SPIRO 1,3,4,6-TETRATHIAPENTALENE-2-THIONES

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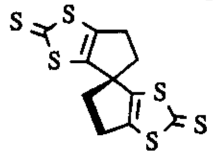
Abstract - Reaction of the geminal α,α-dichloroketones (3) and (5) with the 4,5-dimercapto-1,3-dithiole-2-thione dianion (2) yields the spiro 1,3,4,6-tetrathiapentalene-2-thiones (4) and (6). The structure of 1,3,4,6-tetrathiapentalene-2-thione-5-spiro-3'-benzo[*c*]furan-1'-(3*H*)-one (4) was determined by X-ray crystallography.

A prerequisite for the preparation of new and unusual tetrathiafulvalenes is the availability of the appropriate 1,3-dithiole-2-thiones. Numerous modifications have been introduced in tetrathiafulvalene systems (TTF-systems) in order to maintain or improve the metallic conductivity.[1] The majority of these materials have been based on planer TTF-systems; however, there has been a growing interest in non-planer TTF-derivatives[2] as well as functionalized and macrocyclic TTF-systems.[3] A spiro TTF-system has to the best of our knowledge only been reported once,[4] this system was prepared from the spiro-*bis*-trithiocarbonate (1).



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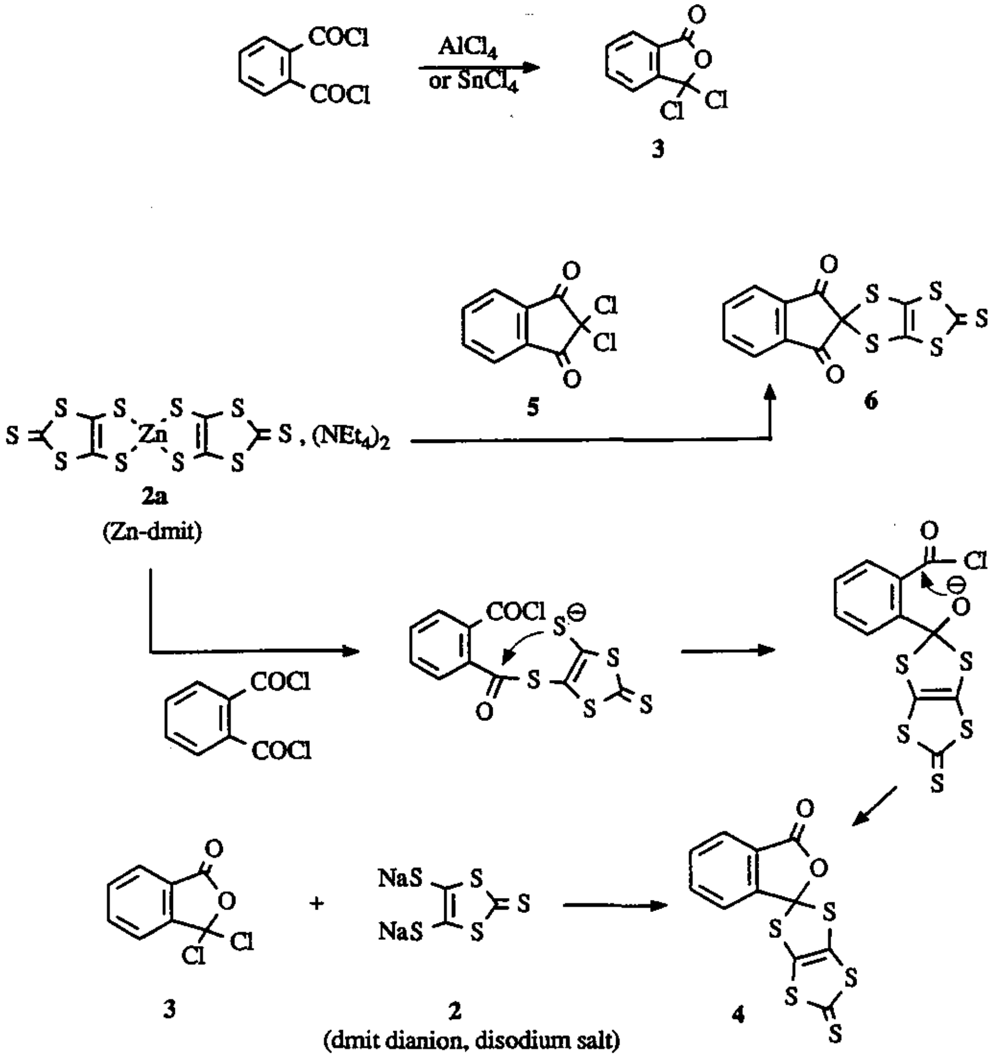
The 4,5-dimercapto-1,3-dithiole-2-thione dianion (dmit) (2) is an important starting material for a number of highly conducting organic charge transfer salts.[5] In this paper we wish to report reaction of the dmit dianion[6] (2) with two examples of geminal α,α-dichloro ketones which leads to new spiro-trithiocarbonate derivatives. In a fast reaction between *o*-phthaloyl dichloride and tetraethylammonium *bis*-(1,3-dithiole-2-thione-4,5-dithio)zinkate[7] (2a) a yellow crystalline product (4) was obtained in high yield. The elementary composition of this compound was $C_{11}H_4O_2S_5$ corresponding to the M^+ peak at m/z = 328 in the ms, the ir spectrum revealed the presence of an ester group C=O (1790 cm^{-1}) and a C=S function (1068 cm^{-1}), while the ^{1}H nmr spectrum confirmed that the protons originated from an unsymmetrically 1,2-substituted benzene system. With Lewis acids symmetric *o*-phthaloyl dichloride will rearrange into the "unsymmetric" isomer;[8]

