Organic Electronic Conductors and Precursors;[1] Reaction of Hexasodium Benzenehexathiolate and Benzenehexathiol with Carbon Disulfide

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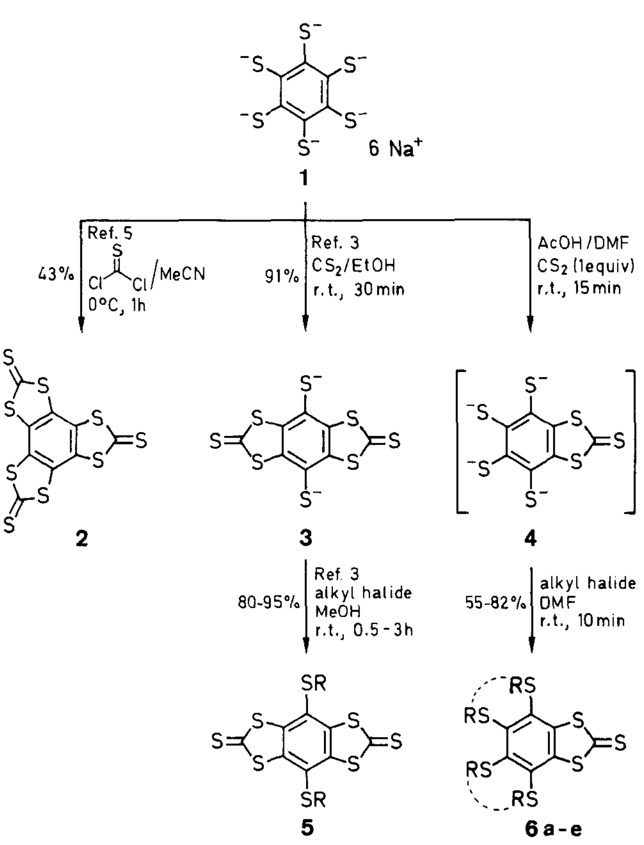
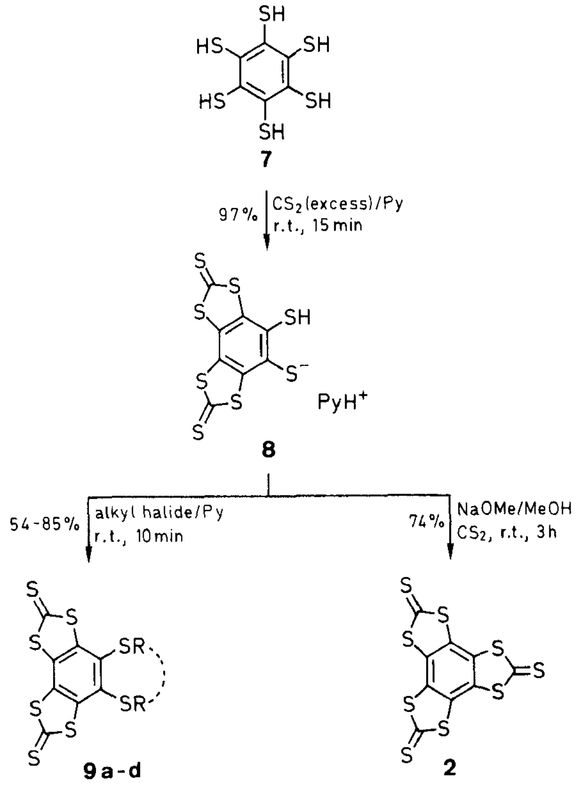
The reaction of hexasodium benzenehexathiolate (**1**) and benzenehexathiol (**7**) with carbon disulfide is studied. Depending on the reaction conditions and the molar ratio of **1** or **7** to carbon disulfide the 1,3-benzodithiole-2-thiones **6**, the 2,6-dithioxobenzo[1,2-*d*: 4,5-d']- **5**, the 2,5-dithioxobenzo[1,2-*d*: 3,4-*d'*]bis[1,3]dithiole **9** or the 2,5,8-trithioxobenzotris[1,3]dithiole (**2**) are obtained.

With the aim of synthesizing 2,5,8-trithioxobenzotris[1,3]dithiole (**2**) we treated hexasodium benzenehexathiolate (**1**)[2] with carbon disulfide. However, the product obtained was 2,6-dithioxobenzo[1,2-*d*: 4,5-*d'*]bis[1,3]dithiole-4,8-dithiolate (**3**), which can be alkylated to give the 4,8-bis(alkylthio) derivative **5**.[3,4] The compound **2**, subsequently prepared by reaction of **1** with thiophosgene,[5] is of interest as precursor for the synthesis of potential organic electronic conductors and ferromagnets. The surprising formation of **3** induced us to investigate the reaction of hexasodium benzenehexathiolate with carbon disulfide in more detail.

