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4,7-Bis(dimethylamino)benzimidazoles and twin-type derivatives: reversible two-stage redox system modulated by proton-transfer☆

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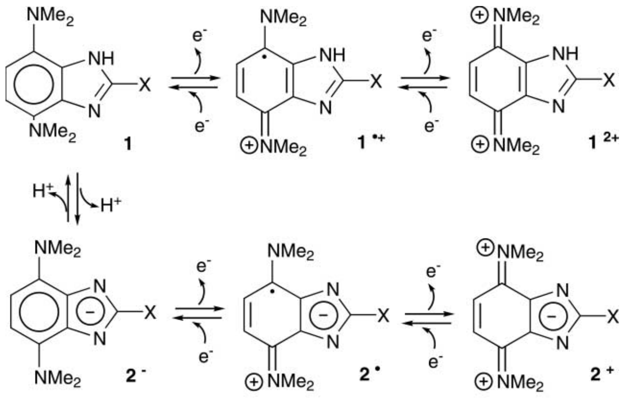
Abstract—The title electron donors **1** as well as their conjugate bases $\mathbf{2}^-$ undergo reversible two-stage one-electron oxidation. ESR analysis indicated the important contribution of zwitterionic structure for radicals $\mathbf{2}^\bullet$. Bis(zwitterionic) but not quinoid structure was suggested for *p*-**4**, generated from the twin-type dianionic donor *p*-$\mathbf{4}^{2-}$ with a *p*-phenylene spacer.

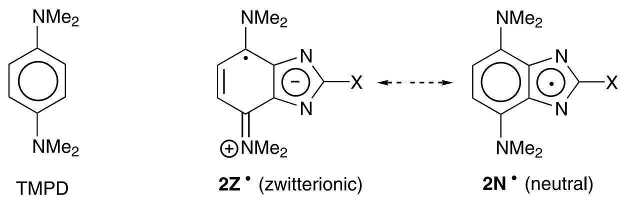
N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine (TMPD) has been known as a representative Wurster-type redox system.[1] Due to its strong electron-donating properties as well as stability in its oxidized form,[2] TMPD serves as a versatile building block in developing functionalized materials such as electroluminescent devices[3] or nonlinear optical materials.[4,5] We have now designed and prepared the title TMPD derivatives fused with an imidazole ring **1** in anticipation that not only the neutral donors **1** but also their conjugate bases $\mathbf{2}^-$ would undergo reversible two-stage one-electron oxidation (Scheme 1). These materials are promising candidates in realizing the multi-input response systems, in which two independent external stimuli (e.g. e^- and H^+) control the physical properties of the molecule.[6,7] On the other hand, the electronic structure of neutral radical $\mathbf{2}^\bullet$ is another concern to be addressed (Scheme 2) in terms of recent interests in the polarizable radicals.[8] Twin-type donors **3** containing two TMPD units connected through a phenylene spacer are also prepared. Their redox behaviors are studied along with their conjugate bases $\mathbf{4}^2$ (Scheme 3) to shed the light on the issue of diradical–quinoid equilibrium[9] in *p*-**4** (Scheme 4).

2,3-Diamino-1,4-bis(dimethylamino)benzene was prepared from *o*-phenylenediamine in 7 steps,[5] and used as



[**a**: X = H; **b**: X = C_6H_5 ; **c**: X = *p*-$NO_2C_6H_4$; **d**: X = Mes (2,4,6-$Me_3C_6H_2$)]

Scheme 1.



Scheme 2.

Keywords: electron donor; proton transfer; phenylenediamine; radical; zwitterion; redox system; electrochromism; response system.

☆ Supplementary data associated with this article can be found at doi:10.1016/j.tetlet.2003.09.012

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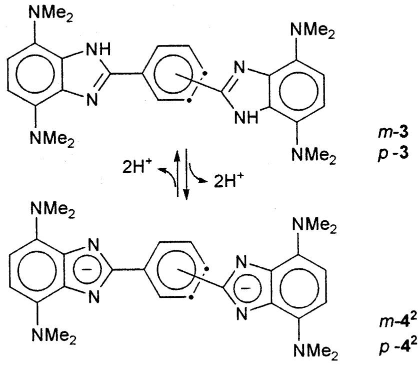
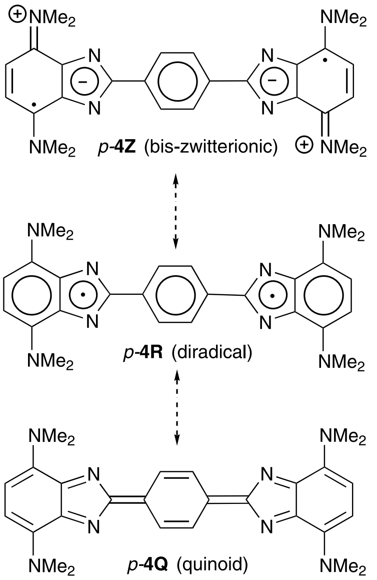


Scheme 3.



