

## Electronic Structure of 1,4-Dihydro-1,2,4,5-tetrazines and of Related 1,4-Dihydroaromatic Compounds

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1,4-Dihydro-1,2,4,5-tetrazine (1) and its 1,4-dimethyl (2) and 1,4-bis(trimethylsilyl) (3) derivative have been studied by photoelectron spectroscopy and cyclic voltammetry. The compounds are electron-rich, albeit not as much as the corresponding 1,4-dihydropyrazines. Electrochemical data illustrate the stability of the 1,4-dihydro form in the tetrazine system and of the radical cation oxidation state in the pyrazine system. Results of MNDO calculations for (1) and for 1,4-dihydro-benzene (4), -pyrazine (5), and -hexazine (6) indicate a contraction of bonds in the six-membered ring upon consecutive replacement of CH by N, accompanied by increasing deviation from planarity and decreasing  $\pi$  electron conjugation.

In the pyrazinium-1,4-dihydropyrazine redox system the reduced and potentially antiaromatic  $8\pi$  electron form C of the parent species ( $X = H$ ) is not persistent.<sup>1</sup> While simple organic derivatives ( $X = R$ ) are only metastable,<sup>1,2</sup> steric hindrance in highly substituted systems<sup>3</sup> as well as organometallic substituents ( $X = SiR_3, GeR_3$ ) may stabilize this oxidation state.<sup>4</sup>

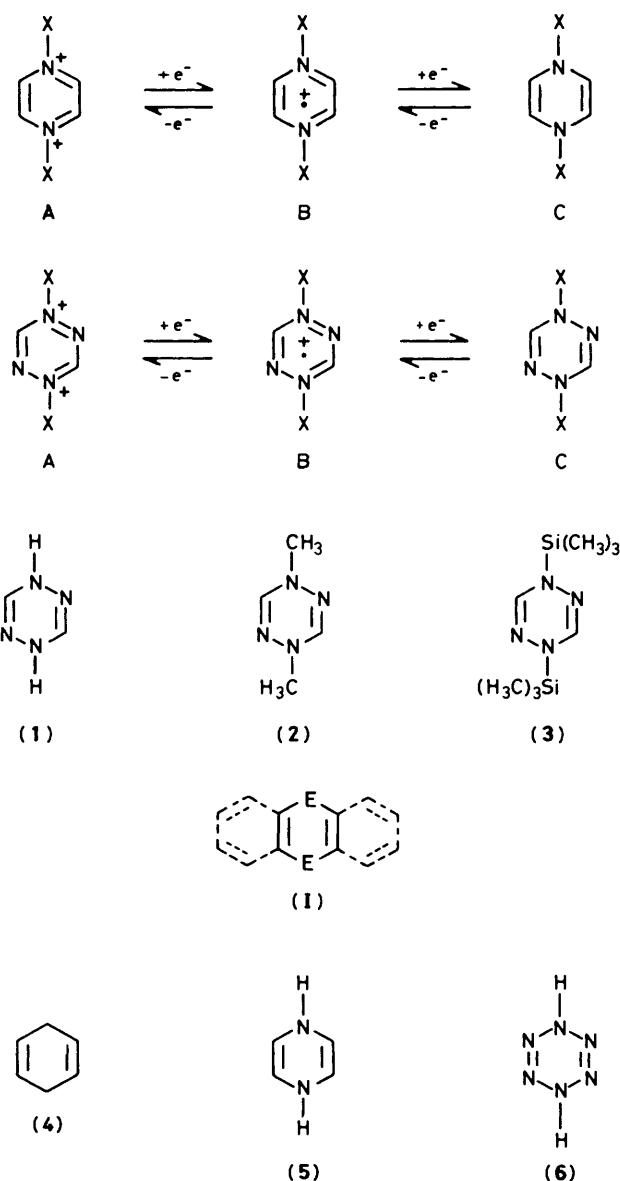
In contrast, reduced forms such as (1) and (2) have long been known<sup>5,6</sup> for the related 1,2,4,5-tetrazine system, and recently, some of them have been structurally characterized.<sup>7</sup> In addition to compounds (1) and (2) we have now prepared the corresponding bis(trimethylsilyl) derivative (3) in order to study the effect of different substituents on chemical and spectroscopic properties and to compare these species with their 1,4-dihydropyrazine analogues.

