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

A. Yu. Koshevaya¹, V. A. Starodub¹, and D. Fenske²

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 ¹³C 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, ¹H and ¹³C 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 (C₅H₄S₅) [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 [(H₅C₂)₄N][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 (C₅S₅)ₓ. As we established in [12], isotrithionedithiol, synthesized by oxidation of a solution of sodium isotrithionedithiolate Na₂C₅S₅ in DMF by a methanol solution of iodine at 0°C, has a dimer structure: C₆S₁₀, 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.

¹ V. N. Karazin Kharkov National University, Kharkov 61077, Ukraine; e-mail: vladimir.a.starodub@univer.kharkov.ua. ² Institute of Inorganic Chemistry, Technical University of Karlsruhe, Karlsruhe, Germany. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 429-434, March, 2005. Original article submitted February 11, 2003; revised November 22, 2004.
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}\text{S}, \(^{33}\text{S}, \) and \(^{34}\text{S}\); 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 \([\text{C}_7\text{H}_9\text{N}]^+\) (14), 106 \([\text{C}_7\text{H}_8\text{N}]^+\) (98.7), and 105 \([\text{C}_7\text{H}_7\text{N}]^+\) (100). In the mass spectra of compounds 2 and 3, we observe molecular ion peaks 301.1 (100); the major fragmentary ions are \([\text{Sn}]^+, n = 1-8\) (12-18); \([\text{CS}_2]^+\) (100), and \([\text{CS}]^+\) (20). The mass spectrum of the conjugated compound 4 contains the molecular ion peak 299 (100).

In the IR spectra of compounds 2-4, we observe bands for stretching vibrations \( \nu(\text{C=S}) \) 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 \( \text{HC}=\text{CPy} \) bond. According to [14], the \( \nu(\text{C=C}) \) 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 \( \text{C}_5\text{S}_3 \) moiety (their position and intensity in compounds 2-4 are practically identical) and the pyridyl substituent respectively [16]. Thus the pyridyl and isotriothionedithiol 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 \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra unambiguously confirm the correctness of the hypothesized structures for compounds 2-4 (see Experimental).