

**N-METHYL DERIVATIVES OF [1,2,5]THIADIAZOLO[3,4-b]QUINOXALINE  
AND THE SELENIUM ANALOGS**

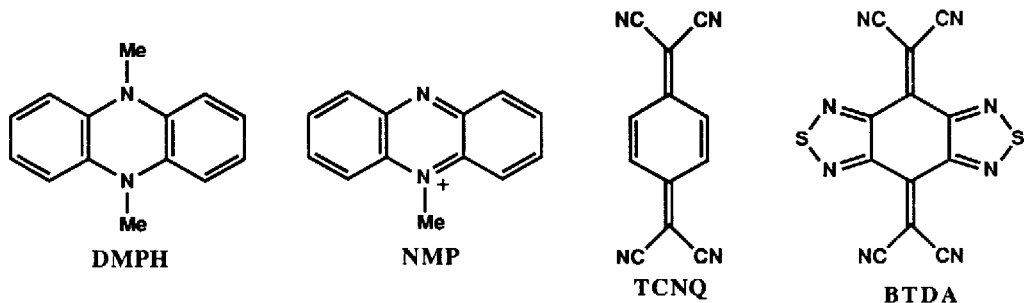
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Summary: A benzene ring of 5,10-dimethyl-5,10-dihydrophenazine (DMPH) was replaced by 1,2,5-thiadiazole or selenadiazole to give a new type of electron donors with electron withdrawing heterocycles. The similar replacement of a benzene ring of N-methylphenazinium (NMP) gave heterocyclic cations with extremely high electron affinities.

N-methyl derivatives of phenazine are known to show interesting physical properties. For example, the dimethyl derivative, 5,10-dimethyl-5,10-dihydrophenazine (DMPH), is a strong electron donor due to the  $16\pi$ -electron system.<sup>1</sup> The mono-methyl derivative, N-methylphenazinium (NMP), is a famous cation whose tetracyanoquinodimethane (TCNQ) anion radical salt is an organic metal.<sup>2</sup> On the other hand, we have prepared novel electron acceptors such as BTDA containing 1,2,5-thiadiazole rings, which have characteristic properties attributable to the heterocycle.<sup>3</sup> It seems interesting to replace a benzene ring of DMPH and NMP with a 1,2,5-thiadiazole or selenadiazole ring for the following reasons. First, introduction of the electron withdrawing heterocycles is expected to enhance the stability of the donor. Second, the chalcogen atom of the heterocycle is helpful to stabilize cationic species. Third, the replacement makes the molecules planar by canceling steric interactions between the peri-hydrogens of the benzene ring and the methyl



groups.<sup>4</sup> Finally, intermolecular interactions leading to unique molecular assemblies can be expected by S---N or Se---N heteroatom interactions as found in BTDA.<sup>5</sup> We report here the preparation and properties of title compounds which are formed by the replacement.

