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Crystal structure of 4,5-(ethoxyethylenedithio)-1,3-dithiole-2-thione, $C_7H_8OS_5$

G. Xue, W.-T. Yu and Q. Fang*

Shandong University, State Key Laboratory of Crystal Materials, Jinan, Shandong Province, 250100 P. R. China

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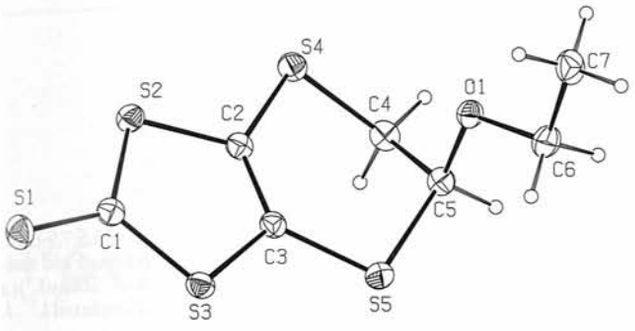

Abstract

$C_7H_8OS_5$, monoclinic, $P12_1/c1$ (No. 14), $a = 8.3699(7)$ Å, $b = 17.573(2)$ Å, $c = 7.5305(7)$ Å, $\beta = 103.584(7)°$, $V = 1076.6$ Å^3, $Z = 4$, $R_{gt}(F) = 0.033$, $wR_{ref}(F^2) = 0.082$, $T = 293$ K.

Source of material

$(Bu_4N)_2[Zn(dmit)_2]$ was stirred with 1,2-dibromoethyl ethyl ether in excess acetone at room temperature. The orange solid was obtained, and it was extracted with benzene, washed with aqueous sodium hydrogencarbonate, and then with water. After drying over Na_2SO_4, the benzene was evaporated, and the residue recrystallized from a mixed solvent of petroleum ether and chloroform (3:2) to give the title compound [1].

Discussion

Electronic donor BEDT-TTF [bis(ethylenedithio)-tetrathiafulvalene] and its variety of charge-transfer salts have attracted great interest for their electronic conductivity or superconductivity [2]. A replacement of the two ethylene units of BEDT-TTF with carbon-carbon double bonds can give rise to another attractive donor named as BVDT-TTF [bis(vinylenedithio)-tetrathiafulvalene] [3]. In the course of researching new BVDT-TTF based molecular electronic conductors, we obtained the crystal structure of title compound which serves as the precursor of BVDT-TTF .

In title compound, the terminal S1—C1 bond length of 1.647(3) Å is slightly longer than a typical S=C double bond. The C2—C3 bond is a double bond with the length of 1.349(3) Å. The bond lengths of S4—C4 and S5—C5 to the methylene carbon atoms are 1.801(3) Å and 1.835(2) Å, respectively, showing a characteristic of single S—C bond.The remaining six S—C bonds are in the range of 1.720(3) Å – 1.754(2) Å which are between typical single S—C and double S=C bonds. Thus, the 4,5-dimercapto-1,3-dithiole-2-thione (dmit) moiety in title compound is highly conjugated, which is similar to the case of other dmit derivatives [4-6]. Least-squares planes calculations show that the planarity of dmit moiety in the title compound is quite good. There are many S···O, S···C interactions between neighboring molecules. The distances of S3···O1, S4···O1 and S3···C2 are 3.320(2) Å, 3.182(2) Å and 3.464(2) Å, respectively. Above intermolecular distances between the molecules are shorter than the sum of the van der Waals radii, so the crystal packing is considerably stabilized.

Table 1. Data collection and handling.

Crystal:	pale-yellow plate, size 0.08 × 0.24 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.32 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	54.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3202, 2465
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1834
$N(param)_{refined}$:	119
Program:	SHELXTL [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(4A)	4*e*	0.4932	0.5686	0.3484	0.052
H(4B)	4*e*	0.5241	0.5390	0.2173	0.052
H(5A)	4*e*	0.7623	0.5700	0.2951	0.048
H(6A)	4*e*	0.9271	0.5615	0.0918	0.064
H(6B)	4*e*	0.8931	0.6490	0.0606	0.064
H(7A)	4*e*	0.9730	0.5976	–0.1882	0.082
H(7B)	4*e*	0.7916	0.6270	–0.2500	0.082
H(7C)	4*e*	0.8265	0.5397	–0.2185	0.082

* Correspondence author (e-mail: fangqi@icm.sdu.edu.cn)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*e*	0.1517(1)	0.90920(4)	–0.0029(1)	0.0611(5)	0.0498(4)	0.0610(5)	0.0121(3)	0.0122(4)	0.0051(4)
S(2)	4*e*	0.17686(8)	0.73991(4)	–0.01138(9)	0.0376(3)	0.0460(4)	0.0449(4)	–0.0038(3)	0.0089(3)	–0.0032(3)
S(3)	4*e*	0.45681(8)	0.82697(3)	0.17200(9)	0.0437(3)	0.0368(3)	0.0441(4)	–0.0042(3)	0.0112(3)	–0.0061(3)
S(4)	4*e*	0.33451(8)	0.58917(4)	0.0582(1)	0.0405(3)	0.0368(3)	0.0551(4)	–0.0086(3)	0.0154(3)	–0.0047(3)
S(5)	4*e*	0.68031(8)	0.69669(4)	0.2883(1)	0.0398(3)	0.0438(4)	0.0508(4)	–0.0028(3)	0.0047(3)	–0.0075(3)
O(1)	4*e*	0.6899(2)	0.58769(9)	0.0349(2)	0.0324(8)	0.047(1)	0.043(1)	–0.0027(7)	0.0120(7)	–0.0025(8)
C(1)	4*e*	0.2560(3)	0.8295(1)	0.0485(3)	0.044(1)	0.043(1)	0.036(1)	–0.001(1)	0.014(1)	0.000(1)
C(2)	4*e*	0.3518(3)	0.6873(1)	0.0891(3)	0.039(1)	0.037(1)	0.039(1)	–0.004(1)	0.014(1)	–0.002(1)
C(3)	4*e*	0.4842(3)	0.7282(1)	0.1743(3)	0.038(1)	0.038(1)	0.037(1)	–0.001(1)	0.013(1)	–0.002(1)
C(4)	4*e*	0.5119(3)	0.5585(1)	0.2283(3)	0.050(1)	0.038(1)	0.046(2)	–0.003(1)	0.018(1)	0.003(1)
C(5)	4*e*	0.6716(3)	0.5971(1)	0.2136(3)	0.042(1)	0.036(1)	0.041(1)	0.000(1)	0.009(1)	0.003(1)
C(6)	4*e*	0.8554(3)	0.5986(2)	0.0175(4)	0.033(1)	0.067(2)	0.063(2)	–0.006(1)	0.015(1)	–0.007(2)
C(7)	4*e*	0.8622(3)	0.5900(2)	–0.1770(4)	0.043(1)	0.062(2)	0.066(2)	0.000(1)	0.024(1)	–0.002(2)

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