BENZIDINE TYPE ELECTRON DONORS FUSED WITH 1,2,5-CHALCOGENADIAZOLE UNITS

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Abstract - The title electron donors (1 and 2) were prepared from 4-bromo-7-dialkylaminobenz[c][1,2,5]thiadiazole (3). They are electrochemically amphoteric, and the absorption maxima in the 500-550 nm region were assigned to the intramolecular charge-transfer (CT) bands. The X-ray analyses of 1b and 1b+PF6− revealed that the twisted geometry of 1b became planar upon one-electron oxidation, and a coplanar "ribbon"-like network was formed by S⋯N interactions in the crystal of 1b+PF6−.

Aromatic amines have been known as strong electron donors, and p-phenylenediamines and benzidines are the representative examples of the Wurster-type redox systems. Recently considerable attention has been focused on organic redox systems due to their intriguing behaviors such as electrical conduction and ferromagnetism in the solid. Because these properties are largely affected by the molecular arrangement in crystal, prediction and regulation of crystal structures are the central problems to be explored in detail. The "engineering" of molecular arrangements is also of significant importance in other areas such as solid-state reactions, and weakly attractive intermolecular interactions can be used for the crystal engineering. In this connection, the electrostatic interaction between heterocycles may be a useful tool for this purpose, which is suggested by various types of molecular networks formed by the chalcogen - nitrogen contacts in the crystal of 1,2,5-chalcogenadiazole derivatives. We report here the preparation and properties of benzidine derivatives fused with chalcogenadiazole units, which were designed in anticipation of the interheteroatom interactions affecting their crystal structures.
Scheme I

\[
\begin{align*}
\text{Br} & \quad \text{Me}_2\text{NH} / \text{DMI} \\
{\text{C}}_6\text{H}_4\text{N}=\text{S} & \quad \text{or pyrrollidine} \\
(5) & \quad \text{Ni}(0) \\
\quad & \quad \text{Br} \\
& \quad \text{NR}_2 \\
(3a,b) & \quad \text{Se} \\
\quad & \quad \text{NR}_2 \\
& \quad \text{Se} \\
(2a,b) & \quad \text{NH}_2 \\
(4a,b) & \quad \text{H}_2\text{N}_2 \\
\quad & \quad \text{H}_2\text{N}_2 \\
& \quad \text{NR}_2 \\
\end{align*}
\]

Scheme II

\[
\begin{align*}
\text{NR}_2 & \quad \text{(CF}_3\text{CO})_2\text{O} \\
{\text{C}}_6\text{H}_4\text{N}=\text{S} & \quad \text{Br-}(\text{CH}_2)_4\text{Br} \\
(6): \text{R}_2\text{N}=\text{H}_2\text{N}^{-} & \quad \text{KOH} \\
(7): \text{R}_2\text{N}=\text{-NHCOCF}_3 & \quad \text{LUMO} \\
(8): \text{R}_2\text{N}=\bigg\{ & \quad \text{HOMO} \\
\end{align*}
\]

Figure 1. HOMO and LUMO of 1 (R_2N^- = H_2N^-) obtained by the simple HMO method. The areas of the circles are proportional to the squares of the LCAO coefficients.
RESULTS AND DISCUSSION

Preparation. Reactions of 4,7-dibromobenzo[c][1,2,5]thiadiazole (5) with dimethylamine in 1,3-dimethyl-2-imidazolidinone (DMI) and with neat pyrrolidine afforded 7-dialkylamino derivatives (3a) and (3b), respectively (Scheme I). They were subjected to the reductive coupling by using a Ni(0) catalyst to give benzidine derivatives fused with 1,2,5-thiadiazole units (1a,b). Reductions of 1a and 1b with LiAlH4 afforded air sensitive hexamines (4a,b), and subsequent reactions with Se gave 2a and 2b fused with 1,2,5-selenadiazole rings. 4-(1-Pyrrolidinyl)benzo[c][1,2,5]thiadiazole (8) was prepared from 4-aminobenzol[c][1,2,5]thiadiazole (6) in order to compare the spectral properties with those of 1b possessing the same chromophore.

