Sci. USA **1988**, *85*, 5409–5413; c) R. Roy, D. Zanini, J. Meunier, A. Romanowska, *J. Chem. Soc. Chem. Commun.* **1993**, 1869–1873.

[11] C. Grandjean, C. Rommens, H. Gras-Masse, O. Melnyk, *Tetrahedron Lett.* **1999**, *40*, 7235–7238.

[12] Such a labelling is envisaged to study the mannose-receptor mediated internalization of the constructs by flow cytometric or confocal analysis. We recently disclosed the fluorescein-labeling of related trees on this position: see ref. [11].

[13] G. B. Fields, R. L. Noble, *Int. J. Pept. Protein Res.* **1990**, *35*, 161–214.

[14] a) O. Melnyk, J.-S. Fruchart, L. Bourel, H. Gras-Masse, FR-9905024, **1999**; b) J.-S. Fruchart, H. Gras-Masse, O. Melnyk, *Tetrahedron Lett.* **1999**, *40*, 6225–6228.

[15] The hydrazino function might not have survived the HF cleavage conditions required by the Boc/benzyl strategy: D. Bonnet, F. Samson, C. Rommens, H. Gras-Masse, O. Melnyk, *Int. J. Pept. Protein Res.* **1999**, *54*, 270–278; for RP-HPLC purification, isopropanol was used as solvent as α-hydrazinoacetyl peptides are unstable in CH_3CN/TFA mixtures.

[16] L. J. Wilson, M. Li, D. E. Portlock, *Tetrahedron Lett.* **1998**, *39*, 5135–5138.

[17] For examples of hydrazone chemical ligations, see: a) T. P. King, S. W. Zhao, T. Lam, *Biochemistry* **1986**, *25*, 5774–5779; b) J. C. Spetzler, J. P. Tam, *Int. J. Pept. Protein Res.* **1995**, *45*, 78–85; c) O. Melnyk, M. Bossus, D. David, C. Rommens, H. Gras-Masse, *J. Pept. Protein Res.* **1998**, *52*, 180–184; d) F. Samson, D. Bonnet, C. Rommens, H. Gras-Masse, O. Melnyk, *J. Pept. Sci.* **1999**, *5*, 352–359.

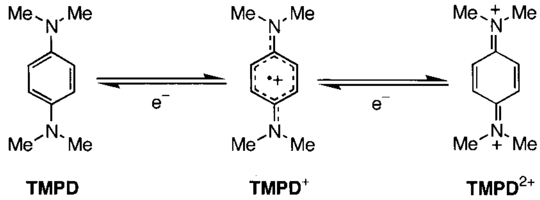
[18] For precise thioetherification procedure, see: C. Grandjean, C. Rommens, H. Gras-Masse, O. Melnyk, *J. Chem. Soc. Perkin Trans. 1* **1999**, 2967–2976.

The Tetraaza[1.1.1.1]*m*,*p*,*m*,*p*-cyclophane Dication: A Triplet Diradical Having Two *m*-Phenylenediamine Radical Cations Linked by Twisted Benzenes[**]

Akihiro Ito, Yukiharu Ono, and Kazuyoshi Tanaka[*]

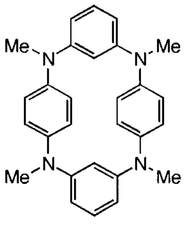
Many kinds of cyclophanes have been synthesized so far for the purpose of investigating the peculiar electronic and spectroscopic properties, which result from the interesting stereochemistry, as well as the effective binding properties for use as host molecules in molecular recognition chemistry.[1] Although carbon is the most common bridging element in useful macrocyclic compounds such as porphyrins[2] and calixarenes,[3] other elements such as nitrogen, oxygen, silicon, phosphorus, and sulfur can be used to obtain additional chemical and physical properties. Indeed, over the past few years, a considerable number of studies have been devoted to the syntheses of various heteroatom-bridged [1_n]cyclophanes.[4]

