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PYRIDYL-SUBSTITUTED [1,3]DITHIOLO-[4,5-*b*][1,4]DITHIINE-2-THIONES

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We have obtained 5-(2-pyridyl)[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione for the first time by cycloaddition of 2-ethynylpyridine to 4,5-dihydro-1,3-dithioltrithione (isotrithionedithiol). We have studied this thione, 5-(2-pyridyl)- and 5-(4-pyridyl)-5,6-dihydro[1,3]dithiolo[4,5-b][1,4]dithiine-2-thiones by mass spectroscopy and also IR, UV, ^1H and ^{13}C NMR spectra. We have determined the crystal and molecular structure of 5-(2-pyridyl)-5,6-dihydro[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione.

Keywords: 4,5-dihydro-1,3-dithioltrithione (isotrithionedithiol), 5-(2-pyridyl)[1,3]dithiolo[4,5-*b*][1,4]-dithiine-2-thione, 5-(2-pyridyl)-5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione, 5-(4-pyridyl)-5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione, IR, ^{1}H and ^{13}C NMR spectra, X-ray diffraction analysis.

4,5-Dihydro-1,3-dithioltrithione, or isotrithionedithiol (dmit), is widely used to obtain derivatives of tetrathiafulvalene: components of synthetic metals and superconductors [1-3] and also many mononuclear and polynuclear metal complexes [4, 5] which can be used to obtain synthetic metals and superconductors. In recent years, interest has also grown in the chemistry of complexes based on 4,5-ethylenedithio-1,3-dithiol-2-thione ($C_5H_4S_5$) [6-8]. In this connection, the work of J. Becher et al. [9] on functionalization of dmit with alkylpyridyl groups is of interest. The Becher method makes it possible to obtain derivatives of dmit that contain two alkylpyridyl substituents at the 4 and 5 positions. Thus in reaction of the complex $[(H_5C_2)_4N]_2[Zn(dmit)_2]$ with 2-vinylpyridine, the compound 4,5-bis(2-pyridylethylsulfanyl)-1,3-dithiol-2-thione (**1**) is obtained.

Another reaction route is also possible. In [10], 4,5-(2-pyridylethylenedithio)-1,3-dithiol-2-thione (**2**) and 4,5-(4-pyridylethylenedithio)-1,3-dithiol-2-thione (**3**) are described, the products of cycloaddition of respectively 2- and 4-vinylpyridine to isotrithionedithiol. Such compounds are of significant interest as ligands in polynuclear complexes and clusters.

A method has been described for obtaining substituted 4,5-ethylenedithio-1,3-dithiol-2-thiones, based on the reaction observed by the authors of [10,11] between alkenes and isotrithionedithiol, a compound to which they assigned a polymeric structure $(C_3S_5)_x$. As we established in [12], isotrithionedithiol, synthesized by oxidation of a solution of sodium isotrithionedithiolate $Na_2C_3S_5$ in DMF by a methanol solution of iodine at 0°C, has a dimer structure: C_6S_{10}, which is consistent with X-ray diffraction data [13] and allows us to hypothesize the possibility of a Diels–Alder type reaction between isotrithionedithiol and alkenes (Scheme 1).

Accordingly, the aim of this work was to study the products of condensation of isotrithionedithiol with 2- and 4-vinylpyridines, obtained by the method of O. Neiland and J. Becher, and also with 2-ethynylpyridine. In the latter case, a bicyclic conjugated system is formed.

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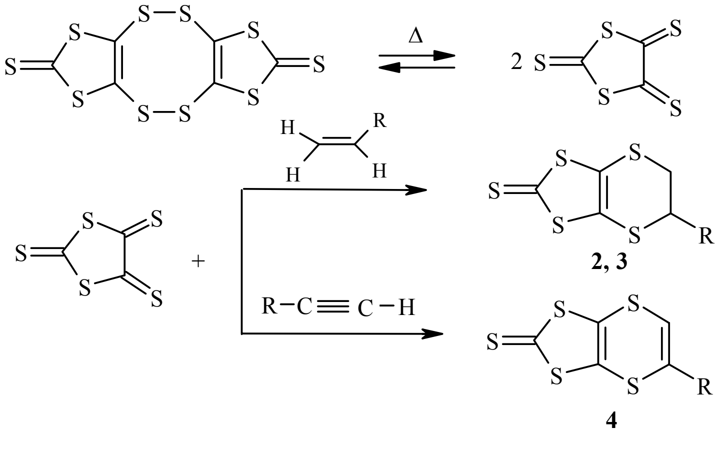
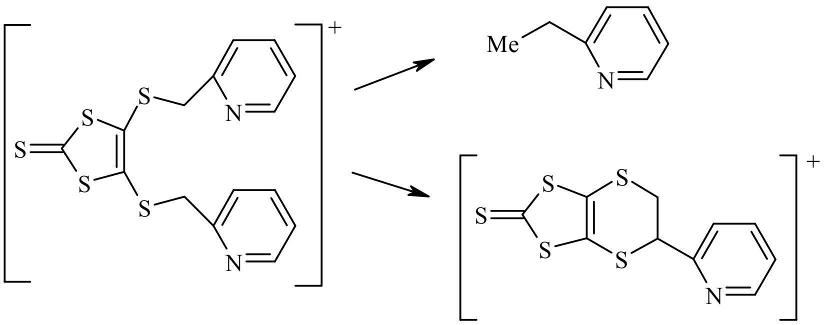
Scheme 1