Redox properties and electronic spectra. As shown in Table 1, the first oxidation potentials ($E_{1\text{ox}}$) of 1 and 2 are the nearly same as that of $N,N,N',N'$-tetramethylbenzidine (TMB), and the cation radical of 1b was successfully isolated as PF6- and I3- salts by electrochemical oxidation in THF. The lower oxidation potentials of 1b and 2b than 1a and 2a are due to the stronger electron donating property of the pyrrolidinyl group than the dimethylamino group. It is noteworthy that the difference ($\Delta E_{\text{ox}}$) between $E_{1\text{ox}}$ and $E_{2\text{ox}}$ is much smaller in 1 or 2 than in TMB, showing that 1++ and 2++ can be oxidized more easily to the dications than TMB++. Because 1++ and 2++ are expected to possess planar geometries (vide infra), smaller $\Delta E_{\text{ox}}$ values indicate the reduced Coulombic repulsion by the annelation of heterocyclic $\pi$-systems, and the effect is larger in 2 containing Se with larger polarizability than S. On the other hand, 1 and 2 underwent reversible one-electron reduction, exhibiting their amphoteric character. Their stronger electron affinities than TMB may arise from the annelation of electron-withdrawing heterocycles, and comparisons of $\Delta E_{\text{sum}}$ values indicate that the selenadiazole derivatives (2) possess higher amphotericity than the thiadiazole derivatives (1). This finding is in accord with the fact that unsubstituted benzo[c][1,2,5]selenadiazole has a smaller $\Delta E_{\text{sum}}$ value than benzo[c][1,2,5]thiadiazole.

In the electronic spectra of 1 and 2, broad absorption maxima appeared in the 500-550 nm region and absorption coefficients were not affected by concentration. These absorptions were assigned to the intramolecular CT bands from the benzidine skeleton to the electron-withdrawing heterocycles by considering the orbital coefficient distribution in HOMO and LUMO (Figure 1). The similar absorption in the visible region was observed in the spectrum of 8 although its absorption maximum (460 nm in CH2Cl2) is shifted hypsochromically by 60 nm compared with 1b possessing the same chromophore. This shift implies the presence of $\pi$-conjugation between two chromophores through the C4-C4' bond in 1b, so that the perpendicularly twisted structure seems inappropriate for 1b.
Table 1. Redox potentials\(^a\) and absorption maxima of benzidine type donors, 1a, 1b, 2a, 2b, and TMB

<table>
<thead>
<tr>
<th></th>
<th>(E_{1\text{ox}})</th>
<th>(E_{2\text{ox}})</th>
<th>(\Delta E_{\text{ox}})(^b)</th>
<th>(E_{1\text{red}})</th>
<th>(\Delta E_{\text{sum}})(^c)</th>
<th>(\lambda_{\text{max}})(^d)</th>
</tr>
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<tbody>
<tr>
<td>1a</td>
<td>+0.56(\pm)0.59 (+0.59)</td>
<td>- (+0.75)</td>
<td>- (0.16)</td>
<td>-1.50</td>
<td>2.06</td>
<td>488</td>
</tr>
<tr>
<td>1b</td>
<td>+0.43 (+0.48)</td>
<td>+0.52 (+0.71)</td>
<td>0.09 (0.23)</td>
<td>-1.60</td>
<td>2.03</td>
<td>520</td>
</tr>
<tr>
<td>2a</td>
<td>+0.45(\pm)0.59 (ca.0.50)</td>
<td>- (+0.63)</td>
<td>- (ca. 0.13)</td>
<td>-1.40</td>
<td>1.85</td>
<td>504</td>
</tr>
<tr>
<td>2b</td>
<td>+0.34(\pm)0.34</td>
<td>- (+0.51)</td>
<td>- (ca. 0.17)</td>
<td>-1.49</td>
<td>1.83</td>
<td>552</td>
</tr>
<tr>
<td>TMB</td>
<td>+0.49 (+0.49)</td>
<td>+0.64 (+0.76)</td>
<td>0.15 (0.27)</td>
<td>&lt;2.0</td>
<td>&lt;2.49</td>
<td>-</td>
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</tbody>
</table>

\(^a\) \(E \)/V vs SCE, 0.1 mol dm\(^{-3}\) Et\(_4\)NClO\(_4\) in DMF, Pt wire, scan rate 100 mV s\(^{-1}\). \(E_{\text{ox}}\) of ferrocene is +0.45 V. Values in parentheses are those measured in CH\(_2\)Cl\(_2\) (0.1 mol dm\(^{-3}\) nBu\(_4\)NCIO\(_4\), \(E_{\text{ox}}\) of ferrocene is +0.52 V).

