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One-step synthesis and redox properties of dodecahydro-3a,9a-diazaperylene—the most easily oxidized *p*-phenylenediamine

Abdel Monem M. Rawashdeh, Chariklia Sotiriou-Leventis,* Xuerong Gao and Nicholas Leventis*

Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65409, USA.
E-mail: cslevent@umr.edu (CSL); Fax: +1 573 341 6033; Tel: +1 573 341 4353(CSL);
E-mail: leventis@umr.edu (NL); Tel: +1 573 341 4391(NL)

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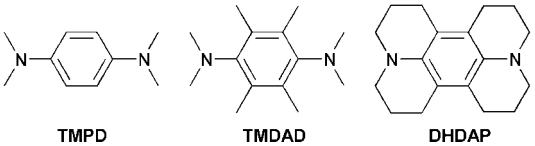
Dodecahydro-3a,9a-diazaperylene (DHDAP) was prepared in one step from *p*-phenylenediamine and 1-bromo-3-chloropropane, and its first redox potential is 292 mV more negative than the first redox potential of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), thus becoming the most easily oxidized *p*-phenylenediamine homologue.

The quest for structure–function relationships in redox chemistry finds an expression in tuning and control of redox potentials. In this context, alkylation is known to increase the electron density and render aromatic systems more easily oxidized. For example, the redox potentials of decamethylmetallocenes are shifted by about 0.5 V to more negative values relative to the corresponding metallocene–metallocenium couples.[1] Similarly, conducting polymer precursors such as *N*-methylpyrrole and 3-methylthiophene are easier to oxidize by 0.06 and 0.20 V relative to pyrrole[2] and thiophene,[3] respectively.

N,N,N′,N′-tetraalkyl-*p*-phenylenediamines, and particularly *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), are among the most well-known redox systems, typically undergoing two well-separated (*vide infra*) chemically and electrochemically reversible one-electron oxidations.[4] Consequently, this class of compounds has been considered for fundamental studies in electrochemical[5] and photoinduced electron transfer,[6] as derivatizing agents for electrodes in conjunction with redox mediation of biological reagents,[7] as electrochromic materials,[8] and more recently as flow indicators in electrochemically generated magnetohydrodynamic convection.[9] The structures of three representative *p*-phenylenediamines pertinent to the ensuing discussion are:



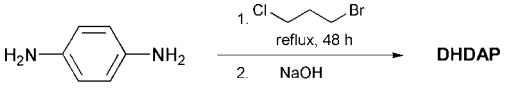
In general, the various derivatives of the parent *p*-phenylenediamine demonstrate the typical pattern of lower redox potentials as the degree of methylation increases (Table 1). TMPD has been the easiest to oxidize homologue in that series of compounds, and in fact it is one of the most easily oxidizable organic compounds. Importantly, methylation of the phenyl ring of TMPD does not lower the redox potential any further: *N,N,N′,N′*-tetramethyl-3,6-diaminodurene (TMDAD) is not only more difficult to oxidize than TMPD, but also according to Evans and Hu,[10] the second one-electron oxidation occurs at a less positive potential than the first one, so electrochemical oxidation of TMDAD yields directly the two-electron oxidized form. Evans and co-workers have proposed that this redox potential reversal is due to large conformational changes occurring during the oxidation of TMDAD, but not of TMPD. The essence of Evans' theory is that if any of the redox forms of TMDAD were planar, the H-atoms of the *N*-methyl groups would compete for space with the H-atoms of the aromatic methyl groups. The neutral form of TMDAD avoids these steric repulsions by twisting the dimethylamino groups out of planarity with the aromatic system. This is supported by the blue-shifted absorption spectrum of TMDAD relative to that of TMPD (Table 1). The two-electron oxidized form of TMDAD avoids the steric repulsions by adopting a boat-like conformation.[10] At this point, we reasoned that if the *N*-methyl and the aromatic methyl groups of TMDAD were bridged by a single atom, the competition for space by the aforementioned H-atoms would no longer exist, and the steric reasons for the abnormal behaviour of TMDAD would be eliminated. The resulting molecule, DHDAP, should demonstrate redox chemistry analogous to that of TMPD, but it should be much easier to oxidize than the latter. These expectations are justified fully by the following results.

