Charge Localization in a Dihydrazine Analogue of Tetramethyl-*p*-phenylenediamine Radical Cation

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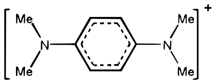
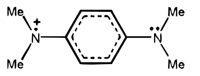
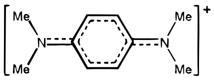
Tetramethyl-*p*-phenylene diamine (TMPD) radical cation ($\mathbf{1}^+$) has been important in the development of radical cation chemistry.[1] It was the first organic radical cation prepared (Wurster, 1879), was first formulated as a radical cation by Weitz in 1928, and was one of the first organic radicals to be studied by ESR (Weissman and co-workers, 1953).[1] Its rate of intermolecular "self" electron exchange (between $\mathbf{1}^0$ and $\mathbf{1}^+$) was one of the first measured,[2a] and the solvent and temperature effects have been studied thoroughly by Grampp and Jaenicke,[2b−d] and have played a central role in the application of ET theory[3] to organic compounds. $\mathbf{1}^+$ could in principle exist instantaneously in a "localized" structure, with one dimethylamino group planar and bearing most of the charge and the other remaining in the slightly pyramidalized geometry of $\mathbf{1}^0$ (see $\mathbf{1}^+$**(loc)** for a diagramatic representation). Instead, $\mathbf{1}^+$ clearly has its charge delocalized over the eight atom π system and has equivalent, planar nitrogen atoms (see $\mathbf{1}^+$**(deloc)**). In the nomenclature used for transition metal intervalence complex studies, $\mathbf{1}^+$**(loc)** would be an organic analogue of Robin−Day Class II system,[4] having a separate energy well for the charge being principally located on each nitrogen, a barrier to ET between the wells, and would show a charge transfer (CT) band for which $\lambda_{\max}$ converted to energy units would measure the intrinsic barrier for ET (Marcus's λ), and for which the separation of the ground and excited state energy surfaces at the ET transition state (2V) could be estimated by a Hush theory analysis.[3−5] In contrast, $\mathbf{1}^+$**(deloc)** is Robin−Day Class III system with a single ground state energy well, for which $\lambda_{\max}$ measures 2 V for the delocalized system.[5c] The delocalization energy gained by having both nitrogens assume the same geometry for $\mathbf{1}^+$ is clearly larger than the reorganization energy required for changing the geometry at both dimethylamino groups, instead of just at one, which is all that would be required to form $\mathbf{1}^+$**(loc)**.



1⁺

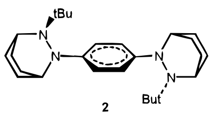


1⁺(loc)



1⁺(deloc)

We report here studies of a dihydrazine analogue of **TMPD**, *p*-phenylene bis(2-*tert*-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl), **2**, prepared in the expectation that the much larger reorganization energy of a hydrazine than a dialkylamino group[6] would result in a localized radical cation structure. This proves to be the case, and we believe that $\mathbf{2}^+$ provides the first system for which different charges on like units of a radical ion conjugated para to each other on a benzene ring is caused by internal structural features instead of by ion pairing.[7]



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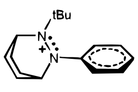
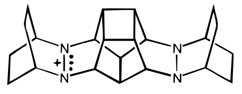