R = 2-pyridyl (**2, 4**), 4-pyridyl (**3**)

In the mass spectrum of compound **1**, we observe a molecular ion peak *m*/*z* 408 (I_{rel}, 16%) with a corresponding isotope distribution for ^{32}S, ^{33}S, and ^{34}S; the molecular ion peak for compound **2**, formed as a result of fragmentation (Scheme 2); and also the peaks for pyridine derivatives with *m/*z: 107 $[C_7H_9N]^+$ (14), 106 $[C_7H_8N]^+$ (98.7), and 105 $[C_7H_7N]^+$ (100). In the mass spectra of compounds **2** and **3**, we observe molecular ion peaks 301.1 (100); the major fragmentary ions are $[Sn]^+$, *n* = 1-8 (12-18); $[CS_2]^+$ (100), and $[CS]^+$ (20). The mass spectrum of the conjugated compound **4** contains the molecular ion peak 299 (100).

Scheme 2



In the IR spectra of compounds **2-4**, we observe bands for stretching vibrations ν(C=S) respectively at 1059 cm^{-1} (**2**), 1065 cm^{-1} (**3**), and 1075 cm^{-1} (**4**). The band at 1259 cm^{-1} in the spectrum of compound **4**, which is missing in the spectra of compounds **2** and **3**, may be assigned to vibrations of the HC=CPy bond. According to [14], the ν(C=C) vibration band is observed in dithiolate compounds in the 1250-1550 cm^{-1} region. Other intense bands in the spectra of compounds **2-4** are assigned to stretching vibrations of the pyridine ring (1420-1600 cm^{-1}) and to bending vibrations of the C–H bonds [15].

In the electronic spectra, we observe two absorption maxima in the ranges 392-408 nm and 255-270 nm, which may be assigned to the C_3S_5 moiety (their position and intensity in compounds **2-4** are practically identical) and the pyridyl substituent respectively [16]. Thus the pyridyl and isotrithionedithiol moieties are weakly coupled even in the conjugated system **4**. The reason for this is obvious in the case of compounds **2** and **3**; in compound **4**, this is possibly explained by the appreciable dihedral angle between the planes of these moieties. The ^{1}H and ^{13}C NMR spectra unambiguously confirm the correctness of the hypothesized structures for compounds **2-4** (see Experimental).

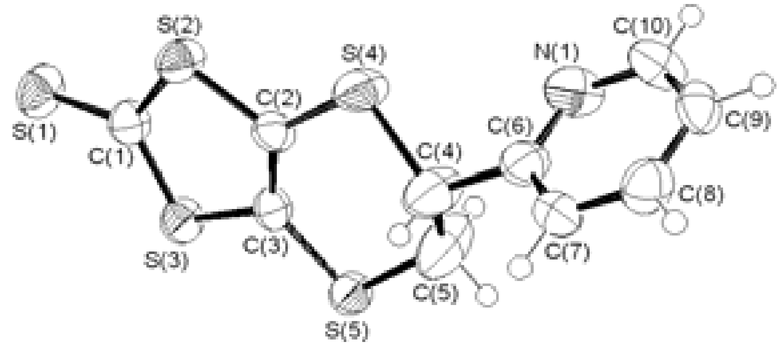


Fig. 1. Numbering of atoms and thermal vibration ellipsoids (50% probability level) in the structure of compound **2**.