3,3-dichloroisobenzofuran-1-one (3) and consequently old samples of *o*-phthaloyl dichloride can contain varying amounts of 3 (as seen in the ^{1}H-nmr spectrum). We first supposed the reaction product (4) described above using *o*-phthalloyl dichloride to result from the "unsymmetric" isomer (3), although this could not explain the relative high yield of 4. However when the reaction was repeated using pure 3, the spiro-isobenzofuran (4) was obtained in 88% yield after recrystallisation. Similarly 2,2-dichloroindan-1,3-dione (5) yielded the corresponding spiro-indan (6) in fair yield. These results are summarised in the following Scheme, which also give a likely mechanism for the reaction of 2a and *o*-phthaloyl dichloride:



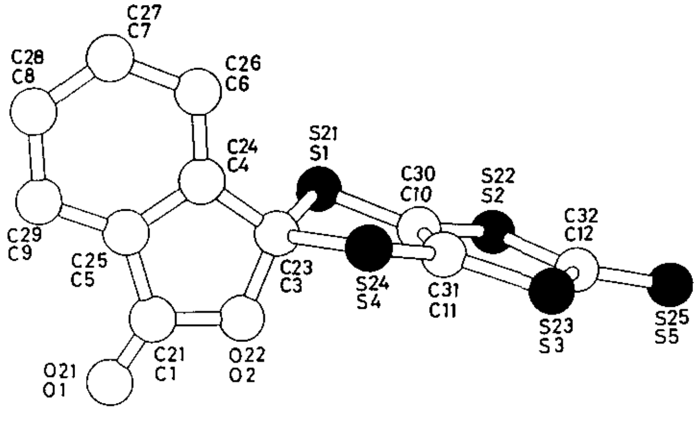
Scheme *Preparation of spiro 1,3,4,6-tetrathiapentalene-2-thiones via reaction from dmit.*

A range of related heterocyclic and alicyclic geminal α,α-dihalo compounds also yields spiro- dithiolethiones, and a full account will be reported elsewhere.

X-RAY STRUCTURE DETERMINATION OF 4

The structure of spiro isobenzofuran (**4**) was confirmed by X-ray diffraction. The corresponding bond distances in the two symmetry independent molecules of **4** are equal within the standard deviations, except for two of the bonds (S5-C12:1.620(3)Å; S25-C32:1.644(4)Å and S3-C12:1.745(3)Å; S23-C32:1.721(3)Å. This is probably caused by a very short intermolecular contact distance between S25 and S1 (S25···S1:3.342(1)Å), resulting in transfer of π-electron density from C32-S25 to C32-S23 and possibly S1-C10. The two parts of the molecules connected through C3/C23 are nearly perpendicular to each other (Table 1), dihedral angles (B)(C); (B)(D); (F)(G) and (F)(H)). The molecules are bent around the lines S1-S4/S21-S24 with fairly different values (Table 1), dihedral angles (B)(A) and (F)(E)). A bent (envelope) conformation for dithiole rings with a apical sp^3-hybridized carbon has been reported previous-ly.[9, 10] The atomic coordinates for **4** are given in Table 2.

Figure 1



Perspective drawing of **4** *with the atomic numbering scheme. Top and bottom numbers are connected to each of the two symmetry independent molecules.*

Table 1 Dihedral angles (°) between some least square planes.