Since there has been a great interest<sup>8-12</sup> in the conformation of molecules of the general formula (I;  $E = CR_2, SiR_2, NR, PR, O,$  or  $S$ ) we have performed MNDO calculations<sup>13,14</sup> for (1) and for the as yet unknown 1,4-dihydrohexazine (6). MNDO calculations have been reported recently for the first two members of that series, for cyclohexa-1,4-diene (= 1,4-dihydrobenzene) (4)<sup>9</sup> and 1,4-dihydropyrazine (5).<sup>12</sup>

**Spectroscopic Properties of 1,4-Dihydro-1,2,4,5-tetrazines.**— In addition to the known compounds (1)<sup>5</sup> and (2)<sup>6</sup> we have prepared the organometallic derivative (3). Surprisingly, reductive silylation of the electron-poor<sup>15</sup> 1,2,4,5-tetrazine proved to be unsuccessful, hence we had to employ the base-assisted substitution of compound (1). Characterization of compounds (1)–(3) by <sup>1</sup>H n.m.r. did not exhibit any significant effects from different substitution at the 1,4-nitrogen atoms. This suggests that cyclic  $8\pi$ -electron conjugation is no longer as effective as in some of the 1,4-dihydropyrazines which exhibit a paramagnetic ring current.<sup>16</sup>

The electron-rich character of the compounds has been studied by cyclic voltammetry in solution and by photoelectron (p.e.) spectroscopy in the gas phase. The p.e. spectra (*cf.* Figure 1) of the species (1)–(3) show decreasing ionization potential (i.p.) in the order i.p. (1) > i.p. (2) > i.p. (3) (Table 1). In particular, the difference between the methyl (2) and the trimethylsilyl derivative (3) is quite large and exceeds similar effects in simple amines.<sup>17</sup> This result may indicate some remaining degree of cyclic  $\pi$ -electron interaction in (3) due to a more planar configuration at the silyl-substituted nitrogen atoms.<sup>18</sup>

When comparing the p.e. data of (3) and of the corresponding 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (7),<sup>4</sup> the loss of the unusual properties typical of (7) becomes apparent: i.p. (3) is *ca.* 1 eV higher than i.p. (7), *i.e.*, compound (3) should be less susceptible to oxidation. In fact, in contrast to the pyrophoric 1,4-



dihydropyrazine (7), the corresponding 1,4-dihydro-1,2,4,5-tetrazine derivative (3) is stable in a dry atmosphere. Further-

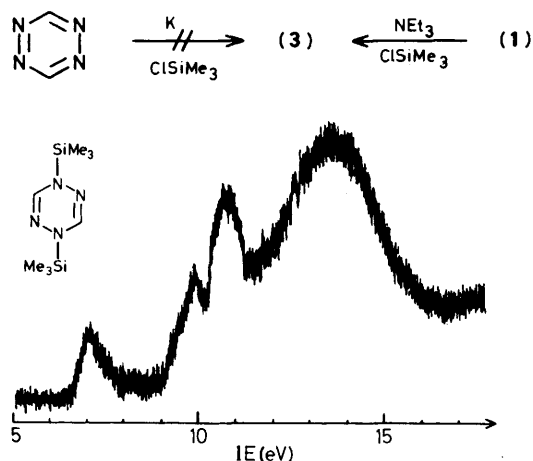
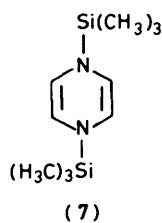


Figure 1. Photoelectron spectrum of compound (3)

Table 1. First vertical<sup>a</sup> ionization energies IE (eV) of 1,4-dihydro-1,2,4,5-tetrazines and 1,4-dihydropyrazines as determined by photoelectron spectroscopy

Compound	IE <sub>1</sub>	IE <sub>2</sub>	Δ = IE <sub>2</sub> - IE <sub>1</sub>
(1)	8.2	10.7	2.5
(2)	7.85	10.3	2.45
(3)	7.15	10.0	2.85
(7)	6.16	9.5	3.34

<sup>a</sup> Band maximum.



more, the difference Δ between the first (i.p. = IE<sub>1</sub>) and the following ionization energy IE<sub>2</sub> has been reduced for (3) relative to (7). Thus, the frontier molecular orbital (HOMO) associated with i.p.<sup>16</sup> no longer exhibits the 'anti-bonding' character<sup>16,19</sup> typical for (7). Although this difference between the 1,4-diazine and the 1,2,4,5-tetrazine system may be rationalized in a Hückel MO perturbation approach (Figure 2), showing that the LUMO of the aromatic (6π) form (possibly becoming the HOMO of the 1,4-dihydro 8π electron form) is stabilized in the tetrazine system, the structural data<sup>7</sup> and the MNDO calculation results presented in the following section demonstrate that the requirement of planarity for such a simple Hückel MO treatment is clearly no longer valid for the 1,4-dihydro-1,2,4,5-tetrazines.