We are interested in aza-bridged cyclophanes[5] in connection with the chemistry of high-spin organic molecules; several cyclophane-based high-spin molecules have been prepared to date.[6] Chemically and thermally stable polyradicals often contain heteroatoms that serve as spin-bearing sites[7] and are connected to each other through *m*-phenylene units, which have proven to be effective ferromagnetic couplers.[8] For example, a *p*-phenylenediamine (PD), such as *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD; Scheme 1), can be readily converted by one-electron oxidation into a stable semiquinone radical (Wurster's blue), in contrast to the instability of ammonium radicals. Therefore, the use of this type of radical as a spin-bearing unit is pertinent to the exploitation of novel high-spin organic molecules.[9]



Scheme 1. Conversion of TMPD into the stable semiquinone radical (Wurster's blue) as well as the dication.

When PD is to be employed as a spin-bearing site, **1** is a promising precursor of high-spin azacyclophanes with the smallest ring size possible. In addition, **1** can be regarded as *m*-phenylene-tethered version of **2**. We have already reported the spin preference of **2**$^{2+}$ and also pointed out the presence of several conformational isomers.[10] On the other hand, **1** is anticipated to retain only one conformation in which the two PD moieties are juxtaposed. Such a conformation is not feasible for **2** because of steric repulsion between the methyl groups. Here, we report on the synthesis, structure, and redox properties of cyclophane **1**. Furthermore, the electronic structure of its dication is described on the basis of EPR and quantum-chemical studies.



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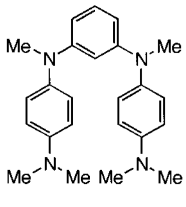

2

Palladium-catalyzed condensation of *m*-dibromobenzene with *N*,*N*′-dimethyl-*p*-phenylenediamine gives the desired **1** in an abysmal yield of 0.28%[11] (Scheme 2), but in a one-pot reaction. The UV/Vis spectrum of **1** in cyclohexane measured at room temperature shows two absorption maxima at λ_{max} = 236 and 302 nm, which are slightly blue-shifted to those of

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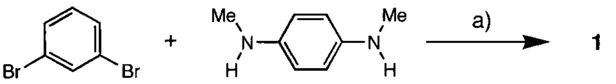


Scheme 2. Synthesis of **1**: a) NaO*t*Bu, $[PdCl_2[P(o\text{-tolyl})_3]_2]$, toluene, 100 °C, 16 h, 0.28 %.

TMPD.[12] Colorless plates were obtained by slow evaporation of a dilute solution of **1** in ethyl acetate at room temperature. The X-ray structure analysis (see the Experimental Section) designates an alternate *meta-para*-linked macrocyclic structure for **1** (Figure 1). Cyclophane **1** has an approximate C_{2v} symmetry, and the *m*-phenylene and *p*-phenylene planes are inclined in the range of 13–21° and 57–59°, respectively, to the plane defined by the four nitrogen atoms.

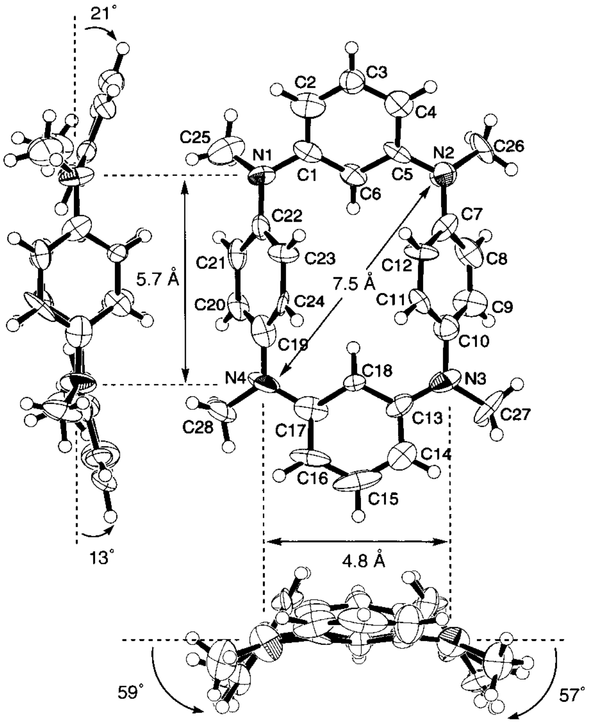


Figure 1. Side (top left and bottom right) and plan views (top right) of the molecular structure of **1** in the solid state. Thermal ellipsoids have been drawn at the 50 % probability level.

