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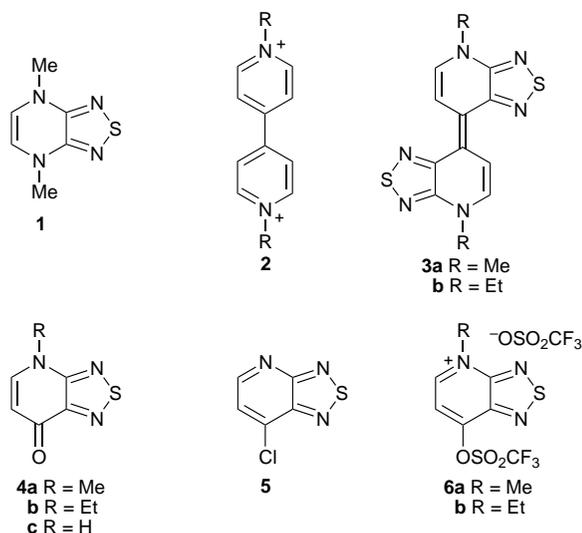
Synthesis and characterization of new electron donors containing 1,2,5-thiadiazole and 1,1'-dihydro-4,4'-bi(pyridylidene) units

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Novel electron donors composed of the title heterocycles are highly polarized and afford cation radical salts and charge transfer complexes with interesting crystal structures.

Molecules containing 1,2,5-thiadiazole rings have been used as components of organic conductors.¹ Introduction of this electron-withdrawing heterocycle to strong electron-donating skeletons leads to novel highly-polarized electron donors.^{2–4} In some cases, interesting molecular networks are formed by intermolecular interactions between the heteroatoms of the thiadiazoles. For example, 4,7-dimethyl-4,7-dihydro-



[1,2,5]thiadiazolo[3,4-*b*]pyridine **1** is a highly-polarized strong electron donor which forms a sheet-like network in the crystal.² On the other hand, viologens **2** are widely used as electron-transfer reagents since they are easily prepared and show well-defined redox processes.⁵ Although viologens are stable in air, their cation radical and neutral states are unstable toward oxygen due to their very low oxidation potentials. We have now fused 1,2,5-thiadiazole rings to the dihydropyridine skeleton in order to enhance the stability of the neutral state of viologens. The compounds **3** are expected to be highly polarized and form a tape-like network with short S...N contacts, as are found in the related bis[1,2,5]thiadiazole derivatives.⁶ We report here the preparation and properties of **3** and its cation radical salts and charge-transfer complexes.

Thiadiazolopyridone derivative **4a** was obtained from chloropyridine derivative **5**.⁴ The ethyl derivative **4b** was prepared by ethylation of **4c**, which was obtained by hydrolysis of **5** with hydrochloric acid. Reaction of **4a,b** with trifluoromethanesulfonic anhydride afforded pyridinium compounds **6a,b**. The bi(pyridothiadiazolyliene)s **3a,b** were obtained by reduction of **6a,b** with zinc in acetone. The yields of **3** were 20–40% over two steps. The donors **3a,b** are stable in air, in contrast to the unstable neutral viologens. They have absorption maxima in the long wavelength region (**3a**:

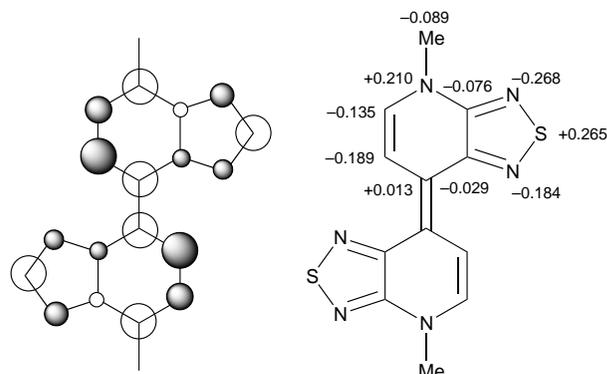


Fig. 1 HOMO and net atomic charges of **3a** calculated by the PM3 method

623, **3b**: 627 nm in CH₂Cl₂), which are regarded as the intramolecular charge-transfer bands. Their cyclic voltammograms showed reversible two-stage one-electron oxidation waves (**3a**: 0.27, 0.57 V, **3b**: 0.26, 0.56 V).[†] Their oxidation potentials are higher than those of methylviologen (−0.40, −0.81 V),⁵ leading to the stability of **3**. This is attributed to the electron-withdrawing properties of the thiadiazole ring. However, the values are lower than those of tetrathiafulvalene (TTF) (0.46, 0.87 V) measured under the same conditions, indicating that they are stronger electron donors than TTF. The difference between the first and second oxidation potential in **3** (0.30 V) is smaller than that in TTF (0.41 V), methylviologen (0.41 V) and **1** (0.80 V),² indicating that the on-site Coulomb repulsion in **3** is decreased due to extended π-conjugation.