A discussion of electrochemical redox potentials will focus on the 1,4-dimethyl derivative (2), since data are also available for related 1,4-dialkylpyrazines.<sup>2</sup> The other 1,4-dihydro-1,2,4,5-tetrazines proved to be less suitable for electrochemistry, either because of the pronounced acid-base sensitivity<sup>20</sup> of the potentials [(1)] or because of complications arising from adsorption processes at the electrode [(3)].<sup>13</sup> Compound (2), however, shows two oxidation peaks in DMF (Figure 3); the first reversible oxidation to the radical cation occurring at

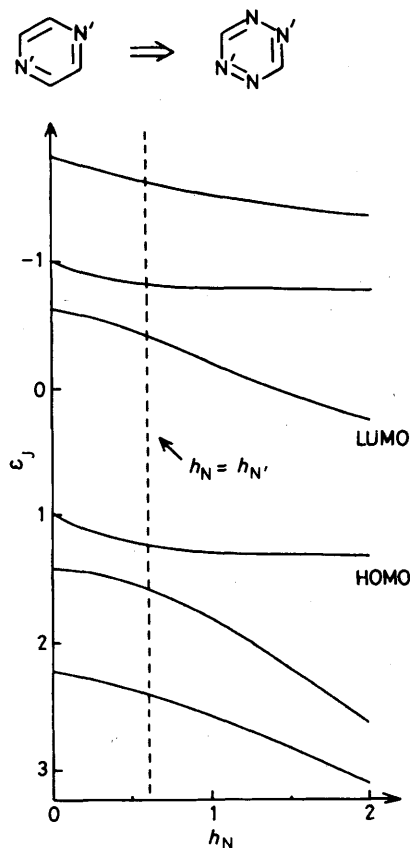


Figure 2. Hückel MO correlation of π orbital energies ε<sub>j</sub>(β) versus the Coulomb integral parameter h<sub>N</sub> for the transition pyrazine → 1,2,4,5-tetrazine → 1,4-dihydro-1,2,4,5-tetrazine (h<sub>N</sub> remains constant at 0.6)

+ 0.40 V versus saturated calomel electrode (s.c.e.) is apparently followed by further oxidation around E<sub>pa</sub> ~ 1.4 V which already occurs in the region of solvent oxidation. Although this second oxidation step is not well defined, the difference of > 1 V between both potentials is typical for 1,2,4,5-tetrazine two-step redox systems.<sup>21</sup> In agreement with the large range of stability of the radical cation intermediate, such species are also conveniently generated by comproportionation or chemical oxidation in various solvents.<sup>6,7,22</sup>

Despite the low ionization potential of (3) we have not been able so far to generate a persistent radical cation thereof. In agreement with the poor electrochemical behaviour, the *intra muros* electrolysis of (3) in an e.s.r. spectrometer produced only (1)<sup>++</sup> after prolonged anodic oxidation [coupling constants of (1)<sup>++</sup> in DMF: a<sub>N</sub> 450 and 717, a<sub>H</sub> 894 μT]. Even the well established<sup>23</sup> one-electron oxidation procedure using AlCl<sub>3</sub>\* in dichloromethane failed to give a radical cation of (3), presumably because the Lewis-acidic species AlCl<sub>3</sub> can co-ordinate to the 2,5-(imine)-nitrogen lone pairs in the molecule, rendering such a σ complex no longer electron-rich enough to lose a π electron.† Conversely, such σ co-ordinations have been shown to favour one-electron reduction and to stabilize anion π radicals.<sup>1,26</sup>

\* A bonus of the one-electron oxidant AlCl<sub>3</sub> is to trap, i.e. to co-ordinate to nucleophilic impurities which would otherwise deactivate reactive cation radicals.<sup>24</sup>

† This complexation does not affect the oxidation of donors where lone pairs can become part of the open-shell π system such as amines, hydrazines,<sup>25</sup> or disulphides.

