

Preparation and Properties of 7-(1,3-Dithiol-2-ylidene)-4-methyl-4,7-dihydro[1,2,5]thiadiazolo[3,4-*b*]pyridines: Novel Donor Molecules containing a 1,2,5-Thiadiazole Unit

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The title compounds are strong electron donors and the parent compound whose structure is revealed by X-ray structural analysis gives a highly conducting charge-transfer complex with tetracyanoquinodimethane (TCNQ).

Molecules containing 1,2,5-thiadiazole units are of interest as components of organic conductors.¹⁻³ The most interesting feature is that the heteroatoms of the thiadiazole rings make intermolecular interactions strong.³⁻⁵ 4,7-Dimethyl-4,7-dihydro[1,2,5]thiadiazolo[3,4-*b*]pyridine **1**, which is a strong electron donor due to the 12 π -electron ring system, afforded conducting charge-transfer (CT) complexes with electron acceptors.⁵ The crystal structure of **1** shows a sheet-like network by S...N interheteroatom contacts. On the other hand, 4-(1,3-dithiol-2-ylidene)-1-methyl-1,4-dihydropyridine **2** has not been prepared except for the dibenzo derivative⁶ because of an instability of the ring system. We have now replaced one amino group of **1** with a 1,3-dithiol-2-ylidene unit to give a derivative of **2**, 7-(1,3-dithiol-2-ylidene)-4-methyl-4,7-dihydro[1,2,5]thiadiazolo[3,4-*b*]pyridine **3a**, which is expected to have a good electron-donating ability and intramolecular CT interactions based on a donor- π -acceptor system. The crystal structure is also of interest to investigate intermolecular interactions caused by heteroatom contacts. We report here the preparation, properties, and structure of **3a** and its derivatives **3b-d**.

4-Methyl-4,7-dihydro[1,2,5]thiadiazolo[3,4-*b*]pyridin-7-one **4** was obtained by methylation of chloropyridine **5** with methyl trifluoromethanesulfonate followed by hydrolysis with hydrochloric acid. Compounds **3a-d** were prepared by a Wittig-Horner reaction of the pyridone **4** with carbanions derived from phosphonate esters **6a-d** in 27-55% yields. The

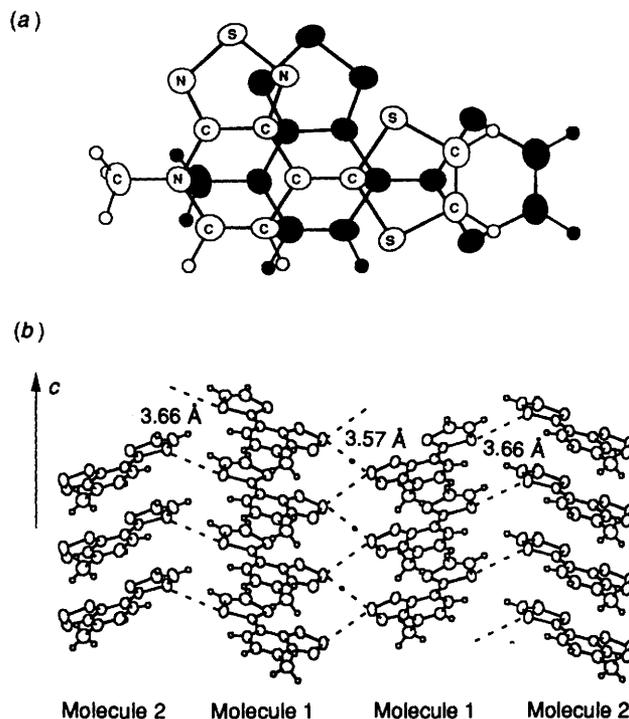


Fig. 1 Crystal structure of **3a** (a) overlap mode of molecule 1; (b) stacking along the *c* axis

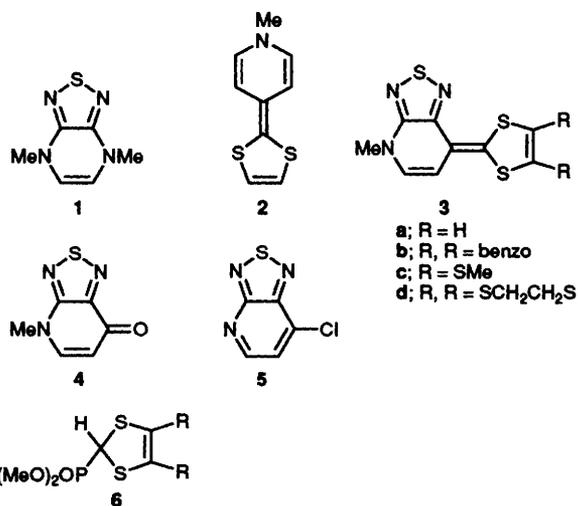


Table 1 Oxidation potentials^a and absorption maxima of donors **3**

Donor	E_1/V	E_2/V	ΔE	λ_{max}/nm (log ϵ) ^b
3a	+0.22	+0.66	0.44	515(4.20), 487(4.32)
3b	+0.33	+0.76	0.43	509(4.16), 482(4.30)
3c	+0.28	+0.66	0.38	518(4.25), 490(4.34)
3d	+0.27	+0.68	0.41	521(4.23), 493(4.31)
TTF	+0.32	+0.76	0.44	

^a 0.1 mol dm⁻³ Buⁿ₄NPF₆ in PhCN. Pt electrode, scan rate 100 mV s⁻¹, V vs. standard calomel electrode (SCE). ^b In CH₂Cl₂.