\(^b\) \(\Delta E_{\text{ox}} = E_{2\text{ox}} - E_{1\text{ox}}\).

\(^c\) \(\Delta E_{\text{sum}} = E_{1\text{ox}} - E_{1\text{red}}\).

\(^d\) Intramolecular CT bands in CH\(_2\)Cl\(_2\), values in nm.

\(^e\) One-wave two-electron processes.

\(^f\) Irreversible waves. Values were calculated as \(E_p - 0.03\) V.

\(^g\) The exact value would not be obtained because of the small separation of \(E_{1\text{ox}}\) and \(E_{2\text{ox}}\).

**X-ray structural analyses.** The X-ray analysis of 1b revealed that the two molecular halves are related by a crystallographic 2-fold axis, and the molecule possesses a twisted geometry around the central C4-C4' bond (Figure 2). Although the van der Waals (vdW) contacts\(^12\) between the orthohydrogens (H6 and H6') and nitrogen atoms (N2' and N2) of heterocycles may result in a twisted structure, the twisting angle is 43.4\(^\circ\), which is much smaller than those in 8,8'-biquinolyl (83.2\(^\circ\))\(^14\) and 2,2'-dimethyldibenzidine (86\(^\circ\))\(^5\) and rather close to those in 3,3'-dimethylbenzidine (41\(^\circ\))\(^15\) and 3,3'-dichlorobenzidine (21\(^\circ\))\(^16\) having no substituent at the ortho-positions. Furthermore, the bond distance of C4-C4' is 1.478(12) Å, corresponding to 20% of double bond character.\(^17\)

These structural features indicate the \(\pi\)-conjugation between two molecular halves in 1b, which is in accord with the conclusion obtained by comparisons of electronic spectra. On the other hand, molecules are packed in crystal without remarkable intermolecular interactions, and no interheteroatom contact of S==N was observed in neutral 1b. Although the molecular halves are arranged in a face-to-face manner as shown in Figure 3, the \(\pi\)-orbital overlap causing the HOMO-LUMO or NHOMO-LUMO interaction seems less important because the interplaner distance (3.72 Å) and N(3)==C(3) contacts (3.70 Å) are much longer than the sum of vdW radii of N==C (3.25 Å).\(^13\)

The geometry of 1b was drastically changed upon one-electron oxidation. Thus, two crystallographically independent molecules of 1b\(^+\) exhibit planar structures in the 1b\(^+\)PF\(_6\) crystal, and the twisting around the central bond is negligible (4.6\(^\circ\) and 3.6\(^\circ\) for molecule-A and -B, respectively). The enhanced double bond character in the central bond in 1b\(^+\) is expected by the MO consideration and may result in the geometrical change although
this idea could not be supported by comparisons of the bond distances [1.47(4) Å and 1.49(4) Å in molecule-A and -B, respectively] in 1b** with that in 1b because of the large observational errors. On the other hand, intramolecular contacts between orthohydrogens and heterocyclic nitrogens get closer due to the planar geometry in 1b**. Their N•••H distances and C-H•••N angles are 1.9-2.1 Å and 127-134°, respectively, suggesting the C-H•••N hydrogen bonding through these contacts. Both molecule-A and -B are connected by S•••N contacts along the c axis, resulting in the formation of infinite "ribbon"-like networks on the ac plane (Figure 4). Although the S•••N distances (3.33-3.39 Å) are nearly the same as the sum of vdW radii (3.35 Å), the coplanar arrangement of molecules is indicative of the attractive interaction through these contacts. The "ribbon" network of molecule-A and that of molecule-B are stacked alternately along the b axis (Figure 5) affording two different types of molecular overlapping. One is a favorable overlap for the interaction of SOMOs of 1b** (Figure 4) with the short interplanar distance (3.21 Å) and causes the "dyad" formation in the crystal. The other is observed between the "dyads" (Figure 6), and the π-orbitals are scarcely overlapped with the longer interplanar distance (3.44 Å). The low conductivity of this salt (\(\sigma_{\text{powder}} = 9.1 \times 10^{-6} \text{ S cm}^{-1}\)) can be accounted for by the "dyad" formation in the crystal. By changing the counter ion from PF6- to I3- the conductivity was raised by a factor of five (\(\sigma_{\text{powder}} = 4.5 \times 10^{-5} \text{ S cm}^{-1}\)), suggesting the improved π-orbital overlapping in 1b**I3- salt.

