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[1,4]Dithiino[2,3-*b*]-1,4-Dithiin (**3**) has been synthesised in high yield by a one-step procedure starting with sodium 1,3-dithiole-2-thione-4,5-dithiolate (**2**). The X-ray crystal structure shows non-planarity of the fused ring system as well as short intermolecular S...S contacts.

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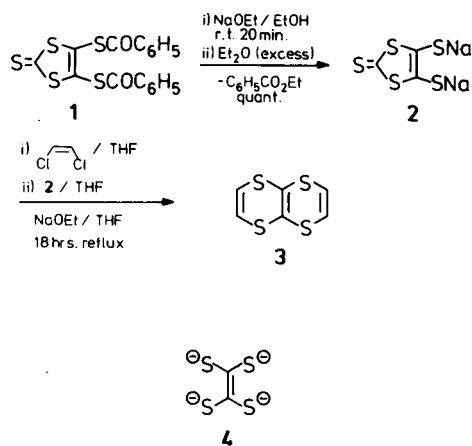
The synthesis of [1,4]dithiino[2,3-*b*]-1,4-dithiin has been reported [1] from sodium 1,3-dithiole-2-thione-4,5-dithiolate **2**. However, the reported [1] synthetic yield for the compound **3** was low and involved three steps as well as the chromatographic separation of the product from its dihydro derivative. In our search for new multisulfur organic  $\pi$ -donor molecules for the preparation of molecular conductors, we have been interested in constructing 1,4-dithiino rings based on "pseudonucleophilic" substitutions of halogens on 1,2-dihaloalkenes by dithiolate nucleophiles [2]. The method described here for the preparation of **3** represents a vastly improved one-step procedure over the previous multi-step synthesis by Cava *et al.* [1]. We also present the results of X-ray crystal structure analysis of the title compound **3** for the first time.

The sodium 1,3-dithiole-2-thione-4,5-dithiolate salt **2** can be prepared conveniently and in excellent overall yield starting with the sodium metal reduction of carbon disulfide. The salt has previously been used for a more efficient route to bis(ethylene dithio)tetrathiafulvalene (BEDT-TTF) [3] - the first sulfur-based organic  $\pi$ -donor to give superconducting charge-transfer salts. The salt **2** can be stored for up to three days under argon using Schlenk techniques [3,4] and has been found to be an ideal 'synthon' for the syntheses and structural elaboration of *N*-heterocycle based multisulfur  $\pi$ -donors for use in preparing organic metals/conductors [5] and metallopolymers [6].

## Results and Discussion.

### Synthesis.

The reactions carried out are outlined in Scheme 1. The dithiobenzoyl ester **1** was easily prepared in excellent yield by a reported procedure [7]. The diester **1** was deprotected by a slight molar excess of sodium ethoxide in absolute ethanol to generate the salt **2** quantitatively in twenty minutes at room temperature. The salt **2** precipitated out



when the ethanolic solution was poured into a large volume of dry diethyl ether and was isolated using a Schlenk apparatus [3,4]. Compound **2** was then allowed to react with *cis*-1,2-dichloroethene in the presence of sodium ethoxide in tetrahydrofuran at high dilution to afford the dithiinodithiin **3** in 88% yield. It must be emphasised that in this step the use of the high dilution technique is crucial as otherwise yields are greatly reduced. This reaction, although having the overall appearance of being a nucleophilic substitution of the chlorine atoms of the dihalo-

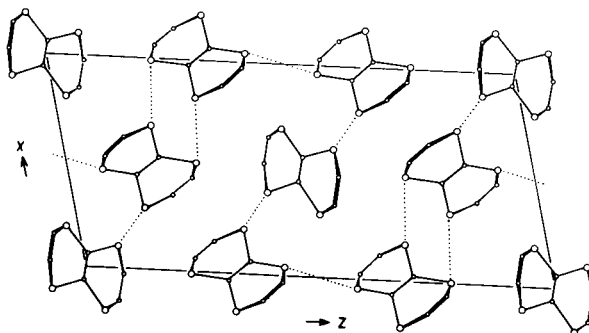


Figure 1. Projection of the crystal structure down the *y*-axis. The dotted lines represent S...S contact distances less than 3.5 Å.