3⁺



4⁺

2 was prepared by addition of 1,4-dilithiobenzene to two *tert*-butyl diazenium cations, a well-established method for making bicyclic hydrazines.[8] It crystallizes in the C_i *anti*-meso form (see Figure 1), and its geometrical parameters about the NN bond are summarized in Table 1. Both nitrogens are strongly pyramidalized, and the twist angle ϕ between the nitrogen lone pair and the aryl ring p orbital is −37.5°. The cyclic voltammogram of **2** shows reversible one-electron oxidation waves at +0.09 and +0.38 V vs SCE in acetonitrile containing 0.1 M $\mathrm{Bu_4N^+BF_4^-}$ at 25 °C. The $\Delta E°$ value of 0.29 V is 51% of the 0.57 V observed under the same conditions for **1**.[9] Oxidation of **2** ($\lambda_{\max}$ 276 nm, $\epsilon = 1.1 \times 10^4\ \mathrm{M^{-1}\ cm^{-1}}$) to $\mathbf{2}^+$ in acetonitrile by silver nitrate causes the intensity of the 276 nm band to decrease about a factor of 2 ($\mathbf{2}^+\mathrm{NO_3}^-$ had $\lambda_{\max} =$ 276 nm, $\epsilon = 6.8 \times 10^3$, and nitrate absorbs some at 276 nm), and the solution turns green because new bands appear at 374 nm ($\epsilon = 5.4 \times 10^3$) and 756 nm ($\epsilon = 3.6 \times 10^3$). We assign the broad ($\Delta\nu_{1/2} = 6410\ \mathrm{cm^{-1}}$) visible band as an "intervalence" CT band, so $h\nu_{\max} =$ Marcus's $\lambda = 13\,230\ \mathrm{cm^{-1}} = 37.8$ kcal/mol. This 756 nm band is clearly associated with the presence of the second hydrazine unit in $\mathbf{2}^+$ because addition of trifluoroacetic acid quenches it instantly. Although intermolecular ET for $\mathbf{2}^+$ is fast on the ESR time scale at room temperature, resulting in the nine-line pattern of ill resolved multiplets expected for four nearly equivalent nitrogens (a(4N) = 6.75 G); it exhibits a broadened five-line pattern at −105(2) °C in 12:1 acetone:acetonitrile, demonstrating that $\mathbf{2}^+$ is localized in solution (Figure 2). Obtaining X-ray crystal structures of class II complexes has been a problem because they usually disproportionate upon crystallization,[5a] as does $\mathbf{2}^+\mathbf{NO_3}^-$, to $\mathbf{2}^{2+}$ and **2**. Nevertheless, crystallization of a sample of $\mathbf{2}^+\mathbf{BPh_4}^-$ containing **2** by addition of water to acetonitrile produced X-ray quality crystals of $\mathbf{2}^+\mathbf{BPh_4}^-$ (see Figure 1 and Table 1). Table 1 compares of the geometries at the reduced and oxidized hydrazine units of $\mathbf{2}^+$ with those of **2** and a model *N*-arylhydrazine radical cation, $\mathbf{3}^+$.

Using Hush's formula to calculate V (eq 1),[5b] with "charge

$$V(\mathrm{cm^{-1}}) = (0.0206/d)(h\nu_{\max}\Delta\nu_{1/2}\epsilon_{\max})^{1/2} \qquad (1)$$

centers distance" d values of 5.657 Å (the X-ray NAr−NAr distance) [or 6.278 Å, the X-ray N−N bond centers distance], produces $V(\mathbf{2}^+)$ of 2012 cm^{-1} (5.8 kcal/mol) [1813 cm^{-1} (5.2 kcal/mol)]. These values are larger than the range $V = 3.5 \pm 0.5$ found by the same method for a series of bis(hydrazine) and bis(hydrazyl) radical cations doubly linked by four saturated

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(1) For the early history of radical ion studies, see: Roth, H. D. *Tetrahedron* **1986**, *42*, 5097.

(2) (a) Bruce, C. R.; Norberg, R. E.; Weissman, S. *J. Chem. Phys.* **1956**, *24*, 473. (b) Grampp, G.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 325. (c) Grampp, G.; Jaenicke, W. *Ibid.* **1984**, *88*, 335. (d) Grampp, G.; Jaenicke, W. *Ibid.* **1991**, *95*, 904.

(3) For reviews of electron transfer theory, see: (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(4) Robin, M.; Day, P. *Adv. Inorg. Radiochem.* **1967**, *10*, 247.

(5) For reviews of the application of Hush theory, see: (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Hush, N. S. *Coord. Chem. Rev.* **1985**, *64*, 135. (c) Reference 5a, p 8, 10. For others using $h\nu_{\max} = 2$ V for Class III complexes, see: (i) Woitelier, S.; Launay, J. P.; Spangler, C. W. *Inorg. Chem.* **1989**, *28*, 758. (iii) Dong, Y.; Hupp, J. T. *Ibid.* **1992**, *31*, 3170. (iii) Reference 10.

(6) For a review on the effects of reorganization energy of amino nitrogen compounds upon ET rates, see: Nelsen, S. F. *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI: Greenwich, CT, 1993; Vol. 3, p 167.

(7) Polynitrobenzene radical anions including that from p-dinitrobenzene provided early examples of ion pairing localizing the spin (and charge) on one unit through the study of ESR splitting constants. For a review of this work, see p 200 of the following: Hudson, H.; Luckhurst, G. R. *Chem. Rev.* **1969**, *69*, 191.