Scheme 4.

the common starting material in this study. Condensation of this tetramine with formic acid gave colorless crystals of **1a** in 37% yield. Other derivatives having an aryl group at 2-position, **1b–d**, were prepared by the reaction of the tetramine with the corresponding aromatic aldehyde followed by oxidation of benzimidazoline intermediates[10] with nitrobenzene[11] in 75%, 58%, and 65% yield, respectively. Twin donors, *m*-**3** and *p*-**3**, were similarly obtained by using isophthal- and terephthalaldehyde, respectively, in 42% and 47% yield. These donors are stable crystalline materials but susceptible to air or acid in solution. X-ray structural analysis[12] of 2-mesityl derivative **1d** at 153 K revealed the detailed geometrical feature of this skeleton (Fig. 1). The diaminobenzimidazole moiety is planar with the largest deviation from the least-squares plane of 0.02 Å. The N(1)-H proton of imidazole appears at the expected position. The bond lengths of N(1)–C(2) [1.376(7) Å] and C(2)=N(3) [1.306(7) Å] clearly show the bond alternation in this unit, and are comparable to those in the parent benzimidazole [1.361(7) and 1.315(8) Å].[13] The geometry of TMPD moiety in **1d** resembles TMPD itself.[14]

Cyclic voltammograms of **1a–d** showed two pairs of reversible waves. Their first oxidation potentials (E_1^{ox}) are close to the value of TMPD, showing the similar electron-donating properties (Table 1). The more positive value in **1c** can be accounted for by the electron-withdrawing nature of nitrophenyl group at 2-position. Due to the reduced Coulombic repulsion in the dications $\mathbf{1}^{2+}$, the second oxidation potentials (E_2^{ox}) of **1a–d** are lower than that of TMPD. At any event, high reversibility of the voltammograms indicates that the oxidized species, $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{2+}$, are stable under the measurement conditions, and deprotonated species, $\mathbf{2}^{\bullet}$ and $\mathbf{2}^{+}$, were not observed during these measurements. Voltammograms of twin-type donors, *m*-**3** and *p*-**3**, also exhibit two pairs of reversible waves, indicating that each wave corresponds to two-electron oxidation. This observation suggests negligible interaction between the two TMPD units through the phenylene spacer in **3**, which is in accord with the very small HOMO coefficient at 2-position in **1a**.

By treatment of neutral donors with a strong base like NaH, their conjugate bases were generated and characterized spectroscopically. ^{1}H NMR spectrum of **1a** in DMSO-d_6 [δ_{ppm} 12.31 (1H, s), 8.00 (1H, s), 6.59 (1H, d, $J=8.0$ Hz), 6.29 (1H, d, $J=8.0$ Hz), 3.00 (6H, s), 2.71 (6H, s)] became very simple after treatment with $NaCD_2SOCD_3$ [7.74 (1H, s), 6.26 (2H, s), 3.11 (12H, s)], which can be assigned to $\mathbf{2a}^-$ of C_{2v}-symmetry. Quite similar changes were observed in the ^{1}H NMR spectra of **1b–d** as well as *m*- and *p*-**3** upon treatment with base ($NaCD_2SOCD_3$/DMSO-d_6, NaH/CD_3CN, and/or NaH/THF-d_8). In the case of nitrophenyl derivative **1c** [$\lambda_{\max}$ (log ε) in THF: 364 (4.31), 454 nm (sh, 3.50); end absorption 600 nm] showing the intramolecular charge-transfer band, base treatment induced red shifts of UV-vis absorption since $\mathbf{2c}^-$ [440 nm (4.31); 650 nm] has the stronger donating properties than **1c** (vide infra). These anions were persistent in solution, but attempts to isolate $\mathbf{2}^-$ and $\mathbf{4}^{2-}$ as pure salts were still unsuccessful due to their high sensitivity toward air, and contact with moisture resulted in regeneration of neutral donors, **1** and **3**.

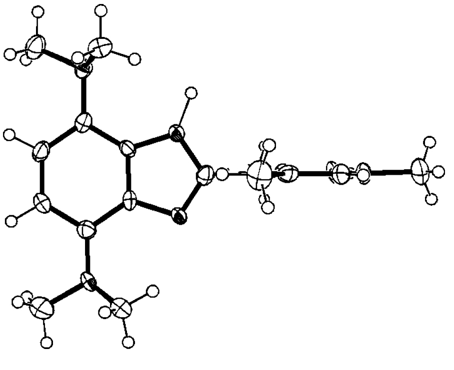


Figure 1. Molecular structure of **1d** determined by X-ray analysis at 153 K. The dihedral angle between benzimidazole and mesityl group is 88.0(2)°.