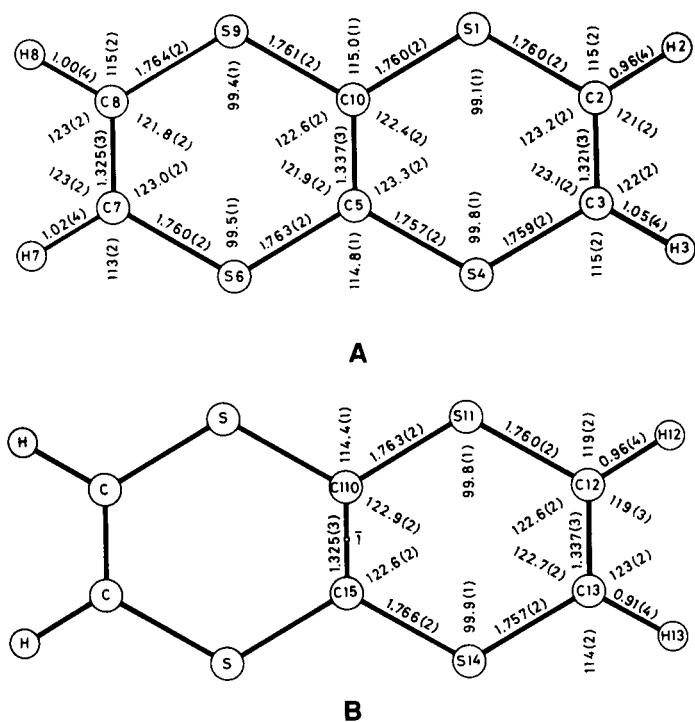


Figure 2. Bond distances (Å), angles (°), and the atom numbering scheme for the two molecules **A**: general position, **B**: special position.

alkene by the dithiolate species, is more likely to involve a sequence of elimination-addition steps similar to the mechanism proposed by Truce *et al.* [8] who have carried out detailed mechanistic work on base-catalysed reactions between *cis*-dichloroethene and monothiolates. It is also very likely that the salt **2** forms the ethenetetrathiolate species **4** after initial ethoxide ion attack on the thione functionality which then reacts 'side-on' with the alkene to give the dithiinodithiin **3**.

Table 1

"Flap"-angles and "boat"-angles for **A** and **B**. The flap angle is the angle between a plane defined by the central  $>S_2C=CS_2<$  fragment and a plane defined by a-S-CH=CH-S- fragment. The boat angle is the angle between a C-S-C plane and the plane of the six olefinic C atoms.

Compound	Plane	Flap angle	Boat angle
<b>A</b>	S1-C2-C3-S4	131.0(5)°	
<b>A</b>	S6-C7-C8-S9	129.0(5)°	
<b>B</b>	S11-C12-C13-S14	130.9(5)°	
<b>A</b>	C10-S2-C1		145.9(6)°
<b>A</b>	C3-S4-C5		149.1(6)°
<b>A</b>	C5-S6-C7		146.6(6)°
<b>A</b>	C8-S9-C10		145.1(6)°
<b>B</b>	C110-S11-C12		147.2(6)°
<b>B</b>	C13-S14-C15		147.1(6)°