The density functional theory (DFT) calculations[13] indicate that the C_{2v}-symmetric structure is favored for a model compound of **1** in which the methyl groups at N are replaced by H ($\mathbf{1}_{NH}$). These results are in accordance with the X-ray crystal structure, except for a small inclination angle of the *m*-phenylene plane (3.0°).[14] More importantly, $\mathbf{1}_{NH}$ (and **1**) can be classified as a coextensive non-Kekulé molecule, judging from its frontier orbitals (HOMO and HOMO − 1), which are composed of two nonbonding MOs ($2a_2$ and $3b_1$) of *m*-phenylenediamine and a HOMO (e_{1g}) of benzene (Figure 2). Hence, when these two frontier MOs are singly occupied, a strong exchange interaction is expected; the energies of the triplet state of $\mathbf{1}_{NH}^{2+}$ (and $\mathbf{1}^{2+}$) lie well below those of the corresponding singlet state. In fact, the singlet–triplet energy difference, ΔE_{S-T}, for $\mathbf{1}_{NH}^{2+}$ is estimated to be 2.2 kcal mol^{-1}, indicating a ground-state triplet. The C_{2v}-symmetric structure of $\mathbf{1}_{NH}$ remains unchanged even in $\mathbf{1}_{NH}^{2+}$, and moreover two PD moieties are close to the semiquinone structure, judging from the optimized bond lengths of $\mathbf{1}_{NH}^{2+}$.

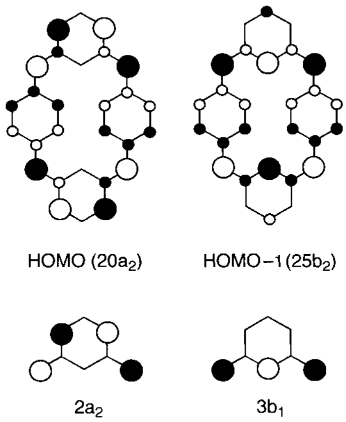


Figure 2. Schematic representation of the frontier orbitals for $\mathbf{1}_{NH}$ on the basis of BPW91/6-31G* calculations. These orbitals are depicted after the expansion of the nonplanar structure onto the plane of the page. Two nonbonding MOs ($2a_2$ and $3b_1$) of *m*-phenylenediamine are also shown at the bottom.

The cyclic voltammogram of **1** in acetonitrile clearly shows four redox couples at $E^{\circ\prime} = -0.03, +0.16, +0.47$, and $+0.62$ V (vs. ferrocene/ferrocenium (Fc/Fc$^+$)), which correspond to $\mathbf{1}^0/\mathbf{1}^+$, $\mathbf{1}^+/\mathbf{1}^{2+}$, $\mathbf{1}^{2+}/\mathbf{1}^{3+}$, and $\mathbf{1}^{3+}/\mathbf{1}^{4+}$, respectively (Figure 3). Whereas a quasi-two-electron transfer takes place in $\mathbf{2}^{2+} \rightarrow \mathbf{2}^{4+}$, the corresponding redox processes for **1** are two separate single-electron transfers, as expected from the macrocyclic structure of **1**. The redox potentials of **1** are summarized in Table 1 together with those of related compounds under the same conditions. Interestingly, the first and second redox potentials of **1** are approximately 0.16 V higher than those of **2**. The decrease of electron-donating ability in **1** is ascribed to the *m*-

