Synthesis and Structure Determination of [1,2]Dithiolo[1,5-*b*][1,2,4]dithiazole-4-$\mathrm{S^{IV}}$ Derivatives

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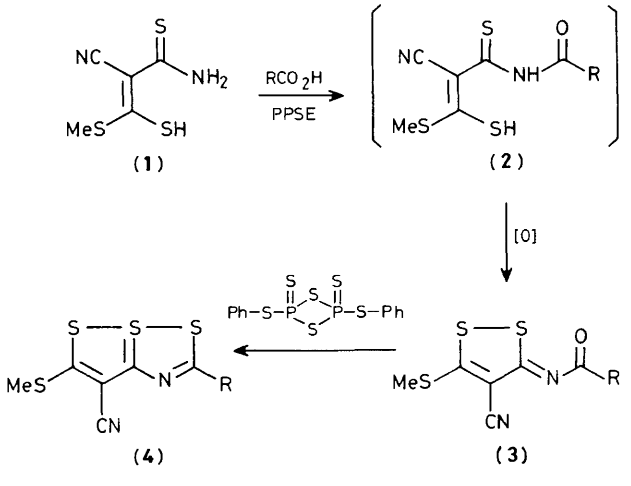
7-Cyano-6-methylthio-2-aryl-[1,2]dithiolo[1,5-*b*][1,2,4]dithiazole-4-$\mathrm{S^{IV}}$ compounds were easily synthesized from the O,S-exchange reaction of (4-cyano-5-methylthio-1,2-dithiole-3-ylidene)aromatic amides and the structure of one of them was determined by single-crystal *X*-ray diffraction.

In recent reports,[1] we have described the chemistry of heteroatom rearrangements. When 2-cyano-3-mercapto-3-(methylthio)thioacrylamide (**1**) was used in similar rearrangement reactions, it was found that compound (**1**) reacted with benzoic acid in the presence of polyphosphoric trimethylsilyl ester (PPSE)[2] to give (4-cyano-5-methylthio-1,2-dithiole-3-ylidene)benzamide (**3a**) in 81% yield and that compound (**3a**) subsequently reacted with 2,4-bis(phenylthio)-1,3-dithia-2,4-diphosphetane 2,4-disulphide[3] under reflux in toluene to afford 7-cyano-6-methylthio-2-phenyl-[1,2]dithiolo[1,5-*b*][1,2,4]dithiazole-4-$\mathrm{S^{IV}}$ (**4a**) as orange crystals of m.p. 225—226 °C in 75% yield. The [1,2]dithiolo[1,5-*b*][1,2]dithioles have been well documented in the literature.[4] To our knowledge, however, the [1,2]dithiolo[1,5-*b*][1,2,4]dithiazole-4-$\mathrm{S^{IV}}$ derivatives have appeared in only one patent.[5] We now report their convenient preparation and the first *X*-ray structure determination of one of these derivatives.



a; R = Ph
b; R = β-naphthyl

The synthesis of (**4a**) was carried out as follows: a mixture of phosphorus pentoxide (2 g), hexamethyldisiloxane (4 ml), and chloroform (8 ml) was heated at reflux for 0.5 h. To the resulting PPSE–chloroform solution were added successively

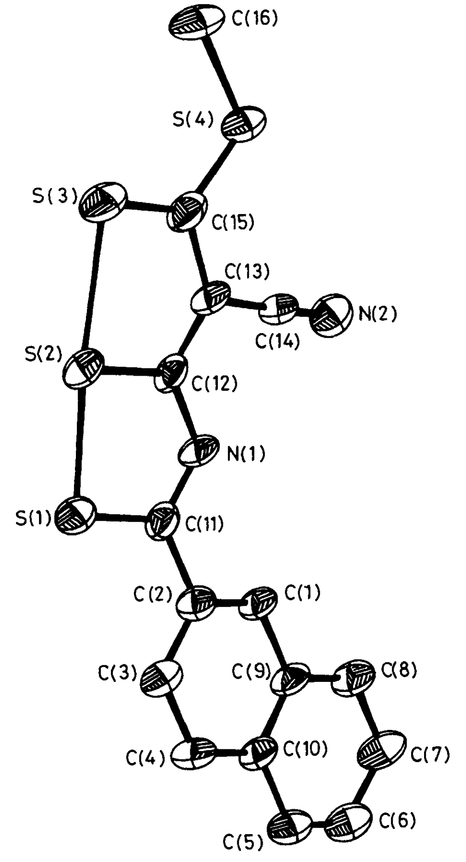
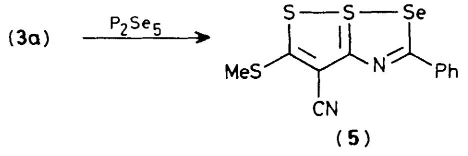
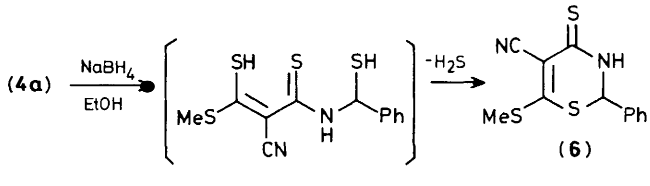