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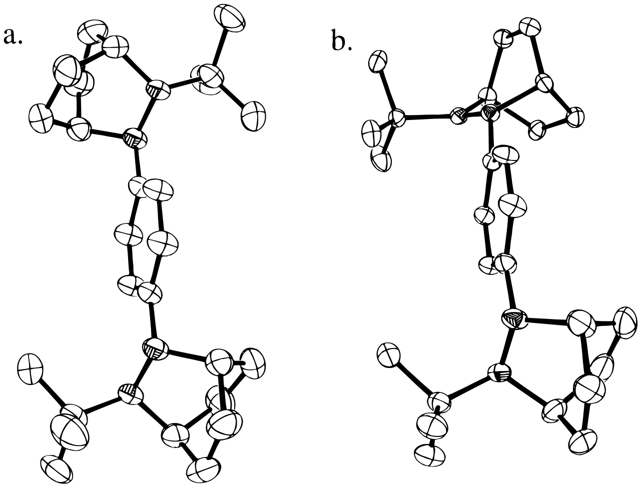

Figure 1. Thermal ellipsoid drawings (50% probability level) of the X-ray crystal structures of (a) $\mathbf{2}$, (b) $\mathbf{2}^{+}$ unit of $\mathbf{2}^{+}(\mathrm{BPh_4}^{-})$. The neutral hydrazine unit is at the bottom.

Table 1. Comparison of Structural Parameters about the Hydrazine Units

	$\mathbf{2}^{a}$ (neutral)	$\mathbf{2}^{+}(\mathrm{BPh_4}^{-})^{b}$ (neutral)	$\mathbf{2}^{+}(\mathrm{BPh_4}^{-})$ (cation)	$\mathbf{3}^{+}\mathrm{NO_3}^{-}$ (cation)
d(N−N), Å	1.461(2)	1.454(3)	1.359(3)	1.355(2)
d(N−Ar), Å	1.440(2)	1.426(3)	1.436(3)	1.440(2)
$\alpha_{\mathrm{av}}(\mathrm{N_{Ar}})$, deg	112.0(1)	112.2(2)	116.2(2)	117.0(1)
$\alpha_{\mathrm{av}}(\mathrm{N_{tBu}})$, deg	113.1(1)	113.6(2)	118.7(2)	119.1(1)
ϕ(N−Ar), deg	−37.5(1)	−32.6(3)	+47.6(3)	−59.7(2)
$\angle \mathrm{C_tN{-}NC_{Ar}}$, deg	−105.8(1)	−107.3(3)	+67.3(3)	−53.6(2)

[a] $d(\mathrm{N_{Ar}{-}N_{Ar}})$ 5.702, $d(\mathrm{N_{tBu}{-}N_{tBu}})$ 7.423 Å. [b] $d(\mathrm{N_{Ar}{-}N_{Ar}})$ 5.657, $d(\mathrm{N_{tBu}{-}N_{tBu}})$ 6.899 Å.

σ bonds,[10] which includes bishydrazine $\mathbf{4}^{+}$, $V = 3.9$ kcal/mol.[11] Finding V to be only 33−49% larger for the π-conjugated benzene-linked system $\mathbf{2}^{+}$ than the saturated bis four σ-bond linked $\mathbf{5}^{+}$ might be initially surprising, but $\mathbf{2}^{+}$ is far from having optimal overlap of its hydrazine units with the benzene ring. An experimental value for V for optimally aligned planar nitrogens linked 1,4 on a benzene ring is available from the optical spectrum of the Type III analogue $\mathbf{1}^{+}$. From the $\lambda_{\mathrm{max}}(\mathbf{1}^{+}) = 616$ nm in acetonitrile,[12] the maximum V for benzene-linked trivalent nitrogen charge-bearing units is 23.3 kcal/mol using Hush's two-site model.[13] A rough estimation of an expected value for $V(\mathbf{2}^{+})$ using the ϕ values for crystalline $\mathbf{2}^{+}$ (which we realize might be different in solution) and assuming that V is scaled by the product of the $\cos^2\phi$ [or $\cos\phi$] values for the two charge-bearing units produces $V(\mathbf{2}^{+}) = 0.32$ [or 0.57]-$V(\mathbf{1}^{+})$, while the numbers obtained from the Hush analysis above are $V(\mathbf{2}^{+}) = 0.22{-}0.25V(\mathbf{1}^{+})$. Increased N pyramidalization, which will also decrease overlap, accompanies increased ϕ so the quantitative angular dependence of V upon ϕ is probably complex. We conclude that the twist of the hydrazine units is crucial for localizing the charge in $\mathbf{2}^{+}$. Charge-bearing units having as good overlap with a benzene ring linking them as the dimethylamino groups of $\mathbf{1}^{+}$ would have to have $\lambda/4 > V(\mathbf{1}^{+})$ to be localized, or $\lambda > 93.2$ kcal/mol. We know of no charge-bearing units with such large reorganization energies. Conversely, the relatively large reorganization energies of the hydrazines are necessary for achieving localization in $\mathbf{2}^{+}$; aromatic or low reorganization energy transition metal charge-bearing units twisted to have the same V as $\mathbf{2}^{+}$ would not have a large enough λ_{in} to be localized.