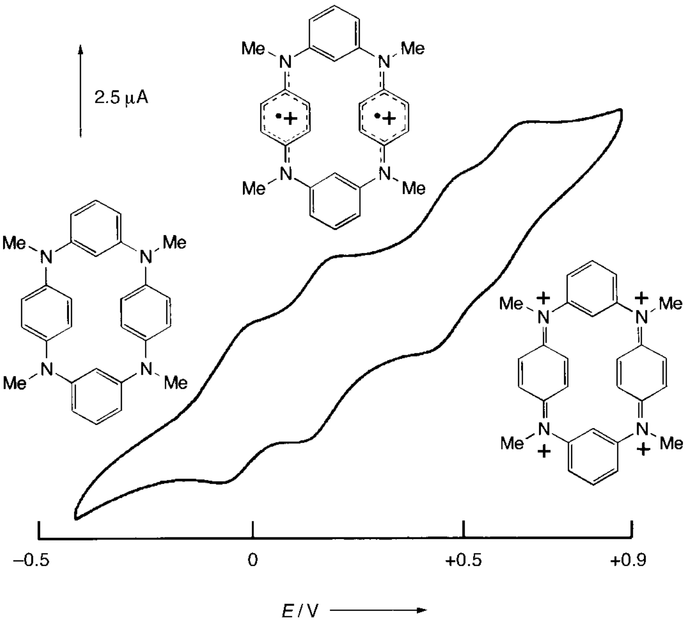


Figure 3. Cyclic voltammogram of **1** in MeCN at 25 °C (scan rate 100 mV s^{-1}).

Table 1. Redox potentials of **1** and related compounds.[a]

Compd	$E_1^{o\prime}$ [V]	$E_2^{o\prime}$ [V]	$E_3^{o\prime}$ [V]	$E_4^{o\prime}$ [V]
1	– 0.03 (– 0.12[b])	0.16 (0.14[b])	0.47 (0.50[b–d])	0.62
2	– 0.19	– 0.01	0.44[d]	
3[b], [15]	0.05	0.55		
4[b], [15]	– 0.09	0.20	0.64[d]	
TMPD	– 0.29	0.29		

[a] Conducting salt 0.1 M $n\mathrm{Bu_4NClO_4}$ in MeCN, potentials given versus Fc/Fc$^+$, Pt electrode, 25 °C, scan rate 100 mV s^{-1}. [b] Measured in CH_2Cl_2. [c] Redox behavior such as the formation and dissolution of chemisorbed hydride and oxide layers on the polycrystalline Pt electrode is observed in this two-electron transfer (C. H. Hamann, A. Hamnett, W. Vielstich, *Electrochemistry*, Wiley-VCH, Weinheim, **1998**, p. 222). [d] Quasi-two-electron oxidation.

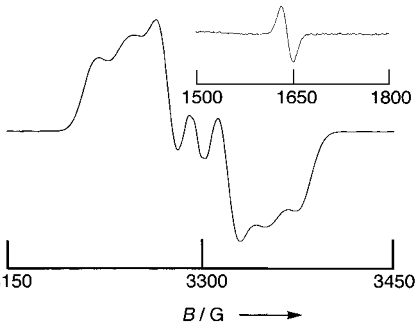
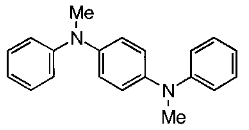


Figure 4. The X-band EPR spectrum of $\mathbf{1}^{2+}$ in *n*-butyronitrile/trifluoroacetate (99/1 v/v) at – 157 °C. The central line is due to some doublet impurity. Inset: The resonance for $\Delta M_S = \pm 2$ at – 157 °C.

phenylene tether. In addition, the donor ability of **1** is comparable to that of a linear *N*-methylated oligoaniline tetramer (**4**) rather than the dimer (**3**).[15]



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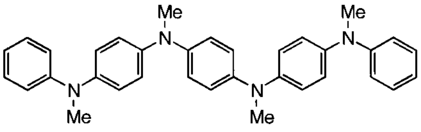

4

Chemical oxidation of **1** (1 mM) with less than one equivalent of tris(4-bromophenyl)aminium hexachloroantimonate[16] in *n*-butyronitrile at – 78 °C yields a blue solution which shows an ESR spectrum (– 157 °C) with a poorly resolved hyperfine structure resulting from ^{14}N and ^1H nuclei at the *N*-methyl groups. The *g* value of 2.0026 suggests fairly large spin densities at the *p*-phenylene units, since nitrogen-centered radicals are typically characterized by large deviation from the *g* value of the free electron (2.003 – 2.004).