Figure 1. ORTEP diagram of (**4b**) showing 50% probability ellipsoids for all atoms. Selected bond lengths (Å) and angles (°): S(1)–S(2) 2.225(1), S(2)–S(3) 2.488(3), S(1)–C(11) 1.696(6), S(2)–C(12) 1.745(7), S(3)–C(15) 1.667(5), C(15)–C(13) 1.434(2), C(13)–C(12) 1.388(8), C(12)–N(1) 1.361(9), N(1)–C(11) 1.306(7); S(1)–S(2)–C(12) 89.5(6), C(12)–S(2)–S(3) 86.0(2), S(2)–S(1)–C(11) 92.1(9), S(2)–S(3)–C(15) 93.0(8), S(3)–C(15)–C(13) 117.5(8), C(15)–C(13)–C(12) 121.1(2), C(13)–C(12)–S(2) 122.0(5), S(2)–C(12)–N(1) 119.8(1), C(12)–N(1)–C(11) 117.2(0), N(1)–C(11)–S(1) 121.0(9).

benzoic acid (256 mg, 2.1 mmol) and (**1**) (400 mg, 2.1 mmol).[6] The mixture was refluxed for 1.5 h, then added to an aqueous $NaHCO_3$ solution, stirred for an additional 1 h, filtered through Celite, and extracted with chloroform. The extract was rotary evaporated to give orange crystals. Recrystallization from acetic acid gave (**3a**)† as orange needles of m.p. 237—239 °C in 81% yield. Next, a mixture of (**3a**) (580 mg, 2 mmol), 2,4-bis(phenylthio)-1,3-dithia-2,4-diphosphetane 2,4-disulphide (450 mg, 1.1 mmol), and dry toluene (7 ml) was refluxed with stirring for 1 h. The reaction mixture was worked up in the usual way by t.l.c. using ethyl acetate–benzene (1 : 1) as eluant to give (**4a**)† in 75% yield.





In a similar way, compounds (**3b**)† and (**4b**)† were obtained from (**1**) and β-naphthoic acid in 61 and 80% yields, respectively. A single-crystal *X*-ray diffraction study‡ was performed for compound (**4b**) (see Figure 1). On treatment of compound (**3a**) with phosphorus pentaselenide[7] in refluxing 1,2,4-trichlorobenzene overnight, the 7-cyano-6-methylthio-3-phenyl-[1,2]dithiolo[1,5-*b*][1,2,4]-thiaselenazole-4-S^{IV} (**5**)† was obtained as orange needles of m.p. 212—213 °C in 62% yield. It is noteworthy that (**4a**) was reduced with $NaBH_4$–EtOH to give the ring-transformed compound, 5-cyano-6-methylthio-2-phenyl-2,3-dihydro-1,3-thiazine-4-thione (**6**)[8] in 55% yield.

Received, 1st July 1985; Com. 918

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† Compound (**3a**): orange needles (AcOH); m.p. 237—239 °C; i.r. (KBr) 3020(w), 2920(w), 2225(s), and 1540 (vs) cm^{-1}; *m/z* 292 (M^+). (**3b**): brown plates (pyridine); m.p. 259—260 °C (decomp.); i.r. (KBr) 3030(w), 2980(w), 2900(w), 2200(m), and 1500 (s) cm^{-1}; *m/z* 342 (M^+). (**4a**): i.r. (KBr) 3020(w), 2900(w), 2200(m), 1630(w), and 1420 (s) cm^{-1}; ^1H n.m.r. ([$^2H_5$]pyridine): δ 8.2 (m, 2H, Ph), 7.4 (m, 3H, Ph), 2.6 (s, 3H, SMe); *m/z* 308 (M^+). (**4b**): orange crystals ($CHCl_3$); m.p. 230—231 °C; i.r. (KBr) 3020(w), 2900(w), 2200(m), 1620(w), 1470(w), 1420(s), and 1330 (vs) cm^{-1}; *m/z* 358 (M^+); ^{13}C n.m.r. ([$^2H_6$]dimethyl sulphoxide): δ 18.2 (SMe), 118 (CN), 124—136 (naphthyl), 145—198 (ring C). (**5**): i.r. (KBr) 2200(s), 1420(vs), 1405(vs), 1325(vs), and 1310(vs) cm^{-1}; *m/z* 356 (M^+).

‡ *Crystal data* for (**4b**): large, well shaped monoclinic crystals were obtained by slow evaporation of a chloroform solution; $C_{16}H_{10}N_2S_4$: space group $P2_1/c$; $a = 12.861(5)$, $b = 8.093(2)$, $c = 15.352(5)$ Å, $\beta = 94.40(4)°$, $U = 1550.7$ Å^3, $D_c = 1.54$ g cm^{-3}, $Z = 4$. Lattice constants and intensity data were measured using graphite monochromated Cu-K_α radiation on a Rigaku AFC-5 diffractometer. A total of 2506 unique reflections with $F(\theta) > 3\sigma(F\theta)$ were obtained using the ω–2θ scanning method with a 2θ scan speed of 4° min^{-1} to θ = 60°. The structure was solved by the RASA system (Rigaku Corp.) based on the direct method, and refined to a final *R* value of 0.14. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.