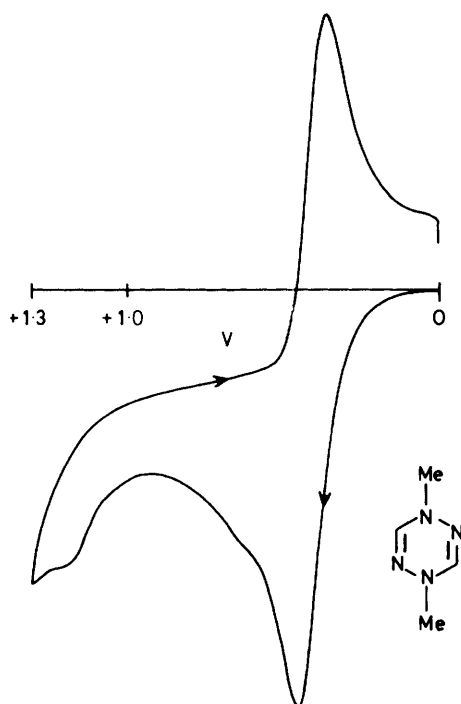
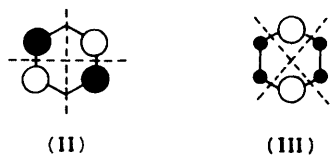


Figure 3. Cyclic voltammogram of compound (2) in DMF, scan rate  $100 \text{ mV s}^{-1}$

The relation between the oxidation potential in solution and the ionization potential in the gas phase of (2) does not fit with correlations<sup>27,28</sup> established for molecules with little geometry change during oxidation. Such a deviation is, however, typical for compounds containing amine nitrogen atoms, it indicates substantial conformational relaxation, most likely planarization at the nitrogen atoms after the loss of an electron.<sup>28</sup>

A comparison between redox potentials of benzene, 1,4-diazine, and 1,2,4,5-tetrazine systems may illustrate the stabilities of the individual oxidation states in those redox systems (Figure 4). The parent molecules benzene ( $E_{\text{red}} -3.42 \text{ V}$  at  $-60^\circ \text{C}$  in DME<sup>29</sup>), pyrazine ( $E_{\text{red}} -2.13 \text{ V}$ <sup>15</sup>) and 1,2,4,5-tetrazine ( $E_{\text{red}} -0.81 \text{ V}$ <sup>15</sup>) show a distinctive decrease of the (negative) reduction potential, *i.e.*, on successive substitution of CH by N. The effects are most pronounced for these particular heteroaromatic isomers because their perturbation pattern coincides with the dominant  $\pi$  frontier orbital coefficients of the benzene system [(II), (III)].



Enhancing the  $\pi$ -electron deficiency by 1,4-bis(acceptor) substitution of benzene or, in the heterocycles, by quaternization of the 1,4-nitrogen atoms allows the observation of the second reduction step to the  $8\pi$  electron systems. These  $6\pi$ – $7\pi$ – $8\pi$  electron redox systems (Figure 4) may then be characterized as follows.

Even on 1,4-distribution with the strongly electron-accepting nitro group (*cf.* Figure 4) the benzene system has both redox potentials in the negative region relative to s.c.e.<sup>30</sup> Accordingly, anion radicals of benzene derivatives are in general sensitive towards oxidation.

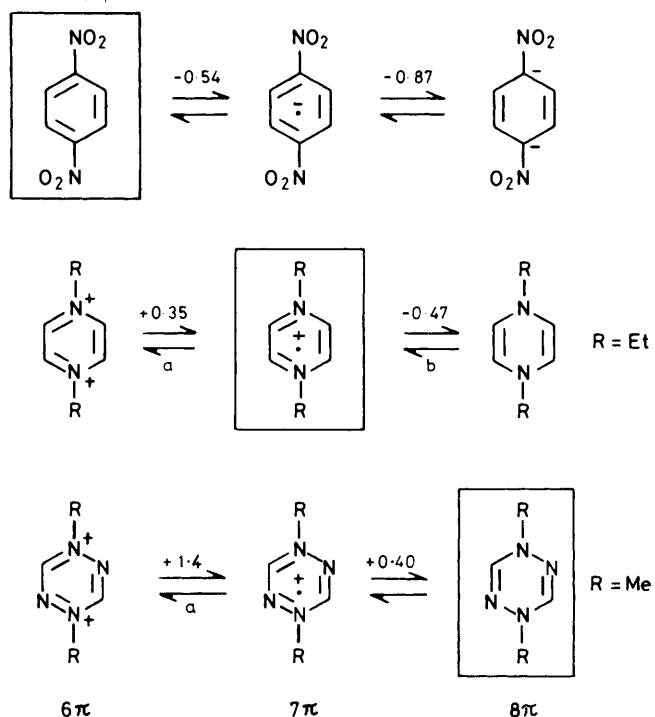


Figure 4. 1,4-Dinitrobenzene, 1,4-dialkylpyrazinium, and 1,4-dialkyl-1,2,4,5-tetrazinium redox systems with their potentials ( $V$  versus s.c.e.) measured in DMF. The most persistent oxidation states are indicated; a, irreversible process (anodic peak potential at  $100 \text{ mV s}^{-1}$  given); b, quasi-reversible process