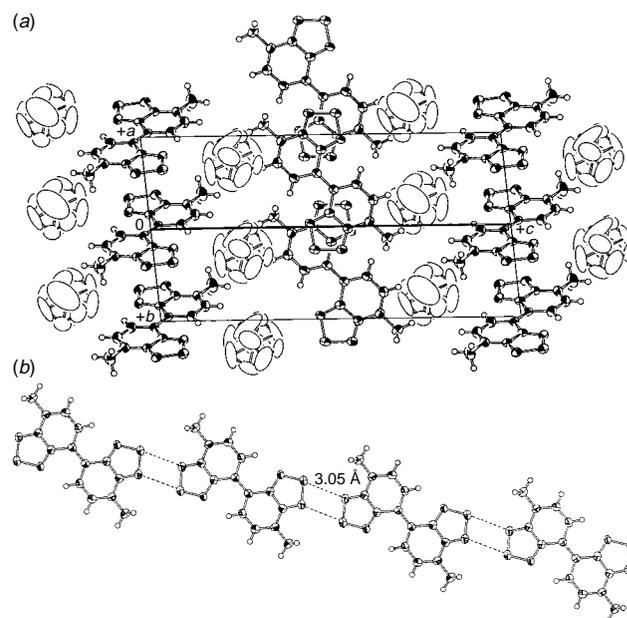


Fig. 2 (a) Crystal structure of **3a**-PF₆; (b) tape-like network

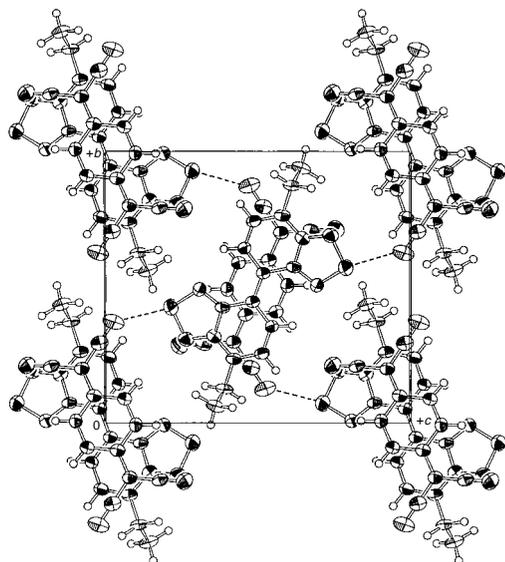


Fig. 3 Crystal structure of **3b**-TCNQ

The HOMO and net atomic charges of **3a** calculated by the PM3 method⁷ are shown in Fig. 1. The charge distribution indicates that the sulfur atom is positively charged and the nitrogen atoms of the thiadiazoles are negatively charged. For this polarized structure, short S...N contacts between the thiadiazole rings are expected to give a molecular network. There may be an electronic interaction through the S...N contacts in the cation radical state since these atoms have fairly large coefficients in the HOMO.

The donor **3a** gave PF₆ and AsF₆ salts of the cation radical upon electrochemical oxidation in CH₂Cl₂. They are 1 : 1 salts and show low conductivities (**3a**-PF₆: 8×10^{-5} S cm⁻¹ as a compressed pellet, **3a**-AsF₆: 5×10^{-4} S cm⁻¹ as a single crystal). The temperature dependence of the conductivity of the AsF₆ salt showed semiconductive behaviour, with an activation energy of 0.27 eV. The structures of the salts are isomorphous.[‡] The crystal structure of the PF₆ salt is shown in Fig. 2. The planar donor molecules are stacked in an interesting mode where one donor molecule bridges two other molecules. Another interesting feature is that a tape-like network of the donor molecules is formed by short S...N contacts (3.05 Å) as expected. The counter anions exist between the molecular tapes which are arranged in two difference directions.

The donors **3a,b** afforded 1 : 1 charge-transfer complexes with tetracyanoquinodimethane (TCNQ). They showed moderate conductivities (**3a**-TCNQ: 1.6×10^{-2} S cm⁻¹, **3b**-TCNQ:

4.9×10^{-3} S cm⁻¹ as compressed pellets). We succeeded in preparing a single crystal of **3b**-TCNQ and carried out an X-ray crystal analysis.[‡] The structure is shown in Fig. 3. The donor and TCNQ molecules form a mixed stack. The C-C bond length of the dicyanomethylene of the TCNQ molecule (1.416 Å) is comparable to that of TCNQ anion,⁸ indicating that almost complete charge transfer occurs in the complex. An interesting feature is that short S...N contacts (3.15 Å) exist between the sulfur of the thiadiazole ring and the nitrogen of the cyano group, forming a two-dimensional network. This finding suggests that the inter-heteroatom interactions can be used for controlling the structures of charge transfer complexes.

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Footnotes and References

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† Conditions: Bu₄NBF₄ (0.1 mol dm⁻³) in PhCN, Pt electrode, scan rate 100 mV s⁻¹, V vs. saturated calomel electrode (SCE).

‡ Crystal data for **3a**-PF₆: C₁₂H₁₀N₆S₂-PF₆, *M* = 447.35, monoclinic, space group *C2/c*, *Z* = 4, *a* = 11.7998(7), *b* = 6.3967(5), *c* = 22.030(2) Å, β = 101.474(6)°, *V* = 1629.6(2) Å³, *D_c* = 1.823 g cm⁻³. The final *R* value was 0.061 for 1663 reflections with *I* > 2σ(*I*). For **3a**-AsF₆: C₁₂H₁₀N₆S₂-AsF₆, *M* = 491.30, monoclinic, space group *C2/c*, *Z* = 4, *a* = 11.8546(3), *b* = 6.3851(6), *c* = 22.429(1) Å, β = 101.51(3)°, *V* = 1663.6(2) Å³, *D_c* = 1.962 g cm⁻³. The final *R* value was 0.088 for 1693 reflections with *I* > 2σ(*I*). For **3b**-TCNQ: C₂₆H₁₈N₁₀S₂, *M* = 534.62, monoclinic, space group *P2₁/n*, *Z* = 2, *a* = 7.1926(4), *b* = 12.3259(9), *c* = 14.1518(7) Å, β = 104.575(4)°, *V* = 1214.3(1) Å³, *D_c* = 1.46 g cm⁻³. The final *R* value was 0.049 for 1029 reflections with *I* > 3σ(*I*). CCDC 182/565.

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