1,3,5,7-Tetrathia-*s*-indacene-2,6-dithione as Potential Building Block for «Polyfulvalenes»

Peter Wolf, Klaus Müllen*, and Michael Przybylski

Abstract: The synthesis of the hitherto unknown title compound [also called «1,2:4,5-benzobis(1,3-dithiole-2-thione)»] (**3a**) and its «3,6»-diisopropyl derivative **3b** is reported. The dithione **3a** can be doubly protonated to yield a dication. **3a** is a potential precursor of poly-conjugated organic conductors of the tetrathiafulvalene series. **3a** is self-coupled with the aid of triethylphosphite to yield the fulvalene 4 (n = 0), which is identified by its FAB-MS- and Raman spectra.

Charge-transfer complexes of tetrathiafulvalenes serve as models for one-dimensional electric conductors[1]. Not much is known about related poly-conjugated donor molecules in which the dimensionality of the conduction process could be increased[1–3]. Extended electron delocalization in these systems might reduce the Coulomb repulsion of the charge carriers and also prevent a Peierls distortion[4].

In our search for suitable precursors of «polyfulvalenes» we realized that benzo[*d*]-1,3-dithiole-2-thione (**1**) can be coupled with triethylphosphite to yield the tetrathiafulvalene **2**[5]. Extension of this reaction to the *di*functional analogue «1,2:4,5-benzobis(1,3-dithiole-2-thione)» (**3**) could, in principle, afford oligomers of structure **4**. Herein we describe the synthesis of the novel dithiones **3a** and **3b**, the coupling to a fulvalene structure, and the characterization of the coupling products by fast-atom-bombardement mass spectrometry (FAB-MS).

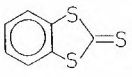
The known 1,2,4,5-tetrakis(isopropylthio)benzene **6a**[6,7] was submitted to reductive dealkylation with sodium in pyridine to yield 1,2,4,5-tetramercaptobenzene (**7a**). In situ reaction of **6a** with carbon disulfide[8] provided the target molecule **3a** in 85% yield[9] [golden-yellow needles after crystallization from dimethylformamide (DMF), *m.p.* > 360 °C; ^{1}H-NMR (90 MHz, [$^2H_7$]-DMF, 130 °C): δ = 8.22; IR (KBr): $\tilde{\nu}$ = 1070 cm^{-1} (C=S); MS (70 eV, 180 °C source temperature): *m/z* 290 (100%, M^+), 246 (87%, $M^+ - CS$)].

As expected from experience with related trithiocarbonates[10], **3a** is sufficiently basic to undergo diprotonation in strong acids (H_2SO_4 or FSO_3H). Quenching into water quantitatively regenerates the starting compound. The dication (**3a**-H_2)$^{2\oplus}$ present in FSO_3H/SO_2ClF-solution was characterized by NMR spectroscopy [^{1}H-NMR (400 MHz, −80 °C): δ = 8.80 (s), 7,25 (s); between −80 °C and −10 °C the latter signal exhibits line broadening effects due to a proton-exchange between solvent and substrate]. Firm evidence for the intact D_{2h} symmetry of the dication (**3a**-H_2)$^{2\oplus}$ came from the observation of three ^{13}C-NMR signals (δ = 211.6, 143.5, 122.0).

In order to improve on the solubility of **3a** and its successors, we synthesized «3,6-diisopropyl-1,2:4,5-benzobis(1,3-dithiole-2-thione)» (**3b**) by an analogous procedure. The generation of the tetrathioether **6b** was achieved by the method of *Tiecco* et al.[7] in 55% yield from 1,2,4,5-tetrachloro-3,6-diisopropylbenzene (**5b**)[7b], which itself was obtained by chlorination of 3,6-diisopropylbenzene in 70% yield[11]. Dealkylation of **6b** and subsequent trapping reaction of **7b** with CS_2 produced **3b** in low yield (8%). The reason for the low yield is not clear; however, incomplete reductive cleavage of the tetrathioether **6b** because of a low solubility of the intermediates seems to play a role[12]. Unfortunately, the alkyl substitution of **3** did not affect the solubility of the compound (**3a** and **3b**: 95 mg in 100 mL of boiling DMF).

The reaction of **3a** with triethylphosphite at 150 °C afforded dark orange products which were isolated by filtration and washed with hot DMF in order to remove any starting compound. The Raman spectra of the remaining samples (irradiation wavelength λ = 633 nm, Ar-laser) exhibited a strong line at $\tilde{\nu}$ = 1667 cm^{-1}. The latter can be assigned to a CC-double bond thus indicating successful coupling to a fulvalene-type compound. Unfortunately, the essential insolubility of the coupling products in organic solvents prevented a further chemical characterization.