In the 1,4-dialkyl-1,2,4,5-tetrazine system *both* potentials are positive versus s.c.e. Obviously, the reduced forms are very persistent in this case, as may also be inferred from their early preparation.<sup>5</sup> The  $7\pi$ -electron (radical cation) oxidation state is accessible by oxidation of the 1,4-dihydro derivatives.<sup>7</sup>

The 1,4-dialkyl-1,4-diazine system exhibits intermediate behaviour. One potential is positive, the other negative relative to s.c.e. This thermodynamically intermediate position finds an equivalent in the reactivity of such systems; in some cases, the cation radical intermediate represents the only persistent oxidation state.<sup>2</sup>

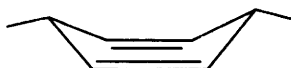
**MNDO Calculations.**—Following reports of MNDO calculations of cyclohexa-1,4-diene (= 1,4-dihydrobenzene) (4)<sup>9</sup> and of 1,4-dihydropyrazine (5),<sup>12</sup> the MNDO geometry-optimization procedure has also been applied to (1) and to the final member in that series, *viz.*, the as yet unknown 1,4-dihydrohexazine (6). In view of the limitations of the MNDO method<sup>13,14,31</sup> the objective could only be to establish characteristic trends in the series (4), (5), (1), (6), *i.e.*, on consecutive replacement of CH by N. Comparing the calculated energy-minimum conformation of (1) with the molecular structure in the crystal, *viz.*, a boat conformation (IV) with equatorial N-hydrogens,<sup>7</sup> should give some clues concerning the reliability of such calculations for the type of molecules at hand. However, considering the relatively shallow energy hypersurfaces of such systems,<sup>9,12</sup> some allowance should be made when calculation results for isolated molecules are compared with data from solid-state structures.

The results given in Table 2 show a reasonable agreement between MNDO, calculated geometries and experimental structures of compounds (4)<sup>9</sup> and (1). Incidentally, much less satisfactory results were obtained by the MINDO/3 method. Encouraged by this qualitative agreement, the calculated data

**Table 2.** Calculated<sup>a</sup> and experimental<sup>b</sup> properties of cyclohexa-1,4-diene (4)<sup>9</sup> and of 1,4-dihydropolyazines

	(4) <sup>b</sup>	(5) <sup>c</sup>	(1) <sup>b</sup>	(6)
Boat angle $\alpha$ (°) <sup>d</sup>	180 (180)	167	154 (147)	149
Sum of angles at $sp^3$ nitrogen (°)		337	336 (339)	335
Length of ring double bond (pm)	134.7 (133.4)	135.4	130.7 (126.5)	123.2
Length of ring single bond (pm)	150.6 (149.6)	143.2	136.6 (138.5) <sup>e</sup>	137.9
			143.9 (143.6)	
I.p. (eV)	<i>f</i> (8.80) <sup>g</sup>	7.85	9.17 (8.3)	10.83
$\Delta H_f^{\text{MNDO}}$ /kcal mol <sup>-1</sup>	<i>f</i>	40.0	64.3	88.8

<sup>a</sup> Complete geometry optimization with MNDO. <sup>b</sup> Experimental values<sup>7,9</sup> in parentheses. <sup>c</sup> Ref. 12. <sup>d</sup> Dihedral angle of molecular halves intersecting at the  $sp^3$  ring atoms. <sup>e</sup> C-N and N-N bond lengths, respectively. <sup>f</sup> Not reported. <sup>g</sup> E. Heilbronner, F. Brogli, and E. Vogel, *J. Electron Spectrosc. Relat. Phenom.*, 1976, 9, 227.



(IV)



(8)

for the series in Table 2 have been compared and have revealed the following effects upon replacement of CH by N.