In summary, multistage redox systems with electrical amphotericity were constructed by the annelation of electron withdrawing heterocycles to the benzidine skeleton. Their planar cation radicals less suffer the Coulombic repulsion due to the enlarged π-electron system, and the infinite network in crystal was formed by the attractive interaction between heterocycles.

Figure 2. Thermal ellipsoids of 1b viewed perpendicular to the least-square plane of the molecular half. In the molecular half, the benzothiadiazole unit and N3, C8, and C10 atoms lie on a coplane with the largest deviation of 0.07 Å at C10. Deviations of C7 and C9 from this plane are 0.3 Å and 0.7 Å, respectively.
Figure 3. Molecular overlapping pattern in 1b. Interatomic distance of N(3)-C(3) is 3.70 Å.

Figure 4. Coplanar "ribbon"-like networks in 1b*PF₆⁻ by S···N contacts (3.33 and 3.39 Å in molecule-A; 3.34 and 3.35 Å in molecule-B). Molecule A and B form a dyad by face-to-face overlapping.

Figure 5. Crystal structure of 1b*PF₆⁻ viewed along the a axis. S···N contacts were not shown for clarity.

Figure 6. Molecular overlapping pattern between dyads in 1b*PF₆⁻.
EXPERIMENTAL SECTION

Preparation of 4-Bromo-7-dimethylaminobenzol[1,2,5]thiadiazole (3a). To a solution of 4,7-dibromobenzol[1,2,5]thiadiazole (5) (720 mg, 2.4 mmol) in 30 ml of 1,3-dimethyl-2-imidazolidinone (DMI) was introduced dry gaseous dimethyamine for 4 h at 180 °C. After cooling, the mixture was poured into water and extracted with CCl₄. The extract was washed with water and brine, and then dried over Na₂SO₄. Evaporation of solvent followed by chromatographic separation on SiO₂ (CH₂Cl₂ / n-hexane, 1:1) afforded 3a (510 mg) as orange needles in 81% yield. mp 91-93 °C; ir (KBr) 2900, 2800, 1578, 1540, 1492 cm⁻¹; ¹H nmr (90 MHz, CDCl₃) δ 7.44 (d, J = 8.1 Hz, 1H), 6.20 (d, J = 8.1 Hz, 1H), 3.11 (s, 6H); ms m/z 257 (M⁺). Anal. Calcd for C₁₅H₁₂N₃BrS: C, 37.22; H, 3.12; N, 16.28. Found: C, 37.11; H, 3.10; N, 16.19.

Preparation of 4,4'-Bis(7-dimethylaminobenzol[1,2,5]thiadiazolyl) (1a). Under a nitrogen atmosphere, a solution of 3a (470 mg, 1.8 mmol) in 3 ml of dry THF was added to a THF solution (3 ml) of Ni(0) prepared by the reduction of (Ph₃P)₂NiBr₂ (440 mg, 0.6 mmol) with Zn powder (190 mg, 2.9 mmol) and Et₄NI (470 mg, 1.8 mmol). The whole mixture was heated at 50 °C for 24 h. After evaporation of the solvent, the residue was extracted with benzene (soxhlet). The reddish extract was chromatographed on Al₂O₃ (CH₂Cl₂ / n-hexane, 1:1), and recrystallization from benzene gave 300 mg of 1a as red plates in 92% yield. mp 225-226 °C; ir (KBr) 2860, 1550, 1494, 1355, 805 cm⁻¹; ¹H nmr (90 MHz, CDCl₃) δ 8.04 (d, J = 9.0 Hz, 2H), 6.71 (d, J = 9.0 Hz, 2H), 3.28 (s, 12H); uv (CH₂Cl₂) λmax (log ε) 266 (4.64), 310 (4.30, sh), 488 nm (4.14); ms m/z (relative intensity) 356 (M⁺, 30), 357 (M⁺+1, 100), 358 (M⁺+2, 18). Anal. Calcd for C₃₆H₂₆N₆S₂: C, 53.91; H, 4.52; N, 23.58. Found: C, 54.06; H, 4.77; N, 23.28.