Direct molecular weight evidence was therefore gathered from the FAB-MS spectra[13]. Homogeneous solutions re-



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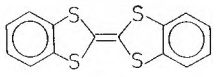

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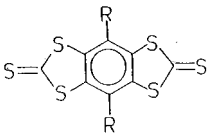
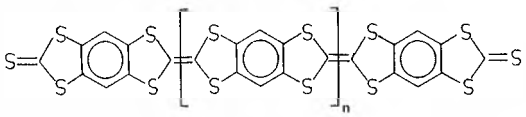


3a: R = H
3b: R = $CH(CH_3)_2$



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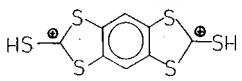
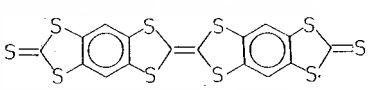
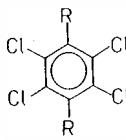


(**3a**-H_2)$^{2\oplus}$



4a



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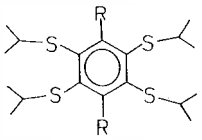

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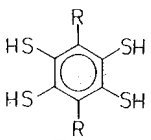
a: R = H
b: R = $CH(CH_3)_2$



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quired for such an analysis were only obtained upon enforced protonation with conc. sulfuric acid. This is the first application of a H_2SO_4-matrix within FAB-MS measurements[14]. The spectra of the coupling products showed abundant ions at m/z 533 and m/z 267 (base peak) which were associated by the respective sulfur isotope ions. The former peak corresponds to the mono-oxygenated, mono-protonated molecular ion and the latter to a diprotonated, doubly charged molecular ion of a «dimeric» condensation product **4a** (n = 0)[15]. These assignments are strongly corroborated by comparison with the spectra in D_2SO_4, which yielded mass shifts to m/z 534 and 268, respectively. Furthermore, addition of Cs-salts to the H_2SO_4-matrix resulted in a mass shift by partial exchange of the doubly protonated ion to m/z 399. Supporting evidence for the occurence of mono-oxygenated products in the present matrix system was obtained (i) from the FAB-MS spectra of the H_2SO_4-matrix itself which showed two series of oligomeric cluster ions, $[M + H]_n^+$ and $[M + O]_nH^+$, and (ii) by comparison with the spectrum of the starting compound **3a** which exhibited an abundant $[M + O]H^+$ ion at m/z 307, in addition to the MH^+ ion at 291.

The synthesis of other substituted analogues of **3** leading to chemically characterizable, *soluble* fulvalene-type coupling products is under way[16].

Experimental

1,3,5,7-Tetrathia-s-indacene-2,6-dithione [«1,2,4,5-Benzobis(1,3-dithiole-2-thione)»] (**3a**): In a 500 mL three-necked flask were placed 22.3 g (60 mmol) of **6a** (prepared according to the method of *Tiecco* et al.[7]) and 300 mL of dry pyridine. The flask was flushed with dry argon and heated to 105°C. Na (9.2 g) was rapidly added with stirring. The mixture was stirred at 100–110°C for 1 h. After cooling, 100 mL of oxygen-free water and 30 mL of CS_2 were added and the mixture was kept at 40–50°C for another 2 h. The yellow precipitate formed was filtered with suction, washed with methanol and ether and dried in vacuo. Yield: 14.8 g (85%)[9]; spectroscopic characterization cf. text.

Coupling of **3a** *to the fulvalene* **4a**: The dithione **3a** (500 mg, 1.7 mmol) was stirred for 1/2 h under reflux in 20 mL of triethylphophite (N_2-atmosphere). The dark-orange solid formed was separated by filtration and washed with hot DMF and with ether and dried to yield 184 mg (42%) of **4a**.

1,2,4,5-Tetrachloro-p-diisopropylbenzene (**5b**): *p*-Diisopropylbenzene (20 g, 123 mmol) was dissolved in 200 mL of chloroform and iron-powder (2 g) was added. A weak flow of chlorine was passed through the solution. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. When the signals of the starting material had disappeared the iron catalyst was removed by filtration and the filtrate extracted three times with water. The organic layer was dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The remaining crystalline material was recrystallized from $CHCl_3$/methanol to yield pure **5b** (26 g, 70%) as colourless needles of *m.p.* 85°C; ^{1}H-NMR ($CDCl_3$, 60 MHz): δ = 4.03 (sept., 2H), 1.41 (d, 12H).

1,2,4,5-Tetrakis(isopropylthio)-3,6-diisopropylbenzene (**6b**): The same procedure as in the case of **6a** was employed, except that the reaction mixture was allowed to react 12 h at 100°C; yield 55%, colourless microcrystals, *m.p.* 79°C; ^{1}H-NMR ($CDCl_3$, 60 MHz): δ = 4.53 (sept., 2H), 3.60 (sept., 4H), 1.45 (d, 12H), 1.12 (d, 24H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 22.1, 22.8, 35.1, 41.5, 142.1,155.6; MS (70 eV): m/z 458 (M^+, 100%), 372 ($M^+ - 2C_3H_7$, 25%), 43 ($C_3H_7^+$, 84%)[9].

4,8-Diisopropyl-1,3,5,7-tetrathia-s-indacene-2,6-dithione [«3,6-Diisopropyl-1,2,4,5-benzobis(1,3-dithiole-2-thione)»] (**3b**): The synthesis was performed as described for **3a**. Yellow crystals, *m.p.* > 280°C (decomp.); ^{1}H-NMR ([$^2H_7$]-MF, T = 130°C, 90 MHz): δ = 1.68 (d, 12H), 4.38 (sept., 2H); MS (70 eV): m/z 375 (M^+, 8%), 332 ($M^+ - C_3H_7$, 100%).

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