The conclusions drawn are confirmed by the X-ray diffraction analysis carried out for crystals of compound **2** (Fig. 1, Tables 1 and 2). As we see from Fig. 1, the C_3S_5 moiety is practically flat; the pyridyl radical is rotated by a 69.12(8)° angle with respect to the C(4)–C(6) bond. The C–C and C–S bond lengths of the C_3S_5 moiety (Table 1) are found within ranges typical of isotrithionedithiols [17, 18]. The molecule consists of two planar moieties: the isotrithionedithiol moiety (the atoms S(1)–S(5), C(1)–C(3), mean-square deviation 0.04 Å) and the pyridine moiety (C(6)–C(10), N(1), mean-square deviation 0.008 Å). The bond lengths, bond angles, and orientation of the thermal vibration ellipsoids in the ethylene group suggest disordering of the C(4) and C(5) atoms. In the packing of the molecules in the crystal, shortened intermolecular contacts $S(2)\cdots S(2)^{-x,3-y,1-z}$ 3.44 Å and $S(4)\cdots H(7)^{x,y+1,z}$ 2.92 Å are formed (the van der Waals radii of S and H are equal to 1.84 and 1.16 Å respectively [19]).

TABLE 1. Bond Lengths (*d*) in the Structure of Compound **2**

Bond	*d*, Å	Bond	*d*, Å
S(1)–C(1)	1.653(3)	S(2)–C(1)	1.708(3)
S(2)–C(2)	1.736(3)	S(3)–C(1)	1.722(3)
S(3)–C(3)	1.747(2)	S(4)–C(2)	1.745(3)
S(4)–C(4)	1.780(4)	S(5)–C(3)	1.739(3)
S(5)–C(5)	1.796(3)	C(2)–C(3)	1.336(4)
C(4)–C(5)	1.376(6)	C(4)–C(6)	1.518(4)
C(6)–N(1)	1.340(4)	C(6)–C(7)	1.370(4)
C(7)–C(8)	1.356(4)	C(8)–C(9)	1.362(4)
C(9)–C(10)	1.370(4)	C(10)–N(1)	1.332(4)

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrometer in the range 400-4000 cm^{-1}. The samples were prepared by pressing in the form of KBr disks. The mass spectra were obtained on a MAT 8200 with ionizing electron energy 70 eV. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AC 250 and Avance 400 spectrometer (operating frequencies 400 MHz and 100 MHz). Internal standard TMS. Elemental analysis

TABLE 2. Bond Angles (ω) in the Structure of Compound **2**

Angle	ω, deg.	Angle	ω, deg.
C(1)–S(2)–C(2)	97.33(13)	C(1)–S(3)–C(3)	97.40(12)
C(2)–S(4)–C(4)	101.32(15)	C(3)–S(5)–C(5)	100.28(16)
S(1)–C(1)–S(2)	123.49(18)	S(1)–C(1)–S(3)	123.35(16)
S(2)–C(1)–S(3)	113.16(15)	C(3)–C(2)–S(2)	116.78(19)
C(3)–C(2)–S(4)	128.7(2)	S(2)–C(2)–S(4)	114.50(15)
C(2)–C(3)–S(5)	128.96(19)	C(2)–C(3)–S(3)	115.2(2)
S(5)–C(3)–S(3)	115.84(14)	C(5)–C(4)–C(6)	116.2(4)
C(5)–C(4)–S(4)	119.2(3)	C(6)–C(4)–S(4)	107.1(2)
C(4)–C(5)–S(5)	122.1(3)	N(1)–C(6)–C(7)	122.8(3)
N(1)–C(6)–C(4)	117.2(3)	C(7)–C(6)–C(4)	120.0(3)
C(8)–C(7)–C(6)	119.2(3)	C(7)–C(8)–C(9)	119.4(3)
C(8)–C(9)–C(10)	118.1(2)	N(1)–C(10)–C(9)	124.0(3)
C(10)–N(1)–C(6)	116.4(3)		

was carried out on an automatic Elementar Vario EL. The electronic absorption spectra were recorded on a Hitachi U 3210 in the range 200-750 nm in acetonitrile.

The X-ray Diffraction Study of the crystals was carried out on a Bruker P4 automatic four-circle diffractometer (MoKα, graphite monochromator). The intensities were measured by the ω-scanning method in the angle range $4° \leq 2\theta \leq 64°$. A total of 8800 reflections were measured, of which 2769 were independent (R_{int} = 0.078) and 2053 were observed with $I > 2\sigma(I)$. Crystallographic data: $C_{10}H_7NS_5$; M_r = 301.47; T = 293 K; monoclinic; $P2_1/c$; a = 11.600(2), b = 6.0010(12), c = 17.964(4) Å; β = 108.27(3)°; V = 1187.5(4) Å^3; Z = 4; d_{calc} = 1.686 g/cm^3; $F(000)$ = 616; μ(MoKα) = 0.943 mm^{-1}·Å.