Preparation of 4,4'-Bis(dimethylamino)-2,2',3,3'-tetraaminobiphenyl (4a). To a suspension of 1a (240 mg, 0.65 mmol) in 50 ml of dry ether was added LiAlH₄ (260 mg, 6.5 mmol) by small portions under nitrogen, and the mixture was stirred for 24 h at room temperature. Excess LiAlH₄ was quenched by adding water-saturated ether, and the mixture was poured into water. The ethereal extract was dried over Na₂SO₄, and evaporation of solvent afforded the crude hexamine (4a) (210 mg, 89%) as a pale orange solid, which was purified by sublimation to give air sensitive colorless rods. mp 57-58 °C; ir (KBr) 3400, 3300, 2930, 2820, 2780, 1485 cm⁻¹; ¹H nmr (90 MHz, CDCl₃) δ 6.67 (s, 4H), 3.60 (br s, 8H), 2.68 (s, 12H); ms m/z 300 (M⁺). Anal. Calcd for C₁₆H₂₄N₆: C, 63.97; H, 8.05; N, 27.98. Found: C, 65.20; H, 8.42; N, 24.65 (Correct analytical values could not be obtained because of its lability).
Preparation of 4,4'-Bis(7-dimethylaminobenzo[c][1,2,5]selenadiazolyl) (2a). Because of the lability of 4a, higher yield of 2a was achieved when 4a was used without isolation and purification. Thus, to the ethereal extract obtained by the reaction of 1a (220 mg, 0.62 mmol) with LiAlH₄ (240 mg, 6.3 mmol) was added an aqueous solution (5 ml) of SeO₂ (300 mg, 2.7 mmol), and the mixture was stirred vigorously for 23 h at room temperature. Most of ether was evaporated, and the mixture was extracted with CH₂Cl₂. Chromatographic separation on Al₂O₃ (CH₂Cl₂) followed by recrystallization from CHCl₃/EtOH (5:1) afforded 142 mg of 2a as red plates in 51% yield over two steps. mp 217-220 °C (decomp.); ir (KBr) 2940, 2830, 2790, 1536, 1480, 1360, 1056 cm⁻¹; ¹H nmr (90 MHz, CDCl₃) δ 7.75 (d, J = 7.7 Hz, 2H), 6.59 (d, J = 7.7 Hz, 2H), 3.23 (s, 12H); uv (CH₂Cl₂) λmax (log ε) 270 (4.37), 326 (4.31), 332 (4.32), 338 (4.32), 504 nm (3.91); ms m/z 450 (M⁺). Anal. Calcd for C₁₆H₁₈N₂O.5H₂O: C, 42.15; H, 3.56; N, 18.32. Found: C, 41.84; H, 3.73; N, 18.30.

Preparation of 4-Bromo-7-(1-pyrrolidinyl)benzo[c][1,2,5]thiadiazole (3b). A solution of 5 (4.59 g, 15.3 mmol) in 10 ml of pyrrolidine was heated under reflux for 8 h under nitrogen. After cooling, reddish needles of 3b (4.10 g, 86%) was filtrated, washed with EtOH, and dried in vacuo. mp 109-111 °C; ir (KBr) 2950, 2850, 1495 cm⁻¹; ¹H nmr (90 MHz, CDCl₃) δ 7.55 (d, J = 9.0 Hz, 1H), 6.10 (d, J = 9.0 Hz, 1H), 3.80 (m, 4H), 2.05 (m, 4H); ms m/z (relative intensity) 284 (M⁺+1, 81), 283 (M⁺, 43), 282 (M⁺-1, 1M)). Anal. Calcd for C₁₀H₁₀N₃BrS: C, 42.27; H, 3.55; N, 14.79. Found: C, 42.67; H, 3.46; N, 14.48.