Table 1. Oxidation potentials[a] of donors (**1** and **3**) and their conjugate bases ($\mathbf{2}^{-}$[b] and $\mathbf{4}^{2-}$[c]) measured by cyclic voltammetry

X	Donor	E_1^{ox}	E_2^{ox}	Anion	E_1^{ox}	E_2^{ox}
H	**1a**	+0.08	+0.48	$\mathbf{2a}^-$	−0.42	+0.05
C_6H_5	**1b**	+0.10	+0.48	$\mathbf{2b}^-$	−0.42	+0.01
p-$NO_2C_6H_5$	**1c**	+0.13	+0.51	$\mathbf{2c}^-$	−0.35	+0.08
mesityl	**1d**	+0.08	+0.47	$\mathbf{2d}^-$	−0.46	+0.03
m-C_6H_4	*m*-**3**	+0.11 (**2e**)	+0.49 (**2e**)	*m*-$\mathbf{4}^{2-}$	−0.35 (**2e**)	+0.06 (**2e**)
p-C_6H_4	*p*-**3**	+0.11 (**2e**)	+0.47 (**2e**)	*p*-$\mathbf{4}^{2-}$	−0.35 (**2e**)	+0.07 (**2e**)
–	TMPD	+0.07	+0.65	2-Phenylbenzimidazolate[b,d]	+0.58 (irrev.)	–

[a] E/V versus SCE, 0.1 mol dm^{-3} Et_4NClO_4 in MeCN; scan rate 100 mV s^{-1}. Ferrocene undergoes **1e**-oxidation at +0.38 V under the same conditions.

[b] Anions were generated in situ by treatment with NaH. Values were obtained in the presence of 18-crown-6.

[c] Anions were generated in situ by treatment with LiH since $(Na^+)_2\mathbf{4}^{2-}$ is insoluble in MeCN.

[d] 2-Phenylbenzimidazole was prepared according to the literature (Ref. 10).

Thus, voltammetric analyses on the conjugate bases were carried out for the in situ generated anions in CH_3CN. The first oxidation waves of $Na^+\mathbf{2}^-$ was ambiguous probably due to tight ion pair formation,[15] and nicely shaped two pairs of reversible waves were observed by addition of 18-crown-6. Far negative E_1^{ox} values were obtained for these anions (Table 1), showing much stronger donating properties of $\mathbf{2}^-$ than the corresponding neutral donors **1**. By considering very weak donating properties of benzimidazolate without amino groups, two-stage one-electron oxidation processes of $\mathbf{2}^-$ are inherent to the TMPD moiety, and the fused imidazolate unit may enhance the donating properties of TMPD by its negative charge. High reversibility again indicates that the oxidized species, $\mathbf{2}^\bullet$ and $\mathbf{2}^+$, are stable under the measurement conditions. These results show that reversible proton-transfer between **1** and $\mathbf{2}^-$ can modulate their reversible oxidation potentials, thus providing the chance to use these molecules to construct multi-input response system. Although the spectral differences between **1** and $\mathbf{2}^-$ or between $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^\bullet$ seem too small to use the present system for dual-mode electrochromism modulated by pH,[7] several isosbestic points observed in the spectroelectrograms of **1d** and $\mathbf{2d}^-$ indicate the clean and quantitative electrochemical transformation into $\mathbf{1d}^{\bullet+}$ [λ_{max} in MeCN: 377, 528 nm] and $\mathbf{2d}^\bullet$ [366, 494, 531 nm], respectively, with the Wurster's Blue-type chromophore (see Supplementary material).

In order to get information on the electronic structure of radicals $\mathbf{2}^\bullet$, the ESR analysis was carried out on $\mathbf{2d}^\bullet$ generated electrochemically (Fig. 2). This spectrum ($g=2.0030$) could be simulated by supposing the following hyperfine coupling constants: a_N (2N, amino) 5.00 G, a_N (2N, imidazole) 2.75 G, a_H (12H, methyl) 4.43 G, a_H (2H, phenylene) 1.65 G. By comparing these values with those of $\text{TMPD}^{\bullet+}$ [$g=2.0031$; a_N (2N) 6.99 G, a_H (12H, methyl) 6.76 G, a_H (2H, phenylene) 1.97 G],[16] substantial spin density in $\mathbf{2d}^\bullet$ is located on the TMPD skeleton, showing the important contribution of the zwitterionic structure $\mathbf{2Z}^\bullet$ (Scheme 2). Similarly, for the two-electron oxidized species of dianion $\mathbf{4}^{2-}$, main contribution would not be the neutral diradical form **4R** but the bis(zwitterionic) structure **4Z** (Scheme 4). In the case of *p*-phenylene derivative *p*-**4**, the quinoid structure *p*-**4Q** is also one of the resonance forms, yet its contribution would be negligible since the redox properties of *p*-**4** are identical to those of *m*-**4**, for which the closed-shell quinoid form does not contribute at all.