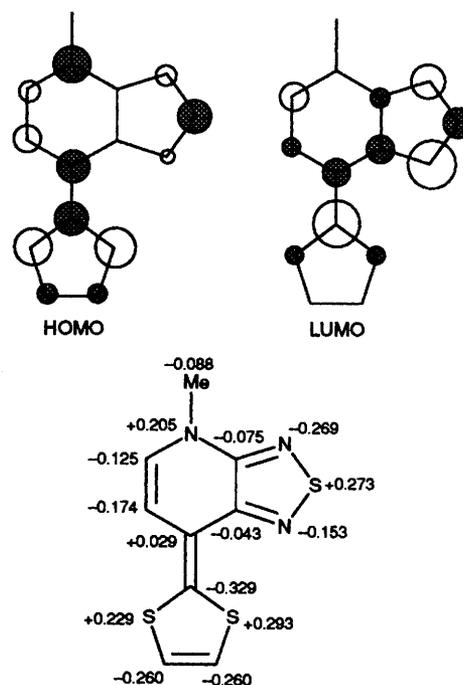


Fig. 2 HOMO, LUMO and net atomic charges of **3a** calculated by the MNDO-PM3 method

donor **3a** (mp 163–164 °C) was sublimed at 120 °C 1 Torr⁻¹ to give a single crystal as red needles. The absorption maxima of **3a–d** were observed around 510 and 490 nm in dichloromethane (Table 1), which are regarded as the intramolecular CT bands due to the donor– π –acceptor system.

The cyclic voltammograms (CV) of **3a–d** showed two reversible one-electron redox waves. The half-wave oxidation potentials in benzonitrile are shown in Table 1. These values are lower than those of the corresponding tetrathiafulvalene (TTF) derivatives, indicating that they are stronger electron donors than TTF. The differences (ΔE) between the first and second oxidation potentials are similar to that of TTF.

In order to investigate the structure of **3**, an X-ray structural analysis of **3a** was carried out.† There exist two crystallographically independent molecules (molecule 1 and molecule 2) in the crystal. They are planar and the intramolecular distances between the S of the dithiole and the N of the thiadiazole (2.86 Å for molecule 1 and 2.89 Å for molecule 2) are shorter than the sum of the van der Waals distances (3.35 Å) as found in the related molecules.^{1,2} The S–N bond lengths (1.641–1.655 Å) are shorter than those of **1** (1.662 and 1.671 Å),⁵ indicating some delocalization of the π -electrons. Both molecule 1 and molecule 2 are uniformly stacked with intermolecular distances of 3.46 and 3.57 Å, respectively. The overlap mode of molecule 1 is shown in Fig. 1(a), which is similar to that of molecule 2. This mode is in accord with that of an effective interaction between the HOMO and LUMO shown in Fig. 2.⁸

The crystal structure is constructed of a set of four columns along the *c* axis shown in Fig. 1(b). These columns interact with each other by S··S contacts. The contact distance between the dithioles is 3.66 Å, and that between the thiadiazole rings in the molecule 1 is 3.57 Å. These values are shorter than the sum of their van der Waals radii (3.70 Å). Although the net atomic charges of **3a** calculated by the MNDO-PM3 method (Fig. 2) show that the molecule is highly polarized, the S··N contacts arising from the electrostatic effect are not observed.

The donors **3a–d** formed conducting CT complexes with tetracyanoquinodimethane (TCNQ) and the properties are summarized in Table 2. The donor **3a** gave a 1:1 CT complex which shows a high electrical conductivity (1 S cm⁻¹) as a

Table 2 Properties of CT complexes of donors **3** with TCNQ

Donor	D:A ^a	σ /S cm ^{-1b}	ν_{CN} /cm ⁻¹
3a	1:1	1	2196
3b	2:1	3×10^{-6}	2198
3c	2:1	2×10^{-3}	2201
3d	4:3	0.2	2195

^a Determined on the basis of elemental analyses; D = donor; A = acceptor. ^b Determined by a two-probe technique on compressed pellets at room temp.

compressed pellet. According to the CN stretching frequency, the degree of CT in the complex is 0.67.⁹ The donor **3d** further gave the ClO₄ salt of the cation radical as a single crystal by an electrochemical oxidation. The molar ratio is 2:1 based on elemental analyses. The salt showed semiconductive behaviour ($E_a = 0.15$ eV) and its electrical conductivity was 4.4×10^{-2} S cm⁻¹ at room temp.

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Footnote

† Crystal data for **3a**: C₉H₇N₃S₃, *M* = 253.39, orthorhombic, space group P2₁2₁2₁, *Z* = 8, *a* = 17.8055(14), *b* = 28.8428(24), *c* = 3.9462(1) Å, *V* = 2026.6(2) Å³, *D_c* = 1.66 g cm⁻³, *F*(000) = 1040, μ (Cu-K α) = 63.32 cm⁻¹. The structure was solved using direct methods (MULTAN-78) and refined by block-diagonal least-squares analysis giving values of *R* = 0.045, $\Delta\rho_{\text{max}}$ = 0.37 e Å⁻³ for 1866 ($|F_o| > 3\sigma|F_o|$) reflections, which were collected using an ENRAF-NONIUS CAD4 diffractometer with graphite monochromated Cu-K α radiation (λ = 1.5418 Å). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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