Preparation of 4,4'-Bis(7-(1-pyrrolidinyl)benzo[c][1,2,5]thiadiazole) (1b). Similarly to the case of 1a, 3b (4.10 g, 14.4 mmol) was reacted with Ni(0) in THF for 42 h at 50 °C. Evaporation of solvent afforded a black solid which was extracted with benzene (soxhlet). The extract was concentrated to dryness and the residue was suspended in 120 ml of hot EtOH. Filtration of the insoluble purple powder gave 2.30 g of 1b in 78% yield. mp 236-238 °C; ir (KBr) 2950, 2840, 1550 cm⁻¹; ¹H nmr (90 MHz, CDCl₃) δ 8.07 (d, J = 8.1 Hz, 2H), 6.46 (d, J = 8.1 Hz, 2H), 3.93 (m, 8H), 2.12 (m, 8H); uv (CH₂Cl₂) λmax (log ε) 274 (4.55), 316 (4.21, sh), 520 nm (4.08); ms m/z 408 (M⁺). Anal. Calcd for C₂₀H₂₀N₆S₂*0.5H₂O: C, 57.53; H, 5.07; N, 20.13. Found: C, 57.26; H, 4.78; N, 19.94.

Preparation of 4,4'-Bis(1-pyrrolidinyl)-2,2',3,3'-tetraaminobiphenyl (4b). To a suspension of 1b (160 mg, 0.39 mmol) in 50 ml of dry ether was added LiAlH₄ (100 mg, 2.5 mmol) by small portions under nitrogen, and the mixture was stirred for 72 h at room temperature. Excess LiAlH₄ was quenched with water, and the mixture was extracted with ether. Evaporation of solvent afforded 128 mg of crude hexamine (4b) as pale orange crystals in 93% yield, which was purified by sublimation (170 °C, 10⁻² Torr) to give colorless plates. mp 209-211
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"C; ir (KBr) 3400, 3320, 2950, 2800, 1480 cm⁻¹; ¹H nmr (90 MHz, CDCl₃) δ 6.67 (s, 4H), 3.53 (br s, 8H), 3.08 (m, 8H), 1.95 (m, 8H); ms m/z 352 (M⁺). Anal. Calcd for C₂₀H₂₈N₂Se: C, 68.94; H, 6.94; N, 24.12. Found: C, 68.47; H, 7.93; N, 23.80 (Correct analytical values could not be obtained because of its lability).

Preparation of 4,4'-Bis(7-(1-pyrrolidinyl)benzo[c][1,2,5]selenadiazolyl) (2b). To a solution of crude hexamine 4b (50 mg, 0.14 mmol) in CH₂Cl₂ (20 ml) was added powdered SeO₂ (78 mg, 0.70 mmol), and the mixture was stirred for 30 min at room temperature. Dark violet filtrate was collected by suction. The insoluble material was thoroughly washed with water and EtOH, and the residue was extracted with CH₂Cl₂ (soxhlet). The extract and the violet filtrate were combined and chromatographed on Al₂O₃ (CH₂Cl₂) giving violet powder of 2b (56 mg) in 79% yield. mp 303-305 °C (decomp.); ir (KBr) 2960, 2860, 1540 cm⁻¹; ¹H nmr (200 MHz, CDCl₃) 8 7.76 (d, J = 7.6 Hz, 2H), 6.30 (br d, 2H), 3.86 (m, 8H), 2.07 (m, 8H); uv (CH₂Cl₂) λmax (log ε) 298 (4.51), 324 (4.36), 552 nm (4.01); ms m/z 502 (M⁺). Anal. Calcd for C₂₀H₂₈N₂Se₂: C, 46.98; H, 4.14; N, 16.44. Found: C, 47.23; H, 4.13; N, 16.20.

Preparation of 4-(Trifluoroacetylamino)benzo[c][1,2,5]thiadiazole (7). To a solution of 4-aminobenzo[c][1,2,5]thiadiazole (6) (2.01 g, 13.3 mmol) in 20 ml of CCl₄ was added (CF₃CO)₂O (8.92 g, 42.4 mmol), and the mixture was heated under reflux for 1 h. After evaporation of solvent, recrystallization of the residue from petroleum ether afforded 2.55 g of faintly orange plates of 7 in 78% yield. mp 85-88 °C; ir (KBr) 3380, 1725, 1619, 1563, 1190-1144 cm⁻¹; ¹H nmr (90 MHz, CDCl₃) δ 9.13 (br s, 1H), 8.47 (d, J = 6.3 Hz, 1H), 7.55-7.95 (m, 2H); ms m/z 247 (M⁺). Anal. Calcd for C₉H₄N₃OF₃S: C, 38.87; H, 1.63; N, 17.00; S, 12.97. Found: C, 39.12; H, 1.36; N, 16.93; S, 13.01.