	(A)	(C)	(D)		(E)	(G)	(H)
(B)	28.4(2)	89.5(1)	89.4(1)	(F)	38.6(3)	93.6(1)	96.8(1)

Definition of least square planes.

(A): S1, C3, S4;
(B): S1, S2, S3, S4, C10, C11;
(C): C1, O2, C3, C4, C5;
(D): C4, C5, C6, C7, C8, C9;
(E): S21, C23, C24;
(F): S21, S22, S23, S24, C30, C31;
(G): C21,O22, C23, C24, C25;
(H): C25, C26, C27, C28, C29.

EXPERIMENTAL

1,3,4,6-Tetrathiapentalene-2-thione-5-spiro-3'-benzo[*c*]furan-1'(3*H*)-one (**4**).

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione[6] 2.03 g (5 mmol) was dissolved in dry ethanol (20 ml) under N_2, whereupon a solution of sodium 0.3 g (13 mmol) in dry ethanol (10 ml) was added. Formation of the dark red dmit anion (**2**) was complete in 30 min whereupon a solution of 3,3-dichlorobenzo[*b*]furan-2(3*H*)-one (**3**)[8] 1 g (5 mmol) was added with stirring at 0°C. The yellow precipitate which was formed at once, was isolated, redissolved in methylene chloride, filtered again whereupon the organic phase was concentrated *in vacuo* (crude yield 1.53 g, 93%). Recrystallisation of the crude product gave the title compound (**4**), 1.45 g (88%) as yellow crystals mp 207 - 210 °C (decomp.) ($CHCl_3$). Alternatively **4** is obtained from dmit-zinkate (**2a**) by stirring a mixture of **2a** 1.44 g (2 mmol) and *o*-phthaloyl dichloride 0.51 g (2.5 mmol) in dry acetone (50 ml) for 30 min at room temperature, followed by work up as described above (yield of recrystallised **4** was 0.46 g, 70%). Ir (KBr) 1790 (C=O), 1068 (C=S) cm^{-1}. ^{1}H-Nmr ($CDCl_3$) 7.74 (1H, dt, *J* = 7.4 and 1.1 Hz), 7.85 (1H, dt, *J* = 7.4 and 1.1 Hz), 7.99 (2H, dd, *J*=7.7 and 7.4 Hz) ppm. ^{13}C-Nmr ($CDCl_3$) 52.74, 124.73, 126.07, 126.53, 132.32, 135.16, 143.03, 165.07, 210.88 ppm. EIms m/z 328 (M^+, 24), 164 (31), 104 (38), 88 (36), 76 (100). Anal. Calcd for $C_{11}H_4O_2S_5$: C, 40.23; H, 1.23; S, 48.81. Found: C, 40.40; H, 1.32; S, 48.81.

1,3,4,6-Tetrathiapentalene-2-thione-5-spiro-2'-indan-1',3'-dione (**6**).

To a suspension of Zn-dmit (**2a**) (0.898 g, 1.25 mmol) in acetone (50 ml, 0°C) was added 2,2-dichloro-1,3-indandione (**5**)[11] (0.538 g, 2.5 mmol), whereupon the reaction mixture was stirred at 0°C for 1 h. Addition of water (50 ml) resulted in a brown precipitate which was filtered, washed with water followed by a small amount of ether. Drying *in vacuo* gave the crude product as brown crystals 0.85 g (100%). Recrystallization from chloroform/methanol gave dark orange crystals of the title compound (6) 0.19 g (22%) mp 195-98°C, a further amount of compound (6) can be obtained from the mother liquor, the spiro-compounds generally crystallize very slowly. Ir (KBr) 1718 (C=O), 1075 (C=S) cm^{-1}. ^1H-Nmr ($CDCl_3$) 8.05 (4H, m) ppm. EIms m/z 340(M^+, 52), 176(44), 104 (82), 88(100), 76(84). Anal. Calcd for $C_{12}H_4O_2S_5$, 0.4 H_2O: C, 41.45; H, 1.39; S, 46.11. Found: C, 41.44; H, 1.21; S, 46.62.