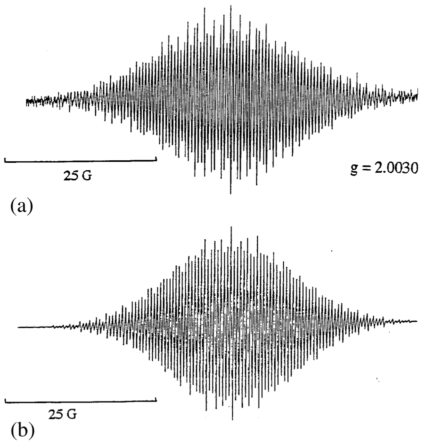
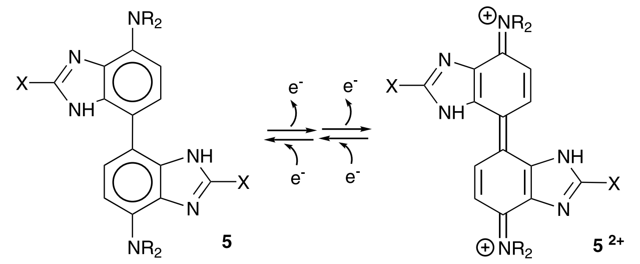


Figure 2. (a) ESR spectrum of $\mathbf{2d}^\bullet$ generated electrochemically from $\mathbf{2d}^-$ in MeCN. This spectrum is quite different from the complicated and unsymmetrical one obtained by electrochemical oxidation of neutral **1d**. (b) Computer simulation.

In summary, the newly prepared TMPD derivatives fused with an imidazole ring are novel electron donors, whose donating properties can be modified by proton-transfer. Upon one-electron oxidation of the conjugate bases $\mathbf{2}^-$ were formed the radicals $\mathbf{2}^\bullet$ with a polarized structure, which is also the case for **4** obtained from the bis(imidazolate) twin-donors $\mathbf{4}^{2-}$. Further studies are now in progress for different type of twin-donors with a biaryl skeleton, e.g. bis(4-aminobenzimidazol-7-yl)s. As depicted in Scheme 5, preliminary study showed that the new donor **5** (NR_2 = 1-pyrrolidinyl, X = Me) undergoes reversible two-stage one-electron oxidation (+0.21 and +0.44 V versus SCE in MeCN). The X-ray analysis[12] of $\mathbf{5}\cdot(EtOH)_2$ revealed that this donor adopts the extended conformation with the biaryl twisting of 140(1)° with both imidazole N–H protons directed inward (Fig. 3). Details on such biaryl systems will be reported elsewhere.



Scheme 5.

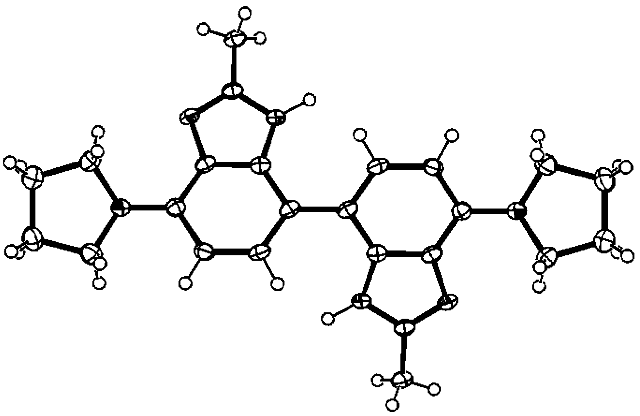


Figure 3. Molecular structure of **5** determined by X-ray analysis at 153 K.

Supplementary material

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 211822 (**1d**) and 216771 (**5**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

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12. Crystal data of **1d**: $C_{20}H_{26}N_4$, M 322.45, orthorhombic, $Pccn$ (No. 56), $a=17.925(9)$, $b=14.724(8)$, $c=13.901(7)$ Å, $U=3668(5)$ Å^3, Dc $(Z=8)=1.167$ g cm^{-1}, $\mu=0.71$ cm^{-1}, $T=153$ K. The final R value is 0.051 for 1048 independent reflections with $I>3\sigma I$ and 217 parameters. Crystal data of **5**$\cdot(EtOH)_2$: $C_{28}H_{40}N_6O_2$, M 492.66, monoclinic, $C2/c$ (No. 15), $a=27.67(7)$, $b=7.44(1)$, $c=13.97(4)$ Å, $\beta=115.29(3)°$, $U=2600(1)$ Å^3, Dc $(Z=4)=1.258$ g cm^{-1}, $\mu=0.81$ cm^{-1}, $T=153$ K. The final R value is 0.050 for 1357 independent reflections with $I>3\sigma I$ and 163 parameters.
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