4,9-Dimethyl-4,9-dihydro[1,2,5]thiadiazolo[3,4-b]quinoxaline (**1a**)<sup>6</sup> was prepared in nearly quantitative yield from dihydro compound **2**, which was obtained by reduction of thiadiazoloquinoxaline **3a**,<sup>7</sup> by treatment with sodium hydride followed by reaction with methyl iodide. On the other hand, the selenium analog **1b**<sup>6</sup> was obtained in 70% yield by reduction of selenadiazoloquinoxaline **3b**<sup>7</sup> with potassium followed by methylation with methyl iodide. These heterocycles are more stable under air than DMPH. They are pale yellow crystals and have absorption maxima at longer wavelengths compared with DMPH [ $\lambda_{\text{max}}$  nm(log $\epsilon$ ) in CH<sub>2</sub>Cl<sub>2</sub>, **1a**; 390sh(3.75), 365(4.18), 349(4.21), **1b**; 398sh(3.92), 377(4.18), 361(4.18), DMPH; 341(3.97), 248(4.73)]. This red shift can be attributed to the contribution of the polarization caused by the electron withdrawing heterocycles. The oxidation potentials measured by cyclic voltammetry are shown in Table 1 along with those of DMPH and dibenzotetrathiafulvalene (DBTTF) measured under the same conditions. The higher values of the first oxidation potentials in **1a,b** compared with that in DMPH reflect the electron withdrawing property of a 1,2,5-thiadiazole ring and a 1,2,5-selenadiazole ring. However, the values are almost the same as that of DBTTF, indicating that the electron donating property of **1a,b** is comparable to that of DBTTF. The differences between the first and second oxidation potentials ( $\Delta E$ ) is larger in **1a,b** and DMPH than in DBTTF, indicating that the cation radicals of **1a,b** and DMPH are thermodynamically more stable than DBTTF. This result can be explained by considering that DBTTF whose dication is stabilized by formation of aromatic dithiolium ions more easily becomes a dication than **1a,b** and DMPH. In fact, the cation radical of **1b** could be isolated as a stable perchlorate salt<sup>8</sup> by electrochemical oxidation of a solution of **1b** and tetrabutylammonium perchlorate in dichloromethane although the corresponding salt of **1a** could not be crystallized due to the high solubility. The donors **1a,b** gave 1:1 charge-transfer complexes with TCNQ and BTDA, whose electrical conductivities were poor as shown in Table 2. They

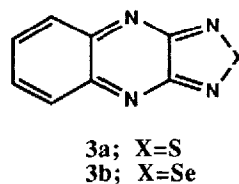
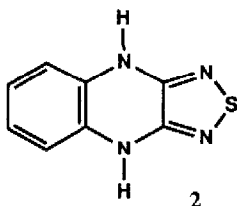
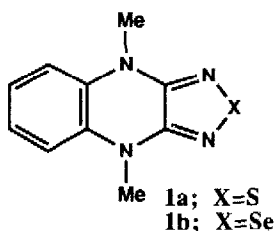


Table 1. Oxidation potentials<sup>a</sup> of donors

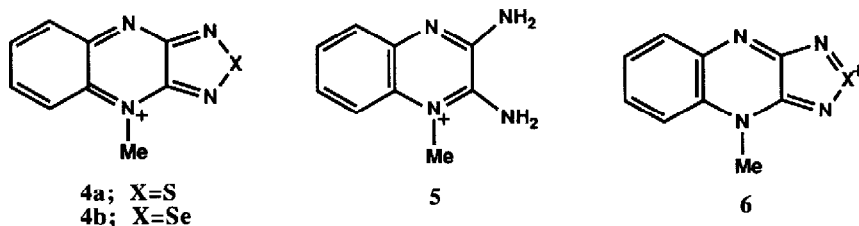
Compound	E <sup>1</sup> /V	E <sup>2</sup> /V	ΔE/V
<b>1a</b>	+0.54	+1.30 <sup>b</sup>	0.76
<b>1b</b>	+0.55	+1.13 <sup>b</sup>	0.58
DMPH	+0.14	+0.87	0.73
DBTTF	+0.54	+0.86	0.32

<sup>a</sup>0.1 mol dm<sup>-3</sup> Et<sub>4</sub>NClO<sub>4</sub> in MeCN, Pt electrode, scan rate 100 mV s<sup>-1</sup>, V vs. SCE. <sup>b</sup>Irreversible. Calculated as E<sub>pa</sub> (anodic peak potential) - 0.03.