The conformation of the six-membered ring changes from a planar arrangement to an increasingly pronounced boat structure. This phenomenon may be traced back to the contraction of bonds which, in turn, leads to enhanced repulsive interactions between ring substituents and/or unshared electron pairs.<sup>12,32</sup>

The configuration at the  $sp^3$  nitrogen atoms remains fairly constant, deviations from a nearly tetrahedral arrangement are disfavoured in all instances (inversion barrier<sup>12</sup>).

As a consequence of increasing deviation from planarity, the calculated ionization potentials increase in the series i.p. (5) < i.p. (1) < i.p. (6), indicating less cyclic  $8\pi$  electron interaction.<sup>16</sup> This result confirms the interpretation of the p.e. data for the bis(trimethylsilyl) derivatives (3) and (7) (Table 1).

The MNDO total energies increase in the series of Table 2 as a consequence of the repulsive interactions described above. Nevertheless, stable minima were obtained for all species, including the 1,4-dihydrohexazine (6). In the current discussion<sup>33</sup> on the structure and stability of the equally hypothetical hexazine (8) (MNDDO/1 energy: 323 kcal mol<sup>-1</sup><sup>34</sup>) the aspect of redox reactivity had not been considered. It must be assumed that (8) would be quite electron-poor and might not, therefore, represent the most persistent form in the presence of electrophiles and reducing agents. Hence, attention is directed to the 1,4-dihydro form (6) and its derivatives which are characterized by a favourable<sup>35</sup> cyclic alternating arrangement of donor (>N-X) and acceptor functions (-N=N-).

In conclusion, the experimental and theoretical results presented here add some new facets to the problem of the electronic and molecular<sup>8</sup> structure of 1,4-dihydroaromatic compounds. The systematic overview now possible exhibits a remarkable variability of this class of compounds, depending critically on the perturbation pattern. The most stable oxidation states range from aromatic  $6\pi$  electron forms via  $7\pi$  radical species to 1,4-dihydro ( $8\pi$  electron) forms, and structures of the latter may vary from fully planar to considerably boat-shaped six-membered ring conformations.

## Experimental

**Materials.**—Compounds (1) and (2) were prepared according to literature procedures.<sup>5,6</sup> 1,4-Dihydro-1,2,4-tetrazine (1) had  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 6.46 (2 H, s, 3,6-H) and 8.02 (2 H, s, 1,4-H); 1,4-dimethyl-1,4-dihydro-1,2,4,5-tetrazine (2) had  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 3.15 (6 H, s, 1,4-CH<sub>3</sub>) and 6.49 (2 H, s, 3,6-H).

**1,4-Bis(trimethylsilyl)-1,4-dihydro-1,2,4,5-tetrazine (3).**—Compound (1) (0.3 g, 3.6 mmol) was dissolved in toluene (10 ml) and was stirred overnight with triethylamine (0.8 ml, 5.5 mmol) and chlorotrimethylsilane (0.7 ml, 5.5 mmol). Evaporation of the solvent and sublimation of the residue at 60–70 °C and 0.1 Torr gave bright yellow (3) (0.17 g, 0.75 mmol, 20%), m.p. 102 °C. The compound is stable in dry atmosphere (Found: C, 41.9; H, 8.7; N, 24.7. C<sub>8</sub>H<sub>20</sub>N<sub>4</sub>Si<sub>2</sub> requires C, 42.1; H, 8.8; N, 24.5%);  $\lambda_{\text{max}}$  (hexane) 225 and 360 nm (sh);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 0.25 (18 H, s, 1,4-SiMe) and 6.32 (2 H, s, 3,6-H).

**Methods.**—<sup>1</sup>H N.m.r.: Varian T60 instrument, CDCl<sub>3</sub> solutions with tetramethylsilane as internal standard. Photoelectron spectroscopy: Leybold Hereaus UPG 200, calibration with Xe(<sup>2</sup>P<sub>3/2</sub>) 12.13 eV and Ar(<sup>2</sup>P<sub>3/2</sub>) 15.76 peaks. Compound (1) showed some decomposition during the measurement.<sup>5</sup> Cyclic voltammetry: Princeton Applied Research system 173/175, glassy carbon working electrode, saturated calomel (s.c.e.) reference electrode. The solvent used was dry dimethylformamide (DMF) containing 0.1M-tetrabutylammonium perchlorate. The cyclic voltammogram of compound (3) was strongly affected by adsorption effects typical for silylated amines.<sup>36</sup> MNDO calculations were performed on a VAX 750/11 system using the available program,<sup>14</sup> including Fletcher–Powell geometry optimization, as described previously.<sup>12</sup>

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