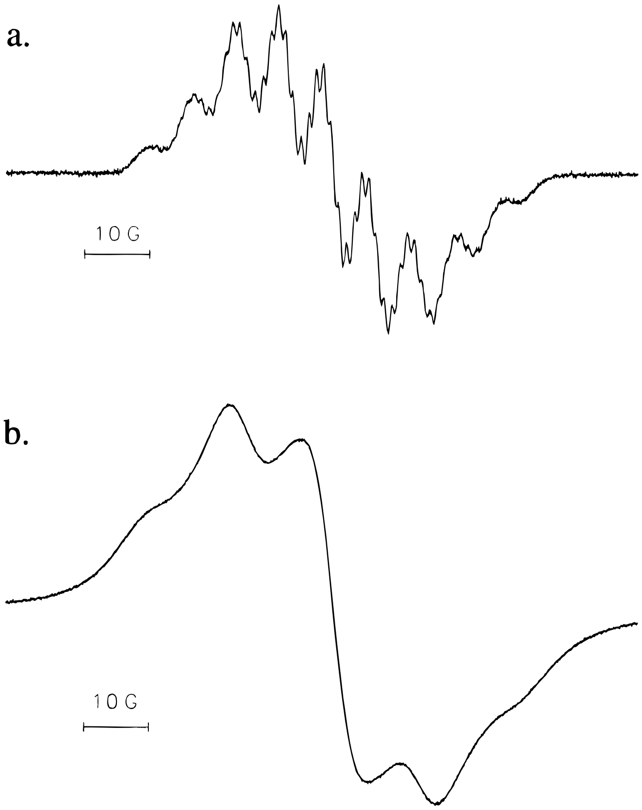

Figure 2. ESR spectra of $\mathbf{2}^{+}$. (a) 23 °C, acetonitrile. (b) −105 °C, 12:1 acetone:acetonitrile.

The CT band position of $\mathbf{2}^{+}$ is sensitive to solvent. In methylene chloride, $\lambda_{\mathrm{max}} = 897$ nm ($\epsilon_{\mathrm{max}} = 5.1 \times 10^3$, $\Delta\nu_{1/2} = 6025$ cm^{-1}, $V = 2130{-}1920$ cm^{-1}), so $h\nu_{\mathrm{max}} = 11\,150$ cm^{-1}, $\lambda = 31.9$ kcal/mol. However, a plot of $h\nu_{\mathrm{max}}$ versus the Marcus solvent parameter $\gamma = 1/n_{\mathrm{D}}^2 - 1/\epsilon$ for $\mathbf{2}^{+}$ shows considerable scatter, and $h\nu_{\mathrm{max}}$ is significantly lower for $\mathrm{CH_2Cl_2}$ than expected from the values found for other solvents (acetone, dimethylformamide, benzonitrile, and pyridine). Quantitative separation of the internal and solvent reorganization energies from a plot of $h\nu_{\mathrm{max}}$ versus γ is therefore unreasonable for $\mathbf{2}^{+}$. Detailed reporting of the complex solvent dependence of $h\nu_{\mathrm{max}}$ for $\mathbf{2}^{+}$ is deferred to the full paper. We are pursuing tests of the applicability of using optical data for delocalized organic radical ions to estimate the reorganization energy required for charge-bearing units to give charge-localized structures,[13] making π-conjugated Class II systems for which the ET rate constant can be measured, how to quantitate the ϕ dependence of V for conjugated links, and how to understand the solvent dependence observed for $h\nu_{\mathrm{max}}$.

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Supporting Information Available: Preparations and crystallographic data for $\mathbf{2}$, $\mathbf{2}^{+}\mathrm{BPh_4}^{-}$, and $\mathbf{3}^{+}\mathrm{NO_3}^{-}$; numbered thermal ellipsoid drawings, tables including heavy atom positions, bond lengths and angles, and anisotropic displacement parameters (20 pages). See any current masthead page for ordering and Internet access instructions.

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(12) Nelsen, S. F.; Yunta, M. J. R. *J. Phys. Org. Chem.* **1994**, *7*, 55.

(13) A two-site model is probably not very accurate for $\mathbf{1}^{+}$ because of charge delocalization into the benzene ring, but we doubt that the real V is very much larger because $\mathbf{2}^{+}$ is clearly localized.