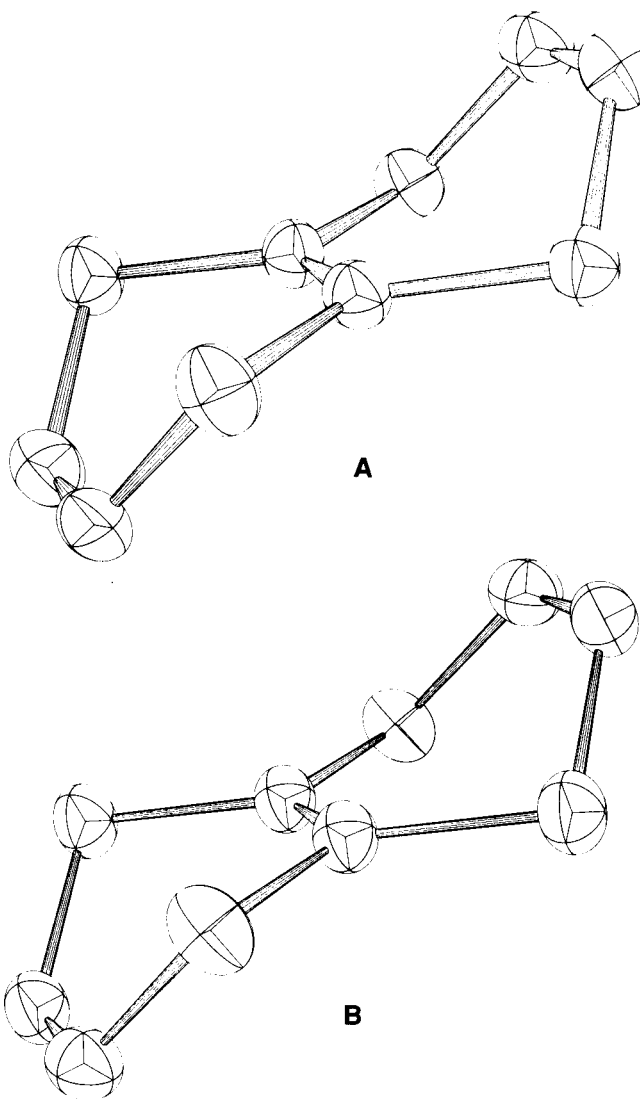


Figure 3. Perspective drawings (ORTEP) of the [1,4]dithiino[2,3-*b*]-1,4-dithiin molecules **A** and **B**.

Table 2

Mean values of non-H bond distances and endocyclic bond angles for the molecules (**A**) and (**B**)

	molecule ( <b>A</b> )	molecule ( <b>B</b> )
C-S	1.761(2) Å	1.762(3) Å
C=C	1.328(7) Å	1.331(6) Å
C-S-C	99.5(3)°	99.9(1)°
C=C-S	122.7(5)°	122.7(1)°

Table 3

Some bond lengths (Å) and angles (°) in [1,4]dithiino[2,3-*b*]-1,4-dithiin compared with corresponding bonds and angles in related 1,4-dithiin derivatives.



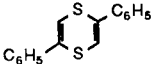
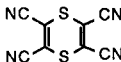
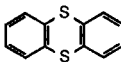
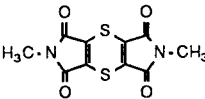
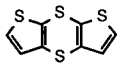
Compound	Reference	C-S (Å)	C=C (Å)	C-S-C (°)	C=C-S (°)	Flap angle (°)	Boat angle (°)
3 		1.757-1.766	1.321-1.337	99.1-99.9	121.8-123.3	129.0-131.0	145.1-149.1
5 	[12] [13]	1.73-1.82	1.24-1.33	100.2	124	137	152
6 	[13]	1.755-1.767		101.8		132.7	147.5
7 	[12] [14]	1.755	1.344	97.3	121.8	124	154
8 	[15]	1.769-1.773	1.394	99.9-100.5	120.5-120.8	128.09	141.8-143.4
9 	[16]	1.736-1.752	1.33-1.34	95.7-96.1	131.3-132.7	179.1	178.4-179.3
10 	[17]	1.747-1.765	1.357-1.360	96.8-99.2	122.3-125.2	130.3	147.1-148.9

Table 4

Fractional coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters of non-H atoms with e.s.d.s. in parentheses

atom	x	y	z	$B_{eq}$
S(1)	110.6(6)	5428(1)	7752.4(2)	2.97(3)
S(4)	-2054.6(5)	7052(1)	6513.9(3)	3.08(4)
S(6)	-377.1(6)	4787(1)	5733.1(2)	3.22(4)
S(9)	1815.2(5)	3345(1)	6957.9(3)	3.31(4)
S(11)	3900.7(5)	-2048(1)	4186.6(2)	3.02(4)
S(14)	6912.9(5)	-247(1)	4732.9(3)	3.17(4)
C(2)	-569(2)	8442(4)	7638(1)	3.2(2)
C(3)	-1459(2)	9097(4)	7137(1)	3.3(2)
C(5)	-585(2)	5469(4)	6487.7(9)	2.5(1)
C(7)	297(2)	1775(4)	5863(1)	3.4(2)
C(8)	1202(2)	1164(4)	6366(1)	3.4(2)
C(10)	325(2)	4845(4)	6995.6(9)	2.5(1)
C(12)	5265(2)	-4064(4)	4260(1)	3.0(1)
C(13)	6510(2)	-3310(4)	4479(1)	3.1(1)
C(15)	5618(2)	357(4)	5114.3(9)	2.5(1)

### X-Ray Structure.

The unit cell contains six molecules in all divided into two symmetry independent categories with four molecules

on the general position (e) and two molecules on the centrosymmetric special position (c) ( $\frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, 0$ ) (Figure 1). Bond distances and bond angles for the two types of molecules (A): (general position) and (B): (special position) are given in (Figure 2). "Flap" angles and "boat" angles for (A) and (B) are listed in (Table 1). The (A) and (B) molecules are nearly identical as can be seen from (Figure 2), (Figure 3) and (Table 1). A comparison of mean values support this point of view (Table 2).