The structure was solved by the direct method and refined by full-matrix least-squares on F^2 in the anisotropic approximation. The hydrogen atoms were introduced geometrically and refined using a *horse and rider* model with $U_{iso} = 1.2\ U_{eq}$ of the corresponding carbon atom. The final reliability indices were R = 0.080, wR = 0.243 with respect to the observed reflections and R = 0.102, wR = 0.276 with respect to all the independent reflections, S = 1.00.

The bond lengths and bond angles are given in Tables 1 and 2. Figure 1 shows the numbering of the atoms used in discussion of the X-ray diffraction data and the thermal vibration ellipsoids in the molecule. We used the programs SHELX-97 and Ortep-3 to do the calculations and prepare the illustrations [20, 21].

4,5-Bis(2-pyridylethylsulfanyl)-1,3-dithiol-2-thione (1) was obtained as in [9]; the IR and ^{1}H and ^{13}C NMR spectra were consistent with the data in [9].

5-(2-Pyridyl)-5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione (4,5-(2-Pyridylethylenedithio)-1,3-dithiolo-2-thione) (2). Obtained according to the method described in [10], but the yield was 32% instead of 20%; mp 126°C. UV spectrum (MeCN), λ_{max}, nm (log ε): 408 (3.65), shoulder 327, 308 (3.61), 257 (3.69). ^{13}C NMR spectrum (CD_2Cl_2), δ, ppm: 35.30 (SCH_2); 49.74 (CHPy); 123.03 ($C_{(3)pyrid}$); 123.75 ($C_{(5)pyrid}$); 124.24 (C=C); 137.50 ($C_{(4)pyrid}$); 150.25 ($C_{(6)pyrid}$); 156.91 ($C_{(2)pyrid}$); 208.88 (C=S).

5-(4-Pyridyl)-5,6-dihydro[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione (4,5-(4-Pyridylethylenedithio)-1,3-dithiol-2-thiol) (3). Obtained by the method described in [10], but the yield was 41% instead of 15%; mp 138°C. UV spectrum (MeCN), λ_{max}, nm (log ε): 406 (3.56), 268 (3.42). ^{13}C NMR spectrum (benzene-d$_6$), δ, ppm: 34.98 (SCH_2); 47.16 (CHPy); 122.54 (C=C); 122.83 ($C_{(3)pyrid}$, $C_{(5)pyrid}$); 124.00 (C=C); 146.69 ($C_{(4)pyrid}$); 151.92 ($C_{(2)pyrid}$, $C_{(6)pyrid}$); 207.87 (C=S).

5-(2-Pyridyl)[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione (4,5-(2-Pyridylvinylenedithio)-1,3-dithiol-2-thione) (4). 2-Ethynylpyridine (0.5 ml, 5.14 mmol) was added to isotrithionedithiol (0.5 g, 1.27 mmol) in benzene (25 ml). The reaction mixture was boiled under reflux for 17 h. After cooling, the solution was filtered, and the solvent was evaporated on a rotary evaporator. The powdery precipitate was washed with acetone. Yield 0.57 g (75%). IR spectrum, ν, cm^{-1}: 1075 (C=S), 1427-1581 (the pyridyl moiety). UV spectrum (MeCN), λ_{max}, nm (log ε): 392 (2.94), 288 (2.98), 256 (3.12). ^{1}H NMR spectrum (benzene-d$_6$), δ, ppm (*J*, Hz): 6.84 (1H, s, HCS); 7.28 (1H, ddd, *J* = 7.5, *J* = 4.8, *J* = 1, $H_{(5)pyrid}$); 7.30 (1H, dd, *J* = 7.5, *J* = 1, $H_{(3)pyrid}$); 7.60 (1H, dt, *J* = 8 and *J* = 1, $H_{(4)pyrid}$); 8.60 (1H, dd, *J* = 4.8 and *J* = 1, $H_{(6)pyrid}$). ^{13}C NMR spectrum (benzene-d$_6$), δ, ppm (*J*, Hz): 120.05 ($C_{(3)pyrid}$); 121.5 ($C_{(6)}$); 122.67 ($C_{(5)pyrid}$); 123.89 ($C_{(3a)}$ or $C_{(7a)}$); 137.18 ($C_{(4)pyrid}$); 142.2 ($C_{(5)}$); 149.84 ($C_{(6)pyrid}$); 156.6 ($C_{(2)pyrid}$); we could not identify $C_{(7a)}$ or $C_{(3a)}$ due to the low signal-to-noise ratio of the C=S signal. Found, %: C 39.42; H 1.92; N 4.57. $C_{10}H_5NS_5$. Calculated, %: C 40.13; H 1.67; N 4.68.

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