When **1** in *n*-butyronitrile (1 mM) is treated with two equivalents of the same oxidant at – 78 °C in the presence of 1 % (v/v) trifluoroacetic acid, the corresponding dark blue di(cation radical) $\mathbf{1}^{2+}$ is obtained. The EPR spectrum of $\mathbf{1}^{2+}$ at – 157 °C (Figure 4) shows a definite six-line pattern characteristic of a randomly oriented non-axial triplet molecule, in contrast to the case of $\mathbf{2}^{2+}$. Corroborating evidence for the triplet state of $\mathbf{1}^{2+}$ is obtained from the resonance at half-field for the forbidden transition $\Delta M_S = \pm 2$ (inset of Figure 4). The generated dication is stable for several weeks in solution at – 78 °C, but decays gradually at higher temperature (lifetime ca. 5 min at room temperature); the resulting solution exhibits an EPR spectrum similar to that observed for $\mathbf{1}^{+}$ at – 157 °C.

Nevertheless, $\mathbf{1}^{2+}$ is far more stable than $\mathbf{2}^{2+}$. From the peak-to-peak linewidth of three pairs of bands, the zero-field parameters of the dipolar electron – electron interaction can be obtained for **1**: $|D| = 77.6$ G (0.0073 cm^{-1}) and $|E| = 7.5$ G (0.0007 cm^{-1}). The value of $|D|$ corresponds to an average distance between the two radical centers of about 7.1 Å within the point dipole approximation. This value is, however, larger than the distance between the centers of two *p*-phenylene moieties estimated from the X-ray structure analysis (ca. 5 Å). The average distance is rather close to the distance between the centers of the two *m*-phenylene moieties (ca. 7 Å). In fact, a reasonable *D* value of 0.0068 cm^{-1} calculated for $\mathbf{1}_{NH}{}^{2+}$ is obtained on the assumption that the largest dipole – dipole interaction is along the direction connecting the two *m*-phenylene moieties.[17] Hence, $\mathbf{1}^{2+}$ can be regarded as two *m*-PD radical cations linked by two *p*-phenylenes rather than two *p*-PD radical cations linked by two *m*-phenylenes. Note that the midpoints of the pairs of bands do not coincide, indicating anisotropy of the *g* factor: $g_{xx} = 2.0021$, $g_{yy} = 2.0008$, $g_{zz} = 2.0028$.[17]

To elucidate the spin multiplicity of $\mathbf{1}^{2+}$ in the ground state, we have carried out variable-temperature EPR measurements (4 – 100 K). The intensity of the resonance for $\Delta M_S = \pm 2$ demonstrates a linear correlation to the reciprocal of the temperature, indicating a triplet ground state or degeneracy of singlet and triplet states for $\mathbf{1}^{2+}$. Consequently, it follows from these results and the calculated ΔE_{S-T} value for $\mathbf{1}_{NH}{}^{2+}$ that the ground state of $\mathbf{1}^{2+}$ is triplet.

In summary, we have described the triplet state of the new azacyclophane-based dication $\mathbf{1}^{2+}$. Moreover, it was confirmed that the stabilization of the di(cation radical) based on Wurster's blue is, to some extent,[19] achieved by macrocyclization due to the *m*-phenylene tether, which is lacking in the conformationally unrestricted $\mathbf{2}^{2+}$. Cyclophane $\mathbf{1}^{2+}$ is a prototype of one-dimensional high-spin ladderlike polymers, so that further work on its oligomer model is now in progress.