The geometry of the [1,4]dithiino[2,3-*b*]-1,4-dithiin (3), molecule can be described in different ways. The molecular framework can be considered as a chair form with  $>S_2C=CS_2<$  as "the seat" and with flap angles of approximately  $130^\circ$  (Table 1). The bending around the S-S axis in related 1,4-dithiin ring systems is well documented (Table 3). By another description compound 3 can be considered as two fused boat-shaped rings with a center of symmetry on the central C=C bond so that the sulfur atoms for each ring are on opposite sides of the plane of the olefinic C-atoms.

The chair conformation of the molecule prevents conjugation, and the C-C bond distances clearly corresponds to normal unconjugated bonds, (simple double bond =  $1.337(6)$  Å [18]) so the molecule is non-aromatic in the solid state.

Bock *et al.* [19] have calculated  $\Delta H_f$  for compound **3** as a function of the flap angle. These calculations shows hardly any significant dependence on the flap angle in the range 180-140°, and the conclusion is that compound **3** should be flexible in the gas phase and in solution.

In nearly all of the reported structures which contains the 1,4-dithiin ring system, a "bent" 1,4-dithiin ring structure is seen (Table 3), however Yamaguchi and Veda [16] have determined the structure of a molecular complex which contains a planar 1,4-dithiin ring system. This, together with the calculations of Bock *et al.* [19], suggests that it may be possible to have planar 1,4-dithiin or [1,4]-dithiino[2,3-*b*]-1,4-dithiin systems under certain "strain" conditions.

The crystal structure is stabilized by intermolecular S...S contact distances, some of which make up spirals centered around the  $2_1$  axes situated at ( $X = 1/4, Z = 3/4$ ) and ( $X = 3/4, Z = 1/4$ ) (Figure 1). The S...S contact distances are in the range 3.454(1)–3.499(1) Å, which are rather short compared to the sum of the van der Waal's radii ( $r$  (sulphur, covalent) = 1.85 Å [20]). The S...S contact distances in compound **3** compare well with those in semi-conducting 3,4,3',4'-bis(ethylenedithio)-2,2',5,5'-tetra-thiafulvalene-hexafluoroarsenate (2:1), [21] (S...S contact distances = 3.447(4)–3.528(4) Å).

## EXPERIMENTAL

Melting points were obtained on a Gallenkamp apparatus and are uncorrected. Proton nmr spectrum was recorded in deuteriochloroform using a Jeol FX-60 spectrometer. All chemical shifts are reported in ppm downfield of tetramethylsilane.

Synthesis of 4,5-Dimercapto-1,3-dithiole-2-thione Disodium Salt (**2**) [3].

To a suspension of finely powdered 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (**1**) 16.24 g (0.04 mole) in 50 ml of absolute ethanol, was added a solution of sodium 1.86 g (0.081 g-atom) in 20 ml of absolute ethanol with stirring and under a nitrogen atmosphere. After twenty minutes the clear red dithiolate solution was poured slowly, with stirring, into 1.5 l of dry diethyl ether. After fifteen minutes the resulting crimson-red precipitate was filtered off under nitrogen using the Schlenk technique [3,4] and washed with 2 x 50 ml portions of dry diethyl ether. The salt **2** was dried *in vacuo* for twenty minutes and then used directly in the next step without further purification. A quantitative yield of 9.68 g of salt **2** was obtained.

Synthesis of [1,4]Dithiino[2,3-*b*]-1,4-dithiin (**3**).

The sodium salt of 4,5-dimercapto-1,3-dithiole-2-thione (**2**) 9.68 g (0.04 mole) obtained from the previous step was dissolved in 250 ml of dry, distilled tetrahydrofuran (THF). *Cis*-1,2-Dichloroethene 7.86 g (0.081) was dissolved in 250 ml of THF. These two solutions were then simultaneously added dropwise, over a period of four hours, into a vigorously stirred and refluxing solution of 750 ml of THF containing sodium 9.43 g (0.41 mole) in 100 ml absolute ethanol. The whole reaction mixture was then left to reflux overnight. After cooling to room temperature, the reaction mixture was poured into 2.5 l of ice-water with stirring and a saturated sodium chloride solution (100 ml) was added slowly to complete the precipitation of the product which was then filtered off, washed with water and dried *in vacuo*. The crude product was recrystallised from benzene-ethanol (2:1) to give lemon yellow crystalline material, 7.18 g (88% yield), mp 126-127° (lit [1] mp 125-126°); ms:  $m/z$  (% relative intensity)

204,  $M^+$  (86), 171 (15), 159 (100), 146 (7), 134 (5), 127 (18), 102 (13), 96 (5), 88 (33), 76 (27), 69 (15), 64 (6), 58 (14), 45 (33);  $^1\text{H-nmr}$  (60 MHz): 6.45 (s, 4H).