Table 1 Redox and electronic absorption data for various *p*-phenylenediamines in acetonitrile[a]

Compound[b]	$E_{1/2}(1)$, V ($\Delta E_{p\text{-}p}$, V)	$E_{1/2}(2)$, V ($\Delta E_{p\text{-}p}$, V)	λ_{max}/nm ($\varepsilon \times 10^{-3}$/M^{-1} cm^{-1})		
p-Phenylenediamine	−0.106 (0.063)	0.429 (0.068)	321 (2.6)	251 (9.9)	
3,6-Diaminodurene	−0.259 (0.068)	0.237 (0.066)	308 (3.9)	245 (9.8)	
TMPD	−0.281 (0.062)	0.294 (0.060)	332 (2.5)	266 (17.4)	
TMDAD	−0.068 (0.443)		264 (3.6)	218 (13.0)	
DHDAP	−0.573 (0.066)	−0.037 (0.065)	338 (27.6)	280 (65.6)	220 (193)

[a] All redox data were determined by cyclic voltammetry in CH_3CN–0.1 M *n*-$Bu_4N^+ClO_4$ (applying 80% compensation for the solution resistance), and are reported *versus* ferrocene. The $E_{1/2}$ values are the mid-points between the anodic and cathodic peak currents. [b] *p*-phenylenediamine, 3,6-diaminodurene, and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) were commercially available and sublimed before use. *N,N,N′,N′*-tetramethyl-3,6-diaminodurene (TMDAD) was prepared according to the literature.[10] Dodecahydro-3a,9a-diazaperylene (DHDAP) was prepared in this study.†

The previously reported preparation procedure for DHDAP involves multistep synthesis.[11] Here, DHDAP was synthesized in high yield from *p*-phenylenediamine and 1-bromo-3-chloropropane in one step (Scheme 1).† DHDAP is stable as a solid,



Scheme 1

and in oxygen-free solutions. Its solubility in CH_3CN is in the 2–3 mM range, but in CH_2Cl_2 is significantly higher. Like TMPD, in non-degassed solvents DHDAP is oxidized slowly, yielding blue solutions. In further analogy to TMPD, DHDAP shows two successive one-electron oxidations, but both of its

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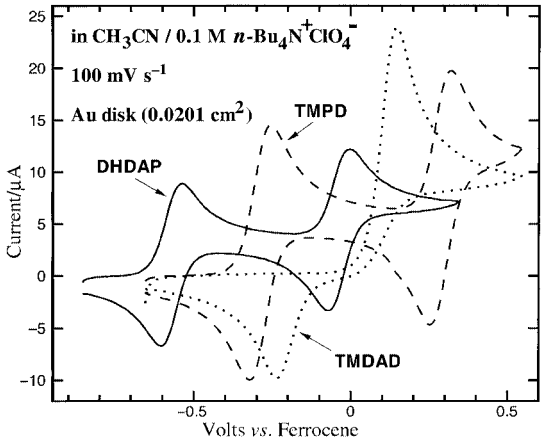

Fig. 1 Cyclic voltammograms of TMPD (1.71 mM), TMDAD (1.59 mM) and DHDAP (1.38 mM) in Ar degassed solutions.

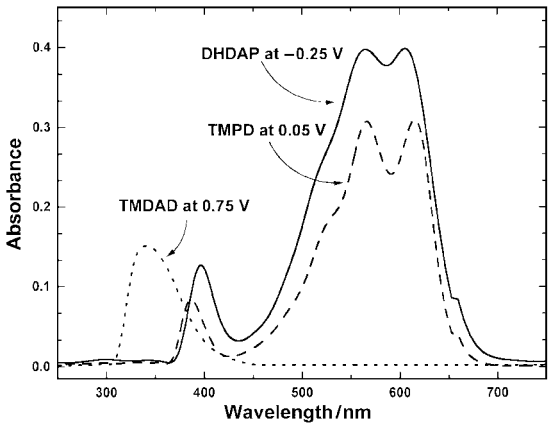

Fig. 2 Absorption spectra of TMPD (10.6 mM), TMDAD (11.1 mM), and DHDAP (7.9 mM) recorded with a dual ITO-electrode thin-layer cell in Ar degassed CH_2Cl_2–0.1 M n-$Bu_4N^+ClO_4^-$.