Experimental Section

1: A mixture of *N*,*N'*-dimethyl-*p*-phenylenediamine (2.7 g, 20 mmol), 1,3-dibromobenzene (4.8 g, 20 mmol), NaO*t*Bu (5.4 g, 56 mmol), and $[PdCl_2(P(o\text{-tolyl})_3)_2]$ (0.61 g, 0.78 mmol) in toluene (180 mL) was heated under an argon atmosphere at 100 °C for 19 h according to the reported procedure.[20] After the usual workup including removal of brown intractable polymeric solid, the crude product was purified by medium-pressure liquid chromatography (MPLC) on SiO_2 (*n*-hexane/ethyl acetate (7/1) as eluent). A fraction ($R_f = 0.5$) afforded **1** as a white solid (12 mg, 0.028 mmol, 0.28 %) after recrystallization from ethyl acetate. M.p. 210 °C (decomp.); ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.26$ (s, 12 H), 5.83 (t, ^4J(H,H) = 2.2 Hz, 2 H), 6.45 (dd, ^3J(H,H) = 8.3, ^4J(H,H) = 2.2 Hz, 4 H), 6.95 (s, 8 H), 7.23 (t, ^3J(H,H) = 8.3 Hz, 2 H); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 39.63$, 106.18, 125.49, 130.05, 130.05, 144.09, 150.33; UV/Vis (cyclohexane): λ_{max} (lg ε) = 236 (4.62), 302 nm (4.57); FT-IR

(KBr): $\tilde{\nu} = 698, 761, 837, 880, 1348, 1510, 1591, 2811, 2876, 2957$; HR-MS: m/z calcd: 420.2314 [M^+]; found: 420.2332.

Crystal data for **1** ($C_{28}H_{28}N_4$): $M_r = 420.56$, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.822(4)$, $b = 17.577(7)$, $c = 15.200(6)$ Å, $\beta = 106.43(3)^\circ$, $V = 2260(1)$ Å^3, $T = 296$ K, $Z = 4$, $\rho_{\text{calcd}} = 1.235\ \text{g cm}^{-3}$, $\mu(\text{Mo}_{K\alpha}) = 0.74\ \text{cm}^{-1}$; of 3911 total reflections, 3689 were independent; $R = 0.084$ and $R_W = 0.090$ for 861 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods and refined with the full-matrix least-squares method of the TEXSAN program (version 1.9, Molecular Structure Corporation). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133430. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] a) F. Diederich, *Cyclophanes*, The Royal Society of Chemistry, Cambridge, UK, **1991**; b) F. Vögtle, *Cyclophane Chemistry*, Wiley, Chichester, **1993**.

[2] B. Morgan, D. Dolphin in *Structure and Bonding*, *Vol. 64* (Ed.: J. W. Buchler), Springer, Berlin, **1987**, p. 115.

[3] a) C. D. Gutsche, *Calixarenes*, The Royal Society of Chemistry, Cambridge, UK, **1989**; b) R. M. Izatt, J. S. Bradshaw, K. Pawlak, R. L. Bluening, B. J. Tarbet, *Chem. Rev.* **1992**, *92*, 1261; c) S. Shinkai, *Tetrahedron* **1993**, *49*, 8933; d) V. Böhmer, *Angew. Chem.* **1995**, *107*, 785; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 713; e) A. Ikeda, S. Shinkai, *Chem. Rev.* **1997**, *97*, 1713.

[4] a) B. König, M. Rödel, P. Bubenitschek, P. G. Jones, *Angew. Chem.* **1995**, *107*, 752; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 661; b) B. König, M. Rödel, P. Bubenitschek, P. G. Jones, I. Thondorf, *J. Org. Chem.* **1995**, *60*, 7406; c) M. Mascal, J. L. Richardson, A. J. Blake, W.-S. Li, *Tetrahedron Lett.* **1997**, *38*, 7639; d) J. Nakayama, N. Katano, Y. Sugihara, A. Ishii, *Chem. Lett.* **1997**, 897; e) N. Katano, Y. Sugihara, A. Ishii, J. Nakayama, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2695, and references therein; f) N. Avarvari, N. Mézailles, L. Ricard, P. Le Floch, F. Mathey, *Science* **1998**, *280*, 1587; g) A. S. Abd-El-Aziz, C. R. de Denus, M. J. Zaworotko, C. V. K. Sharma, *Chem. Commun.* **1998**, 265; h) I. Baxter, H. M. Colquhoun, P. Hodge, F. H. Kohnke, D. J. Williams, *Chem. Commun.* **1998**, 283; i) I. Baxter, H. M. Colquhoun, P. Hodge, F. H. Kohnke, D. J. Williams, *Chem. Commun.* **1998**, 1991; j) T. Fruend, C. Kübel, M. Baumgarten, V. Enkelmann, L. Gherghel, R. Reuter, K. Müllen, *Eur. J. Org. Chem.* **1998**, 555; k) M. Yoshida, M. Goto, F. Nakanishi, *Organometallics* **1999**, *18*, 1465; l) N. Avarvari, N. Maigrot, L. Ricard, F. Mathey, P. Le Floch, *Chem. Eur. J.* **1999**, *5*, 2109.