*Anal.* Calcd. for  $\text{C}_6\text{H}_4\text{S}_4$ : C, 35.26; H, 1.97. Found: C, 35.38; H, 2.0.

## X-Ray Crystal Structure Analyses.

The crystals of [1,4]dithiino[2,3-*b*]-1,4-dithiin (**3**) used in the X-ray investigation were crystallized from a 1/2 benzene/ethanol solution. A crystal with approximate dimensions 0.07 x 0.26 x 0.40 mm was selected for X-ray diffraction. Space group  $P2_1/n$  (No. 14, unique axis *b*) was deduced from systematic extinctions. The reflections were measured from systematic extinctions. The reflections were measured with an Enraf-Nonius CAD-4F diffractometer, using graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å). Lattice parameters were determined from setting angles for 25 reflections with  $10.00 < \theta < 14.03^\circ$ , ( $a = 10.370(1)$ ,  $b = 5.367(1)$ ,  $c = 22.051(3)$  Å and  $\beta = 102.83(1)^\circ$ .  $V = 1196.5(6)$  Å<sup>3</sup>,  $\mu(\text{Mok}\alpha) = 1.05$  mm<sup>-1</sup>. The density was determined by flotation in NaI (aq),  $D_{\text{obs}} = 1.68$  g·cm<sup>-3</sup>,  $D_{\text{calc}} = 1.702$  g·cm<sup>-3</sup>,  $Z = 6$ . The reflections ( $h$  0–14, 0–7, 1-30–29) in the range  $2^\circ < \theta < 30^\circ$  were measured by applying a mixed  $\omega/\theta$  scan technique with  $\Delta\omega = (1.00 + 0.35 \tan \theta)^\circ$ . The scan angle was extended at each side with 25% for background measurements. One-sixth of the scan time was used for background measurements at the beginning and the end of the scan. The reflections were measured with a horizontal variable detector aperture width of  $(2.40 + 1.20 \tan \theta)$  mm. The vertical size of the detector slit was fixed to 4.00 mm. A prescan determined the speed of the final scan so that  $\sigma(I)/I < 0.03$ . Three reflections ( $1\bar{2}11$ ), ( $4\bar{2}\bar{6}$ ), and ( $5\bar{2}\bar{3}$ ) were used for orientation control every 100 reflections. The intensity of ( $4\bar{2}\bar{6}$ ) was checked every 3 hours. A reflection was designated not observed if  $I \leq 2.5 \sigma(I)$ . With this criterion 2408 out of 3482 independently measured reflections were regarded as observed. Lorentz and polarization corrections were applied, but no extinction or absorption corrections were made.

The structure was solved by direct methods, using the SHELX-76 system [9]. Refinement and analysis of the structure were performed with the X-RAY-76 system [10], computer: SPERRY 1100/72. In the full-matrix minimization of  $\sum w(|F_o| - |F_c|)^2$ , the weighting function was  $w = 1$  if  $|F_o| < 32$  else  $w = (A/F_o)^2$  for  $A = 32$ , as this choice gave an acceptable weight analysis. Contributions from unobserved reflections were included if  $F_c > F_o$ . The positional H-parameters were calculated.  $H(x,y,z)$  were refined separately with  $\sin \theta/\lambda < 0.40$  Å<sup>-1</sup> and fixed isotropic H temperature factor. Final  $R = 0.032 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $wR = 0.039 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|)^{1/2}$  with a GOF of 1.28 (quality of fit =  $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{para}})]^{1/2}$ ). Ratio of maximum least-squares shift to error in final refinement cycle = 0.0020. Minimum and maximum in final  $\Delta\rho$  map was -0.44 and 0.43 e/Å<sup>3</sup>. Scattering factors were from International Tables for X-Ray Crystallography [11]. The positional and isotropic thermal parameters are given in (Table 4).

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