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Tetrathiafulvalene with two cyclododecane rings: synthesis of a novel C_{60} complex

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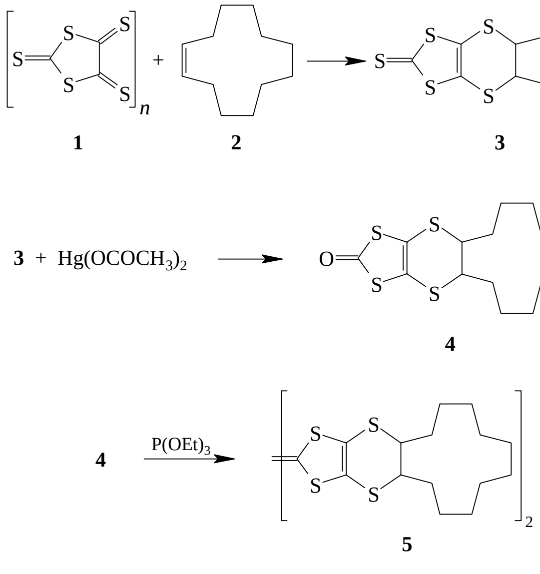
1,3-Dithiolane-2,4,5-trithione **1** has been used as the starting material in the synthesis of the title compound; this tetrathiafulvalene has been found to form a conductive complex with buckminsterfullerene C_{60}.

Recently it has been found that some substituted tetrathiafulvalenes (TTFs) containing four thioalkyl groups exhibit abnormally high electrical conductivities in the neutral non-oxidised state when the aliphatic chains in their molecules contain not less than 10–11 carbon atoms.[1–3] This is due to the strong interaction of aliphatic chains resulting in the mutual attraction of TTFs molecules. Researchers working in the field of organic conductive materials therefore pay considerable attention to TTFs, the molecules of which incorporate macrocyclic moieties.[4] In order to continue studies on the influence of the nature of the macrocycles on the electrophysical properties of the corresponding TTFs, their salts and their complexes with C_{60}, we have synthesised a new tetrathiafulvalene containing two cyclododecane rings.

The reaction of the oligomer of 1,3-dithiolane-2,4,5-trithione **1** with various unsaturated compounds occurs as a 1,4-cycloaddition and serves as a useful synthetic pathway to new thiole–thiones.[5–7] Depending on the structure of the alkene introduced in the reaction, a large variety of stereospecific *cis*- and *trans*-addition products can be obtained. We have chosen cyclododecene **2** as the unsaturated component for this reaction. Benzene was used as the solvent. The reaction afforded compound **3**, which on treatment with mercuric acetate was converted into the oxygen derivative **4**.



Heating of the thiole-2-one **4** in triethyl phosphite for 15 min yielded a new tetrathiafulvalene **5** as fine red needles in a quantitative yield. The product was purified by recrystallization from pyridine.

The 1 : 1 complex of **5** with C_{60} was obtained as fine black lustrous plates by spontaneous slow evaporation at room temperature of a toluene solution containing equimolar amounts of the components.[†]

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[†] *General experimental details*. For **3**: 5,6,7,8,9,10,11,12,13,14,14a,15-dodecahydro-4a*H*-cyclododeca[*e*][1,3]dithiolo[4,5-*b*][1,4]dithiepine-2-thione. A suspension of the oligomer of 1,3-dithiole-2,4,5-trithione **1** (1.96 g, 0.01 M) and cyclododecene (1.66 g, 0.01 M) in 100 ml of benzene was heated under reflux for 30 min. The hot reaction mixture was filtered, cooled and diluted with diethyl ether until the product **3** completely precipitated. Yield 2.03 g (57%). Mp 113–115 °C. Calc. for $C_{16}H_{24}S_5$ (%): S 42.56. Found (%): S 42.48. ^{1}H NMR ($CDCl_3$) δ: 3.40 (m, 4H, 2SCH), 1.31 (s, 20H, 10CH_2). IR (ν/cm^{-1}, KBr): 2930, 2860, 1488, 1465, 1437, 1300, 1058 (C=S), 914, 885, 707, 504.

For **4**: 5,6,7,8,9,10,11,12,13,14,14a,15-dodecahydro-4a*H*-cyclododeca-[*e*][1,3]dithiolo[4,5-*b*][1,4]dithiepin-2-one. Mercuric acetate (1.98 g, 0.005 M) was added to a solution of the thione **3** (1.91 g, 0.005 M) in acetic acid (50 ml) and the reaction mixture was heated for 15–20 min. The black precipitate of HgS was filtered off and the solution was cooled and diluted with cold water. The compound **4** completely precipitated over a period of 1 h. Yield 1.52 g (88%). Mp 55–58 °C. Calc. for $C_{16}H_{24}OS_4$ (%): S 35.56. Found (%): S 35.47. ^{1}H NMR ($CDCl_3$,) δ: 3.45 (m, 4H, 2SCH), 1.35 (s, 20H, 10CH_2). IR (ν/cm^{-1}, KBr): 2932, 2864, 1603, 1658 (C=O), 1627, 1507, 1469, 1442, 900, 783, 746, 711, 465.

For **5**: 2-(5,6,7,8,9,10,11,12,13,14,14a,15-dodecahydro-4a*H*-cyclododeca-[*e*][1,3]dithiolo[4,5-*b*][1,4]dithiepin-2-ylidene)-5,6,7,8,9,10,11,12,13,14,14a,15-dodecahydro-4a*H*-cyclododeca[*e*][1,3]dithiolo[4,5-*b*][1,4]dithiepine. Compound **4** (1 g) was heated in triethyl phosphite (5 ml) for 15–20 min in a flow of dry argon. After being cooled, the product precipitated as fine red needles and was purified by recrystallisation from pyridine. Mp > 250 °C (decomp.). Yield 75%. Calc. for $C_{32}H_{48}S_8$ (%): S 37.21. Found (%): S 37.16. ^{1}H NMR (C_5D_5N) δ: 3.38 (m, 4H, 2SCH), 1.28 (s, 40H, 20CH_2). IR (ν/cm^{-1}, KBr): 2910, 1425, 1301, 990, 973.

The complex of **5** with C_{60} was obtained as fine black plates by spontaneous evaporation of a toluene solution of a mixture of components (1 : 1) over a fortnight.