[5] a) A. Ito, Y. Ono, K. Tanaka, *New J. Chem.* **1998**, 779; b) A. Ito, Y. Ono, K. Tanaka, *J. Org. Chem.* **1999**, *64*, 8236.

[6] a) A. Rajca, S. Rajca, R. Padmakumar, *Angew. Chem.* **1994**, *106*, 2193; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2091; b) A. Rajca, S. Rajca, S. R. Desai, *J. Am. Chem. Soc.* **1995**, *117*, 806; c) K. Matsuda, N. Nakamura, K. Takahashi, K. Inoue, N. Koga, H. Iwamura, *J. Am. Chem. Soc.* **1995**, *117*, 5550; d) A. Rajca, K. Lu, S. Rajca, *J. Am. Chem. Soc.* **1997**, *119*, 10335; e) A. Rajca, J. Wongsriratanakul, S. Rajca, *J. Am. Chem. Soc.* **1997**, *119*, 11674; f) A. Rajca, J. Wongsriratanakul, S. Rajca, R. Cerny, *Angew. Chem.* **1998**, *110*, 1353; *Angew. Chem. Int. Ed.* **1998**, *37*, 1229; g) A. Rajca, S. Rajca, J. Wongsriratanakul, *J. Am. Chem. Soc.* **1999**, *121*, 6308.

[7] A. R. Forrester, J. M. Hay, R. H. Thomson, *Organic Chemistry of Stable Free Radicals*, Academic Press, New York, **1968**.

[8] a) H. Iwamura, *Pure Appl. Chem.* **1987**, *59*, 1595; b) H. Iwamura, *Adv. Phys. Org. Chem.* **1990**, *26*, 179; c) D. A. Dougherty, *Acc. Chem. Res.* **1991**, *24*, 88; d) H. Iwamura, *Pure Appl. Chem.* **1993**, *65*, 57; e) W. T. Borden, H. Iwamura, J. A. Berson, *Acc. Chem. Res.* **1994**, *24*, 109; f) A. Rajca, *Chem. Rev.* **1994**, *94*, 871.

[9] a) M. M. Wienk, R. A. J. Janssen, *Chem. Commun.* **1996**, 267; b) M. M. Wienk, R. A. J. Janssen, *J. Am. Chem. Soc.* **1996**, *118*, 10626; c) M. M. Wienk, R. A. J. Janssen, *J. Am. Chem. Soc.* **1997**, *119*, 4492; d) K. R. Stickley, T. D. Selby, S. C. Blackstock, *J. Org. Chem.* **1997**, 62, 448; e) T. D. Selby, S. C. Blackstock, *J. Am. Chem. Soc.* **1999**, *121*, 7152.

[10] A. Ito, A. Taniguchi, T. Yamabe, K. Tanaka, *Org. Lett.* **1999**, *1*, 741.

[11] Treatment at a moderate dilution (10–50 mM) remedies the yield of **1** (ca. 1%). On the other hand, prolonged reaction time does not improve the yield.

[12] UV/Vis (cyclohexane) for TMPD: $\lambda_{\max}$ ($\lg \varepsilon$) = 265 (4.3), 325 nm (3.5).