Table 2. Molar ratios<sup>a</sup> and electrical resistivities, ρ,<sup>b</sup> of charge-transfer complexes of **1**

Compound	TCNQ		BTDA		I <sub>2</sub>	
	molar ratio	ρ/Ω cm	molar ratio	ρ/Ω cm	molar ratio	ρ/Ω cm
<b>1a</b>	1:1	>10 <sup>8</sup>	1:1	>10 <sup>8</sup>	1:1.5	6.3×10 <sup>5</sup>
<b>1b</b>	1:1	1.1×10 <sup>7</sup>	1:1	>10 <sup>8</sup>	1:1.5	7.7×10 <sup>4</sup>

<sup>a</sup>Based on elemental analyses. <sup>b</sup>Measured as compaction pellets by a two probe technique at room temperature.



also formed moderately conducting complexes with iodine, whose molar ratios show that they are 1:1 salts of I<sub>3</sub><sup>-</sup>.

The analogs of NMP, **4a,b**,<sup>9</sup> were obtained as tetrafluoroborate salts in 89% and 62% yields, respectively, by methylation of **3a,b** with trimethyloxonium tetrafluoroborate. Although they were stable in the solid state, they were easily ring-opened in solution by a nucleophilic attack of water to give diamino derivative **5**. The cyclic voltammograms of **4a,b** showed reversible or quasi-reversible waves at +0.46 and +0.51 V vs. SCE.<sup>10</sup> The values of the reduction potentials are extremely high compared with NMP (-0.12 V) and higher than trityl cation (+0.29 V, irreversible) which is known as a cation with a high electron affinity.<sup>11</sup> The high values can be attributed to the electron

withdrawing property of the heterocycles. The fact that such cations could be isolated may be rationalized by contribution of a resonance structure such as **6** which stabilizes the cation. Another interesting feature is the reversible nature which indicates that radical species are stable on the c.v. time scale. In fact, the radical formed by reduction of **4a** was detected by ESR.<sup>12</sup> The cation **4a** formed 1:1 TCNQ<sup>-</sup> and BTDA<sup>-</sup> salts although they were insulators.

#### References and Notes

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6. **1a**; mp 170.5–171.5 °C; IR (KBr) 1591, 1533, 1485, 1398, 1283, 730 cm<sup>-1</sup>, <sup>1</sup>H NMR (CDCl<sub>3</sub>) δppm 3.25 (s, 6H), 6.37–6.58 (m, 2H), 6.64–6.85 (m, 2H), **1b**; mp 231–232 °C, IR (KBr) 1521, 1505, 1493, 1393, 1299, 732 cm<sup>-1</sup>, <sup>1</sup>H NMR (CDCl<sub>3</sub>) δppm 3.43 (s, 6H), 6.54–6.72 (m, 2H), 6.75–6.91 (m, 2H).
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8. **1b**<sup>+</sup>ClO<sub>4</sub><sup>-</sup>; mp 230–232 °C (dec), UV (MeCN) λmax nm (logε) 577 (3.62), 426 (4.16), 398 (3.88), 372 (3.79), 351 (3.75), 336 (3.65), 230 (4.35).
9. **4a**·BF<sub>4</sub><sup>-</sup>; mp 159–160 °C (dec), IR (KBr) 1517, 1488, 1477, 1423, 1360, 1337, 1286, 1150–950 cm<sup>-1</sup>, MS m/z 204 (100%), 203 (M<sup>+</sup>-BF<sub>4</sub>, 76), 189 (88), 188 (90), **4b**·BF<sub>4</sub><sup>-</sup>; mp 182–185 °C (dec), IR (KBr) 1430, 1363, 1355, 1323, 1288, 1150–950 cm<sup>-1</sup>, MS m/z 252 (90%), 251 (M<sup>+</sup>-BF<sub>4</sub>, 100), 249 (53), 237 (49), 236 (98), 234 (66).
10. The electrochemical criteria for reversibility were satisfied as follows. The half-wave reduction potentials were independent on the scan rate, v. The current ratios, i<sub>pa</sub>/i<sub>pc</sub>, were near unity. The peak currents were proportional to v<sup>1/2</sup>.
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12. The ESR measurement was carried out by Prof. M. Hirayama of Ibaraki University. The result will be reported elsewhere.

(Received in Japan 22 July 1989)