Preparation of 4-(1-Pyrrolidinyl)benzo[c][1,2,5]thiadiazole (8). To a solution of 7 (2.06 g, 8.35 mmol) and 1,4-dibromobutane (7.23 g, 33.5 mmol) in dry acetone (40 ml) was added portionwise 3.1 g (54 mmol) of crashed KOH at 100 °C. After heating under reflux for 7 h, the mixture was concentrated to dryness. The residue was suspended in water and extracted with CH₂Cl₂. Chromatographic separation on Al₂O₃ (CH₂Cl₂) afforded bright orange crystals of 8 (1.28 g) in 75% yield. mp 84-85 °C; ir (KBr) 2950, 2820, 1520, 732 cm⁻¹; ¹H nmr (200 MHz, CDCl₃) δ 7.41 (dd, J = 8.5, 7.5 Hz, 1H), 7.20 (d, J = 8.5 Hz, 1H), 6.23 (d, J = 7.5 Hz, 1H), 3.03 (m, 4H), 2.06 (m, 4H); uv (CH₂Cl₂) λmax (log ε) 266 (4.47), 304 (3.60), 316 (3.56), 460 nm (3.70); ms m/z (relative intensity) 205 (M⁺, 100), 204 (M⁺-1, 14). Anal. Calcd for C₁₀H₁₁N₃S: C, 58.51; H, 5.40; N, 20.47. Found: C, 58.60; H, 5.49; N, 20.35.
Preparation of cation radical salts of 1b. A solution of 1b (20 mg, 0.05 mmol) in 3 ml of THF containing 0.1 mol dm\(^{-3}\) Bu\(_4\)NPF\(_6\) or Bu\(_4\)NI\(_3\) was electrolyzed by applying constant current of 10 \(\mu\)A for 3 d. Cation radical salts of 1bPF\(_6^+\) and 1bI\(_3^+\) were obtained as black thin plates or black rods, respectively.

1bPF\(_6^+\) : mp 149-153°C; ir (KBr) 1560, 1190, 830 cm\(^{-1}\). Anal. Calcd for C\(_{20}\)H\(_{19}\)F\(_6\)N\(_6\)S\(_2\): C, 43.40; H, 3.64; N, 15.18. Found: C, 43.55; H, 4.01; N, 14.83.

1bI\(_3^+\) : mp 150-160°C; ir (KBr) 1555, 1190 cm\(^{-1}\). Anal. Calcd for C\(_{20}\)H\(_{19}\)I\(_3\)S\(_2\): C, 30.44; H, 2.55; N, 10.65. Found: C, 30.79; H, 2.79; N, 10.46.

X-ray structural analysis of 1b. A dark red plate-like crystal with a dimension of 0.3 x 0.3 x 0.08 mm was obtained by recrystallization from chlorobenzene/CH\(_3\)CN, and used for the data collection on an AFC-5R automated four-circle diffractometer with a rotating anode (200 mA, 45 kV) at 13°C. A total of 2157 independent reflections within 20 = 55° was collected by using graphite monochromated MoK\(_\alpha\) radiation (\(\lambda = 0.71049\) Å) with a scan speed of 4° min\(^{-1}\) and the \(\omega - 2\theta\) scan mode of (1.2 + 0.3 tan\(\theta\))°. Crystal data are as follows: orthorhombic, Pbcn (No. 60), a = 13.205(2), b = 7.783(1), c = 18.167(2) Å, V = 1867.1(5) Å\(^3\), Z = 4, \(D_{calc} = 1.453\) g cm\(^{-3}\). The structure was solved by the direct method by using RANTAN81 program with some modification. Atomic parameters of non-hydrogen atoms were refined by the block-diagonal least-squares method with anisotropic temperature factors. Most of hydrogen atoms were picked up from the D-map, and the positions of H5 and H92 were calculated geometrically. They were included in the refinement at the final stage with isotropic temperature factors. The final R value is 7.93% for 946 reflections with |F\(\bar{0}\)| > 3|F\(\bar{o}\)| (No. of parameters, 168). The largest electron density in the D-map after the final refinement is 0.41 e Å\(^{-3}\). No absorption correction was applied (\(
abla = 2.916\) cm\(^{-1}\)). All the calculations were carried out on an ACOS 2020 computer at Tohoku University by using applied library programs of UNICS III system. The estimated standard deviations are 0.007 - 0.015 Å for bond distances and 0.3 - 0.8° for bond angles, respectively, within the non-hydrogen atoms.

