SYNTHESIS AND CHARACTERIZATION OF THIENO[3,4-*c*][1,2,5]THIADIAZOLES†

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Abstract - Thieno[3,4-*c*][1,2,5]thiadiazoles (**1a-b**) were synthesized and characterized based on the spectral and structural data. The most notable structural feature of this "nonclassical" condensed thiophene is the small HOMO-LUMO separation leading to the highly amphoteric redox properties compared with the related "classical" thiophenes. The X-ray structure analysis suggested that this heterocycle has the character of a thiocarbonyl ylide. Short intermolecular S---N contacts were found in the crystal.

Nonclassical thienothiadiazole (**1a**) is of interest in the field of physical organic chemistry because this molecule contains a tetravalent sulfur in the uncharged singlet resonance structures.[1] Theoretical studies have suggested that such heterocycles have a small HOMO-LUMO separation compared with the related "classical" thiophenes.[2] Therefore compounds of this type are one of the promising building blocks for conjugated polymers with narrow bandgap.[3] So far the parent compound (**1a**) has not been well-characterized due to its high reactivity; it was generated by thermal dehydration of the corresponding dihydro sulfoxide, followed by trapping as Diels-Alder adducts.[4] We report here on a new synthetic route to **1a-b**. The electronic and structural characters of this system have been clarified based on the experimental data.

Compounds (**1a-b**) were prepared as shown in Scheme 1. The purifications were carried out by sublimation from the crude products [**1a**: 0 °C (10^{-4} - 10^{-5} torr), **1b**: 35 °C (10^{-2} torr)]. The parent compound (**1a**) was collected as yellow crystals on a cold finger at -50 °C and dissolved in an appropriate solvent under an argon atmosphere for spectral measurements. In the solid state or in the concentrated solutions at room temperature, **1a** decomposed to the insoluble, intractable colorless materials, which precluded recording the ir spectrum.

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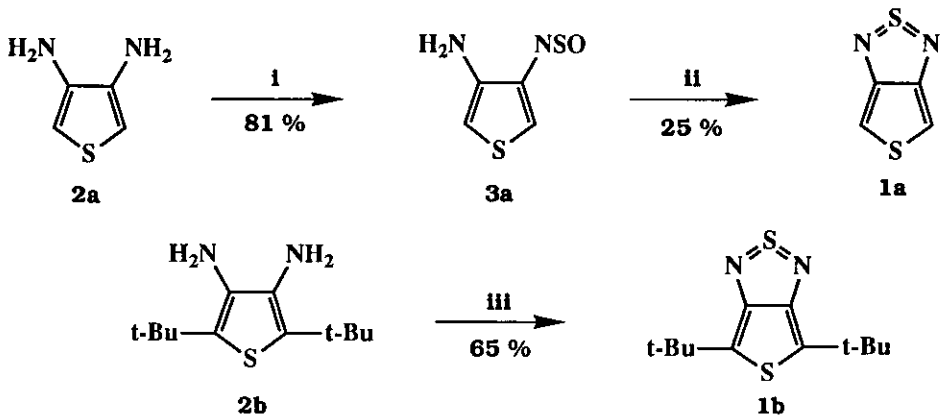
†Dedicated to Prof. Aran R. Katritzky on the occasion of his 65th birthday.



Scheme 1 *Reagents and conditions*: i, Ph-NSO (2 equiv.), Et_3N, 25°C, 1.5 h; ii, Me_3SiCl (4 equiv.), pyridine, 50°C, 2.5 h; iii, Ph-NSO (2 equiv.), pyridine, 50°C, 4 h

The available spectral data, however, clearly supported the structure of **1a**.[5]

The physical data summarized in Table 1 confirm the expected smaller HOMO-LUMO separation of the "nonclassical" system compared with "classical" thiophenes; **1a** shows absorptions at lower energy region and exhibits the smaller difference between the oxidation and reduction steps (higher amphoteric nature) compared to the related heterocycles (**4**[6] and **5**). The X-ray structure of **1b** (Figure 1)[7] reveals the another characteristics of this heterocycle; (i) **1b** has an almost planar ring structure, (ii) the averaged Cα-Cβ and Nα-Cβ bond lengths [1.39 Å and 1.37 Å, respectively[8]] are longer than the corresponding ones of thiophene and 1,2,5-thiadiazole [1.37 Å and 1.33 Å, respectively [9]], which indicates the lower bond order between the α–β positions. In addition the nmr signal of α-carbons of **1a** is shifted upfield by 15.1 ppm compared with that of the isoelectronic system (**4**), which can be attributed to the higher electron densities at these positions. These findings suggest that the contribution of ylide-type resonance structures (**1a'**) inducing the efficient peripheral 10 π-electron delocalization should be significant to the electronic structure of thieno[3,4-*c*][1,2,5]thiadiazole. Furthermore the crystal structure of **1b** reveals an interesting feature; the shortest intermolecular S-N distance [3.17 Å] is shorter than the sum of van der Waals radii [3.35 Å]. In the conjugated polymers possessing this heterocycle, these short S--N contacts are expected to improve the structural order and enhance the charge transport between adjacent polymer chains. We are now searching for the experimental conditions to obtain the conducting and electroactive polymer containing this new class of heterocycle.

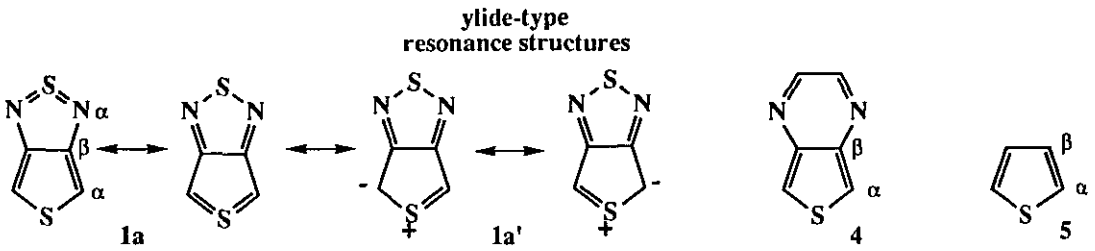


Table 1: Physical properties of **1a** and its related systems.