X-ray structure determination of **4**

Single crystals of **4** suitable for an X-ray investigation were obtained by slow crystallization from $CHCl_3$/MeOH. A crystal of size 0.07 x 0.23 x 0.46 mm was mounted on an Enraf-Nonius CAD-4F diffractometer. Graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) was used. The intensities of 4053 unique reflections were measured ($2.0 < \Theta < 24.0°$). 3036 reflections with $I > 2.5\sigma(I)$ were used in the refinement process together with "less-than" reflections [$I < 2.5\sigma(I)$] with calculated values greater than the observed (3765 contributing reflections). The intensities were corrected for Lorentz and polarization effects. Absorption was ignored. Correction for decay was applied. The structure was solved by direct methods with the SHELXS-86 program.[12] Full matrix least squares refinements as well as the calculations of the geometric parameters were performed with the Xtal3.0 program system.[13] Positional H-atom parameters were calculated and refined with fixed isotropic temperature factors (U = 0.035). The refinement converged to final R = 0.051 and ωR = 0.025. Min. and max. values in the final difference density map were -0.3 and 0.3 $eÅ^{-3}$. Space group, triclinic, $P\bar{1}$. The cell parameters were determined from setting angles for 25 reflections. a = 7.888(2), b = 12.831(2), c = 13.592(2)Å, α = 75.73(1), β = 83.82(2), γ = 77.11(2)°. V = 1298(1)$Å^3$. Density measured by flotation in CCl_4 and CH_2BrCl: 1.69(1) $g\cdot cm^{-3}$. Calculated density: 1.681 $g\cdot cm^{-3}$. Z = 4 corresponding to 2 molecules in the asymmetric unit.

Table 2

	x/a	y/b	z/c	U_{eq}
S1	0.3794(1)	-0.18972(6)	0.97892(6)	0.0535(4)
S2	0.2265(1)	0.05011(6)	0.99234(6)	0.0525(4)
S3	0.2951(1)	0.12519(6)	0.77510(6)	0.0471(4)
S4	0.4476(1)	-0.11346(6)	0.75677(6)	0.0448(3)
S5	0.1524(2)	0.28851(7)	0.90009(7)	0.0631(4)
S21	1.2423(1)	-0.92266(6)	0.52860(6)	0.0464(4)
S22	1.2877(1)	-1.09649(6)	0.39981(6)	0.0475(4)
S23	1.0805(1)	-0.93785(7)	0.24362(6)	0.0479(4)
S24	1.0454(1)	-0.75956(7)	0.36576(6)	0.0515(4)
S25	1.2293(2)	-1.16160(7)	0.21243(7)	0.0627(5)
01	0.1349(4)	-0.3975(2)	0.8263(2)	0.073(1)
02	0.2362(3)	-0.2519(2)	0.8388(2)	0.051(1)
021	1.5557(4)	-0.6493(2)	0.4113(2)	0.086(2)
022	1.3683(3)	-0.7568(2)	0.4075(2)	0.055(1)
C1	0.2563(5)	-0.3609(3)	0.8371(2)	0.047(1)
C3	0.3997(4)	-0.2291(2)	0.8571(2)	0.038(1)
C4	0.5266(4)	-0.3354(2)	0.8618(2)	0.033(1)
C5	0.4390(4)	-0.4125(2)	0.8516(2)	0.036(1)
C6	0.7036(5)	-0.3629(3)	0.8777(3)	0.044(1)
C7	0.7846(5)	-0.4712(3)	0.8828(3)	0.056(2)
C8	0.6964(5)	-0.5487(3)	0.8727(3)	0.056(2)
C9	0.5203(5)	-0.5209(3)	0.8564(3)	0.048(2)
C10	0.3151(4)	-0.0496(2)	0.9253(2)	0.042(1)
C11	0.3479(4)	-0.0154(2)	0.8258(2)	0.039(1)
C12	0.2211(4)	0.1628(2)	0.8896(2)	0.043(1)
C21	1.4224(6)	-0.6781(3)	0.4435(3)	0.060(2)
C23	1.2065(5)	-0.7790(2)	0.4583(2)	0.043(1)
C24	1.1561(5)	-0.6990(2)	0.5262(2)	0.045(1)
C25	1.2885(5)	-0.6438(2)	0.5186(2)	0.052(2)
C26	1.0066(6)	-0.6785(3)	0.5863(3)	0.059(2)
C27	0.9976(7)	-0.5997(3)	0.6423(3)	0.073(2)
C28	1.1324(8)	-0.5459(3)	0.6363(3)	0.084(3)
C29	1.2795(7)	-0.5653(3)	0.5744(3)	0.070(2)
C30	1.2046(4)	-0.9682(2)	0.4228(2)	0.039(1)
C31	1.1117(4)	-0.8940(2)	0.3503(2)	0.040(1)
C32	1.1992(4)	-1.0695(2)	0.2813(2)	0.045(1)

Fractional atomic coordinates and equivalent isotropic thermal parameters ($Å^2$) for (**4**). $U_{eq} = 1/3\ \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

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