X-ray structural analysis of 1bPF\(_6^+\). A black thin plate-like crystal with a dimension of 0.35 x 0.20 x 0.05 mm was obtained by an electrochemical oxidation of 1b in THF, and used for the data collection. A total of 4219 reflections within 20 = 50° was collected on an AFC-5 four-circle diffractometer (25 mA, 50 kV) by using graphite monochromated MoK\(_\alpha\) radiation with the \(\omega - 2\theta\) scan mode of 3° min\(^{-1}\) and scan width of (1.25 + 0.5 tan\(\theta\))°. Intensities of the higher angle reflections (35° < 20 < 50°) were very weak probably because of the small size and low quality of the crystal. Several larger crystals were proved to be twinned. Another data set was collected on an AFC-5R diffractometer (MoK\(_\alpha\), 200 mA, 45 kV) on the same specimen, which was also used for
the structure solution. However, the former data set gave a more satisfactory result in the refinement than the latter. Crystal data are as follows: monoclinic, P2_1 (No. 4), a = 14.125(3), b = 13.355(3), c = 11.656(2) Å, β = 91.69(1)°, V = 2197.9(8) Å³, Z = 4, D_{calc} = 1.658 g cm⁻³. The structure was solved by the direct method and successive R factor method with some difficulty. There are two crystallographically independent molecules in the crystal whose molecular planes are parallel to the ac plane, and coplanar two-dimensional "sheets" are formed at y/b = 0, 1/4, 1/2, and 3/4. Because these molecules cannot be related by a mirror symmetry or an inversion center, the space group is P2_1 but not P2_1/m with higher symmetry. The atomic parameters were refined by using block-diagonal least-squares method with anisotropic temperature factors for S and P, and isotropic ones for C, N, and F. Hydrogen atoms were not included in the refinement because of a small number of reflections available for the refinement. Higher angle reflections (40° < 2θ < 50°) were omitted because of their very weak intensities and large observational errors. The final R value is 12.69% for 1580 non-zero reflections within 2θ = 40° (No. of parameters, 312). The largest residual electron density is 0.81 e/Å³. No absorption correction was applied (μ = 3.728 cm⁻¹). Comparisons of the bond distances and angles of 1b** with those of neutral 1b make no sense because of their large estimated standard deviations (0.03 - 0.08 Å for distances and 1 - 4° for angles, respectively).

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REFERENCES AND NOTES

1. Dedicated to celebrate the 70th birthday of Professor Edward C. Taylor of Princeton University.


10. The stronger donating property of 1,4-bis(1-pyrrolidinyl)benzene ($E_{1}^{ox}$, -0.04 V) than $N$, $N'$, $N'$-tetramethyl-$p$-phenylenediamine ($E_{1}^{ox}$, +0.10 V) was reported. K. Kikuchi, T. Katagiri, T. Niwa, Y. Takahashi, T. Suzuki, H. Ikeda, and T. Miyashi, Chem. Phys. Lett., 1992, 193, 155.

11. $E_{1}^{ox}$, $E_{1}^{red}$, and $\Delta E_{\text{sum}}$ values of benzo[c][1,2,5]selenadiazole are +2.15 V, -1.30 V, and 3.45 V, respectively in MeCN (0.1 mol dm$^{-3}$ $\text{BaClO}_4$; $E_{1}^{ox}$ of ferrocene, +0.38 V). Those for benzo[c][1,2,5]thiadiazole are $> +2.30$ V, -1.53 V, and $> 3.83$ V, respectively, under the same conditions.

12. The distance (2.69 Å) is similar to the sum of vdW radii of $\text{N} \cdots \text{H}$ (2.75 Å), ref. 13).


17. The $\pi$-bond order was calculated from the bond length according to the established equation. G. Hafelingers, Chem. Ber., 1970, 103, 2902.

18. Hydrogen atoms were not included in the structural analysis of 1b$^{+}$PF$_6$. The positions of orthohydrogens were calculated by supposing the idealized sp$_2$ hybridization on carbon and the C-H distance of 1.08 Å.


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