of **2** in *n*-butyronitrile (1 mM) with 2 equiv of oxidant at −78 °C in the presence of 5% trifluoroacetic acid results in the corresponding blue di(cation radical) $\mathbf{2}^{2+}$. The ESR spectrum of $\mathbf{2}^{2+}$ at −150 °C (Figure 2) shows a two-line pattern with no definite fine structure. Direct spectral evidence for the triplet state of $\mathbf{2}^{2+}$ is obtained from the forbidden $\Delta M_S = \pm 2$ resonance at half-field (inset of Figure 2). It should be noted that this spectrum is observed even when 1 equiv of oxidant is used, suggesting a disproportionation reaction such as $2\ \mathbf{2}^{+} \rightarrow \mathbf{2}^{0} + \mathbf{2}^{2+}$. This di(cation radical) is stable for several hours in solution at ≤−80 °C but decays rapidly at higher temperature, and finally the resulting solution exhibits the same ESR spectrum as $\mathbf{2}^{+}$ observed at −150 °C. Given that the zero-field splitting is estimated by the peak-to-peak line width of $\Delta M_S = \pm 1$ resonance, the $|D/hc|$ value of 0.0032 cm^{-1} corresponds to an average distance between the two radical centers of about 9.3 Å within the point dipole approximation. The temperature dependence of the intensity for the signal of $\Delta M_S = \pm 2$ resonance demonstrates a linear correlation to the reciprocal of the temperature, indicating a triplet ground state or degeneracy of singlet and triplet states for $\mathbf{2}^{2+}$ (Figure 3).

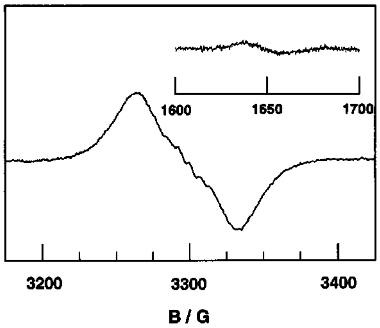

Figure 2. ESR spectrum of $\mathbf{2}^{2+}$ in *n*-butyronitrile/TFA(5%) at −150 °C. The central hyperfine-structured line in the $\Delta M_S = \pm 1$ resonance is due to some doublet impurity.

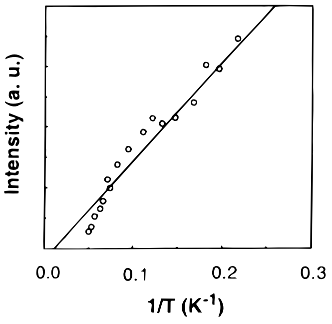

Figure 3. Temperature dependence of the signal intensity for the $\Delta M_S = \pm 2$ resonance of $\mathbf{2}^{2+}$ in *n*-butyronitrile/TFA(5%).

In $\mathbf{2}^{2+}$, at least, two conformers are expected from its molecular structure. Their triplet states[8] are obtained by semiempirical MO calculations (PM3-UHF).[9] The fully optimized structures are shown in Figure 4. The peripheral PD units retain coplanarity and have large torsion angles of about 60° to the *m*-phenylene plane. Moreover, both PD units have the semiquinone structure, in good agreement with the X-ray structure of $\mathbf{1}^{\bullet+}$ perchlorate salt.[1j] The unpaired electrons are delocalized over all the atoms through spin polarization. Note that the spin densities at the nitrogen atoms of dimethylamino groups (ca. 0.6) are large compared with that at the central nitrogen atoms (ca. 0.3). More importantly, the energy difference between two conformers is estimated to be only 2.2 kcal/mol. This indicates that the two conformers are detectable in the ESR measurements. Furthermore, the distances between the centers of two PD moieties in the optimized structures of two conformers **A** and **B** corresponds to $|D/hc|$ values of 0.0029 and 0.0035 cm^{-1}, respectively, under the point dipole approximation. This situation may cause an overlap of the spectra, leading to no definite fine structure.

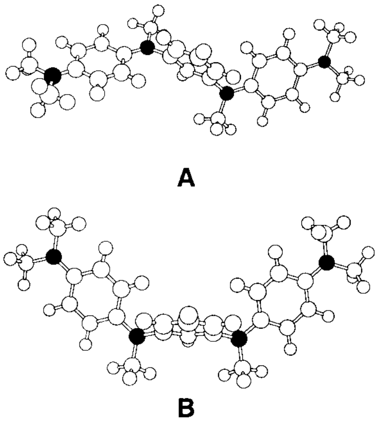

Figure 4. Overviews of the PM3-optimized structures for two conformers of $\mathbf{2}^{2+}$ in the triplet state. Conformer **A** lies 2.2 kcal/mol below conformer **B**.

The present results suggest that Würster's blue-based di(cation radical), $\mathbf{2}^{2+}$, has a triplet ground state. The reason for the unexpected instability of $\mathbf{2}^{2+}$ to ambient temperature is unknown at the present stage. Preparation of an isolable, stable poly(cation radical) of this type is currently the subject of our investigation.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan and is a part of the project of the Institute for Fundamental Chemistry ("Research for the Future" Program), supported by the Japan Society for the Promotion of Science (JSPS Grant No. RFTF96P00206). Numerical calculations were partly carried out at the Supercomputer Laboratory of the Institute for Chemical Research of Kyoto University.

OL990727W