cyclic voltammetric (CV) waves are negative-shifted relative to those of TMPD, by 292 mV for the first and 331 mV for the second (Fig. 1). By comparison, TMDAD (its CV is also included in Fig. 1) is oxidized 0.213 V more positive than TMPD, reflecting its twisted geometry, which limits the extent of conjugation. The anodic-to-cathodic peak current ratios for both waves of DHDAP are equal to 1.0, indicating chemical reversibilty. Bulk electrolysis to $DHDAP^{\cdot+}$ and then back to DHDAP under the conditions of Fig. 1 led to 100% recovery of DHDAP (by ultramicroelectrode voltammetry), showing that $DHDAP^{\cdot+}$ is a stable species. The same experiment yielded the following diffusion coefficient data: $D_{DHDAP} = 1.52 \times 10^{-5}$ $cm^2\ s^{-1}$ and $D_{DHDAP^{\cdot+}}/D_{DHDAP} = 0.89$. By comparison, $D_{TMPD} = 2.58 \times 10^{-5}$ $cm^2\ s^{-1}$ and $D_{TMPD^{\cdot+}}/D_{TMPD} = 0.79$,[12] reflecting the somewhat smaller size of TMPD. (The different sizes of the CV waves of DHDAP and TMPD in Fig. 1 can be accounted for completely by the small differences in the concentrations and the diffusion coefficients.) Bulk electrolysis to $DHDAP^{2+}$ in CH_3CN–0.1 M $NaClO_4$ led to *ca.*. 80% recovery of DHDAP. The peak-to-peak separation of DHDAP is 66 ± 1 mV (*vs.* 59 mV for ferrocene) indicating a nearly reversible redox couple. Indeed, fitting the CV data with the Perkin–Elmer COOL™ software package we obtained as electron transfer coefficient for the first wave, $\alpha = 0.546$ (indicating an almost symmetric transition state) and a relatively high value for the standard rate constant, $k^\circ = 10.7$ cm s^{-1}.

The 292 mV negative shift of the first oxidation wave of DHDAP relative to TMPD indicates that the HOMO of the former is significantly higher in energy. Also, the two lower energy absorptions of DHDAP are red-shifted by only 7–23 mV (6–14 nm) relative to TMPD's (Table 1), suggesting that the HOMO and the LUMO of DHDAP are destabilized simultaneously by comparable amounts of energy.

The blue $DHDAP^{\cdot+}$ and $TMPD^{\cdot+}$ radicals were generated quantitatively in transparent thin layer electrochemical cells,[8] and their absorption spectra are shown in Fig. 2 alongside the spectrum of $TMDAD^{2+}$. The spectrum of $DHDAP^{\cdot+}$ is identical to the spectrum of $TMPD^{\cdot+}$, indicating analogous structures and identical chromophores. Similarly, the spectrum of the yellow $DHDAP^{2+}$ in CH_3CN–0.1 M $NaClO_4$ (not shown here) is identical to the spectrum of $TMDAD^{2+}$. Although energy minimization (AM1 method) yields a boat-like structure for $TMDAD^{2+}$,[10] and a planar structure for $DHDAP^{2+}$, the fact that their absorption spectra are identical implies that the differences in their geometry are not important. In both cases the iminium groups are electronically isolated from one another, probably due to the perturbation imposed by the positive *N*-atoms.

In summary, the preparation of DHDAP has been straightforward. DHDAP demonstrates two well-separated one-electron oxidation waves, shifted negatively by about 300 mV compared with the corresponding waves of TMPD. DHDAP is expected to render itself a main stream redox-active substance, with utility in redox staircases, and as a charge transfer quencher.

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Notes and references

† *Synthesis of dodecahydro-3a,9a-diazaperylene*‡ *(DHDAP)*: *p*-phenylenediamine (0.50 g, 4.6 mmol, Aldrich, purified by sublimation) was added to 1-bromo-3-chloropropane (25 ml, 0.25 mol) and the resulting yellow solution was refluxed under Ar for 48 h. During this time a precipitate was formed and the color of the reaction mixture changed to orange. It was then cooled to rt, filtered under Ar and the pale orange solid was washed with diethyl ether and dried *in vacuo* to give DHDAP2H$^+$Br$^-$Cl$^-$ (1.51 g); ^{1}H NMR (400 MHz, D_2O): δ = 7.35 (s, 2H), 3.39 (t, J = 5.7 Hz, 8H,), 2.66 (t, J = 6.9 Hz, 8H), 2.10 (quint, J = 5.7 Hz, 6.9 Hz, 8H). A solution of the latter in 1 M HCl (50 ml, argon degassed) was made basic with 10% NaOH (argon degassed) and then extracted with diethyl ether (3 × 100 ml). Concentration of the pale yellow ether extracts after adding charcoal (rt) and drying over solid NaOH yielded 0.40 g (32%) of DHDAP as colorless platelets;§ mp 188–190 °C (lit.[11a] mp 190–191 °C; lit.[11b] mp 189–190 °C); ^{13}C NMR (100 MHz, argon degassed $CDCl_3$): δ = 136.4, 119.6, 50.4, 24.9, 22.9 ppm; anal. calcd. for $C_{18}H_{24}N_2$ (268.19): C, 80.55; H, 9.01; N, 10.44; found: C, 80.37; H, 9.06; N, 10.23.

‡ In ref. 11, the name of this compound was reported incorrectly as 1,2,3,3a,4,5,6,7,8,9,9a,10,11,12-tetradecahydro-3a,9a-diazaperylene.

§ The isolation of protonated DHDAP may be bypassed by extraction of the reaction mixture with water, basification and isolation of DHDAP as above.

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