[13] Computational details: The molecular structures of $\mathbf{1}_{\text{NH}}$ and $\mathbf{1}_{\text{NH}}^{2+}$ were calculated using the split-valence 6-31G* basis set on the basis of density functional theory (DFT), which incorporates dynamical correlation, giving reliable results. We employed Becke's nonlocal exchange functional (A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098), and Perdew and Wang's gradient-corrected correlation functional (J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244); BPW91/6-31G* was applied using the GAUSSIAN94 suite of programs (M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94*, Revision D.4; Gaussian, Inc., Pittsburg, PA, **1995**).

[14] The optimized C_{2h}-symmetric conformer, in which two *p*-phenylene moieties are parallel, is 0.5 kcal mol^{-1} less stable than the C_{2v}-symmetric conformer. Furthermore, the energy difference between the two conformers increases upon two-electron oxidation (2.6 kcal mol^{-1}).

[15] T. Moll, J. Heinze, *Synth. Met.* **1993**, *55–57*, 1521.

[16] F. A. Bell, A. Ledwith, D. C. Sherrington, *J. Chem. Soc.* **1969**, 2720.

[17] This assignment is tentative: One of the principal axes for the $\boldsymbol{D}$ tensor, corresponding to the maximum value of $2D$, is probably oriented in the direction connecting the two *m*-phenylene moieties (z axis). According to an approximation method to calculate the eigenvalues of $\boldsymbol{D}$ tensor in the three principal axis directions (K. A. Sandberg, D. A. Shultz, *J. Phys. Org. Chem.* **1998**, *11*, 819), the estimated eigenvalues for $\mathbf{1}_{\text{NH}}^{2+}$ are as follows: 0.0012 (x axis; the direction connecting two *p*-phenylene moieties), 0.0033 (y axis; the direction perpendicular to the molecular plane), -0.0045 cm^{-1} (z axis). Thus, the D and E values are calculated to be 0.0068 and 0.0011 cm^{-1}, respectively. Since the $\boldsymbol{g}$ and $\boldsymbol{D}$ tensors are often coaxial in many organic radicals, we assume that $g_{zz} = 2.0028$. In general, the value for g in the direction perpendicular to the molecular plane of the planar aromatic radicals often gives a small positive or negative value relative to the value for a free electron (R. Angstl, *Chem. Phys.* **1989**, *132*, 435). Moreover, from the calculated (DFT) results for $\mathbf{1}_{\text{NH}}$, the inclination angles of two *p*-phenylene moieties to the plane defined by the four nitrogen atoms tend to decrease through the two-electron oxidation. Therefore, the larger value of g (2.0021) is assigned to g_{xx}, and the smaller one (2.0008) to g_{yy}. Note that the broadening recognized only for y components of the resonance for $\Delta M_S = \pm 1$ is attributed to hyperfine splitting due to ^{14}N nuclei.[18]

[18] a) A. Calder, A. R. Forrester, P. G. James, G. R. Luckhurst, *J. Am. Chem. Soc.* **1969**, *91*, 3724; b) J. F. W. Keana, R. J. Dinerstein, *J. Am. Chem. Soc.* **1971**, *93*, 2808; c) A. Rassat, H. U. Sieveking, *Angew. Chem.* **1972**, *84*, 353; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 303; d) R.-M. Dupeyre, A. Rassat, J. Ronzaud, *J. Am. Chem. Soc.* **1974**, *96*, 6559; e) P. Michon, A. Rassat, *J. Am. Chem. Soc.* **1975**, *97*, 696; f) W. B. Gleason, R. E. Barnett, *J. Am. Chem. Soc.* **1976**, *98*, 2701; g) M. Dvolaitzky, R. Chiarelli, A. Rassat, *Angew. Chem.* **1992**, *104*, 220; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 180.

[19] A reviewer remarked that replacement of the *N*-methyl group by another group without hydrogen atoms restrains deprotonation reactions leading to decomposition of $\mathbf{1}^{2+}$. Preparation of such derivatives is needed to realize further persistency of $\mathbf{1}^{2+}$.

[20] A. S. Guram, R. A. Rennels, S. L. Buchwald, *Angew. Chem.* **1995**, *107*, 1456; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1348.