	1a	**4**	**5**
ε_{HOMO}[a)]	-8.63 eV	-9.22 eV	-9.50 eV
ε_{LUMO}[a)]	-2.40 eV	-1.24 eV	+0.04 eV
$\lambda_{max}(CH_2Cl_2)$	415 nm (2.99 eV)	351 nm (3.53 eV)	231 nm (5.37 eV)
E_p^{ox} *vs* SCE[b)]	+1.45 V	+1.58 V	+2.06 V[10]
E_p^{red} *vs* SCE[b)]	-1.32 V	-1.65 V	< -2.0 V

a) MO energies calculated by MNDO method.[11]

b) Measured at a Pt electrode in 0.1 mol dm^{-3} Bu_4NClO_4-MeCN with a scan rate 100 mVs^{-1}.

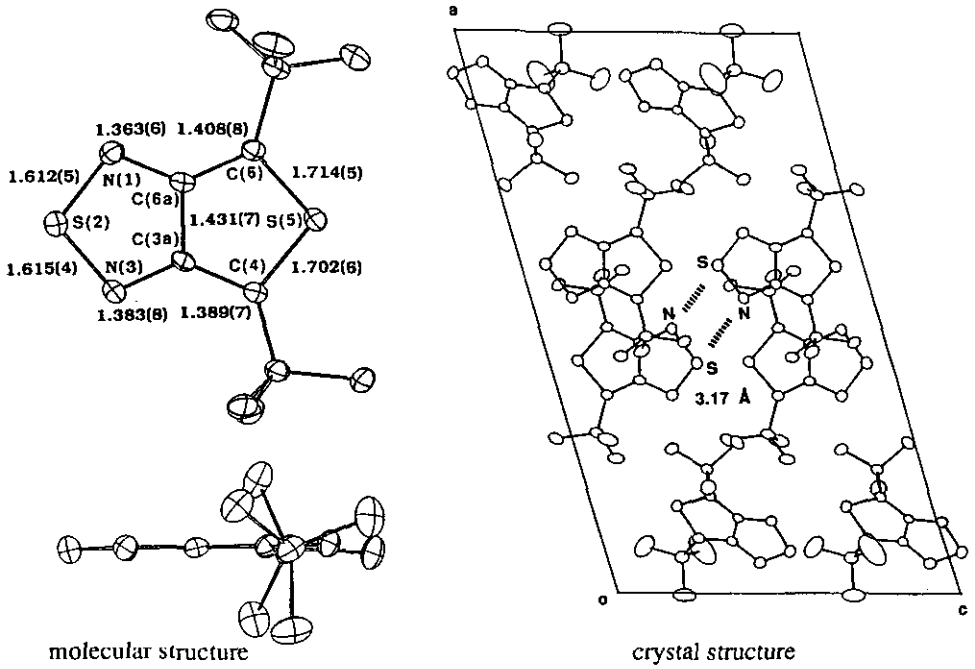


Figure 1. ORTEP drawing of **1b** along with important bond lengths (Å).

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5. **1a:** HRms m/z: Calcd for $C_4H_2N_2S_2(M^+)$: 141.9659. Found: 141.9658; ^{1}H-nmr ($CDCl_3$) δ 7.58 (H-4 and H-6, s); ^{13}C-nmr ($CDCl_3$) δ 160.3 (C-3_a and C-6_a, s), 102.9 (C-4 and C-6, d); uv (Et_2O) λ_{max} (log ε) 249(3.66), 300(4.39), 307(4.33), 413(3.45) nm; **1b:** mp 53.0-53.5 °C (CH_3CN); *Anal.* Calcd for $C_{12}H_{18}N_2S_2$: C, 56.65; H, 7.13; N, 11.01. Found: C, 56.70; H, 7.17; N, 11.09; ^{1}H-nmr ($CDCl_3$) δ 1.58 (*t*-Bu, s); ^{13}C-nmr ($CDCl_3$) δ 156.3 (C-3_a and C-6_a, s), 126.7 (C-4 and C-6, d), 35.2 ($\underline{C}(CH_3)_3$, s), 31.2($C(\underline{C}H_3)_3$, q) ;ir ($CHCl_3$) 2964, 1504, 1462, 1364, 1295, 1192, 906, 840 cm^{-1}; uv(CH_2Cl_2) λ_{max} (log ε) 258(3.78), 305(4.33), 311(4.28), 478(3.53) nm.
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7. **1b** is kinetically stabilized by the *t*-butyl groups to allow the data collection for X-ray structural analysis at room temperature. Crystal data for **1b**: monoclinic, space group $P2_1/c$. a=22.199(9), b=10.072(4), c=12.927(5) Å, β=106.55(3)°, U=2270.6(19)Å^3, Z=8, D_{calcd}=1.22 gcm^{-3}, Mo-Kα radiation. The final R value is 0.089 for 3045 reflections with |Fo|> 3σ|Fo|.
8. The unit cell contains two crystallographically-independent molecules, which are identical in shape within the experimental accuracy. One of them is shown in Figure 1. The averaged bond lengths were calculated from the data for the two independent molecules.
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11. The MO calculations were carried out at the Computer Center of the Institute for Molecular Science, using MOPAC program; J. J. P. Steward, *Q. C. P. E. Bull.*, 1983, **3**, 43.

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