While the reaction of **1** with an excess of carbon disulfide yields near quantitative yields of **3**, a molar ratio of 1 : 1 in methanol gives, after alkylation with methyl iodide a mixture of **5** (R = CH_3; 17%) and the new compound 4,5,6,7-tetrakis(methylthio)-1,3-benzodithiole-2-thione (**6a**) (30%). It seems that the thiolate groups in **4** (not isolated) are sufficiently reactive for the further reaction to **3**. By protonation with acetic acid, their nucleophilicity can be reduced so far, that the formation of **3** is retarded and after alkylation a good yield of compounds **6** can be isolated. The 1,3-benzodithiole-2-thiones **6** can also be prepared by treatment of benzenehexathiol (**7**) with an equimolar amount of carbon disulfide in pyridine.[6]



6	R	**6**	–R...R–
a	Me	**d**	$-CH_2-$
b	Et	**e**	$-(CH_2)_2-$
c	Bn		



9	**a**	**b**	**c**	**d**
R···R	Me	Et	n-C_5H_{11}	$-CH_2-$

In contrast to hexasodium benzenehexathiolate (**1**) compound **7** does not react with an excess of carbon disulfide in pyridine to form the 2,6-dithioxobenzo[1,2-*d*: 4,5-*d'*]bis[1,3]dithiole system **3**, but leads almost quantitatively to the pyridinium salt of 7-mercapto-2,5-dithioxobenzo[1,2-*d*: 3,4-*d'*]bis[1,3]dithiole-8-thiolate (**8**). The pyridinium salt **8** can be alkylated directly to give the 7,8-bis(alkylthio) derivatives **9** or can be isolated in substance.[7] Compound **8** does not cyclize to give compound **2** with carbon disulfide even after a prolonged

Table. Compounds **6** and **9** Prepared

Product	Alkyl Halide	Yield (%)	mp (°C) (solvent)	Molecular Formula[a]	IR (KBr) ν (cm^{-1}) C=S	UV-VIS λ_{max}(nm) (logε) (solvent)	MS (70eV) M$^+$ (%)
6a	MeI	82	167–168 (BuOH)	$C_{11}H_{12}S_7$ (368.6)	1068	379 (4.34)[e] ($CHCl_3$)	368 (100)
6b	EtI	75	69 (MeOH)	$C_{16}H_{20}S_7$ (424.7)	1080	383 (4.45) ($CHCl_3$)	424 (100)
6c	BnI	63	168–170[b] [c]	$C_{35}H_{28}S_7$ (673.0)	1068	383 (4.44) ($CHCl_3$)	672 (27)
6d	CH_2I_2	78	248–251 (1,2-dichloroethane)	$C_9H_4S_7$ (336.5)	1070	395 (4.16) (*o*-dichlorobenzene)	336 (11)
6e	$(CH_2)_2Br_2$	55	292–294 [c]	$C_{11}H_8S_7$ (364.6)	1050	396 (4.13) (*o*-dichlorobenzene)	364 (100)
9a	MeI	85	263–265 (*o*-dichlorobenzene)	$C_{10}H_6S_8$ (382.6)	1055	380 (4.69) ($CHCl_3$)	382 (100)
9b	EtI	65	196–199 (1,2-dichloroethane)	$C_{12}H_{10}S_8$ (410.7)	1085	381 (4.72) ($CHCl_3$)	410 (100)
9c	*n*-$C_5H_{11}I$	60	164–166 (1,2-dichloroethane)	$C_{18}H_{22}S_8$ (494.8)	1060	381 (4.71)[f] ($CHCl_3$)	494 (68)
9d	CH_2I_2	54	310 (subl.) (*o*-dichlorobenzene)	$C_9H_2S_8$ (366.6)	1065	387[d] ($CHCl_3$)	366 (4.5)

[a] Satisfactory microanalyses obtained: C ±0.25, H ±0.2, S ±0.5.

[b] Precipitated from a solution in CH_2Cl_2 with MeOH.

[c] Reaction mixture stirred for 10 min after addition of the alkylating reagent, evaporated to dryness and recrystallized the residue from *o*-dichlorobenzene.

[d] Slightly soluble.

[e] ^{13}C-NMR ($CDCl_3$/HMDS, 90 MHz): δ = 19.9, 21.6 (CH_3S), 135.0, 147.7, 148.3 (C_{arom}), 212.7 (C=S).

[f] ^{13}C-NMR ($CDCl_3$/HMDS, 90 MHz): δ = 22.3, 27.5, 35.5, 38.5 (C_{alkyl}), 131.2, 132.3, 149.1 (C_{arom}), 208.1 (C=S).

reaction time and heating. Probably, the nucleophilicity of the mercapto group in **8** is not sufficient for this reaction. Only after deprotonation with a strong base does the pyridinium salt **8** react with carbon disulfide to give **2** in up to 75% yield. Thus, the preparation of **2** via the pyridinium salt **8** is more efficient due to the higher yield (> 70%) than the "direct synthesis" from **1** and thiophosgene (43%).

The question why compound **1** forms the symmetric benzobis[1,3]dithiole and **7** the corresponding asymmetric system is the subject of our present investigations.

All reagents were of commercial quality from freshly opened containers and were purchased from Laborchemie Apolda, GDR. Reagent quality solvents were used without further purification.

Melting points were taken using a Boetius apparatus and are corrected. Microanalyses were carried out in the Microanalytical Laboratory of the Technical University Merseburg. Mass spectral data were obtained on a Varian CH6. A Carl-Zeiss-Jena Specord M80 and M40 was used to record the IR and UV/VIS spectra, respectively. ^{13}C-NMR spectra were obtained on an Bruker HX-90R instrument.

4,5,6,7-Tetrakis(alkylthio)-1,3-benzodithiole-2-thiones 6; General Procedure:

To a suspension of hexasodium benzenehexathiolate (**1**,[2] 0.66 g, 1.7 mmol) in DMF (100 mL) CS_2 (0.1 mL, 1.66 mmol) is added. Then a mixture of AcOH and DMF (2:5, about 30 mL) is added dropwise until the solid dissolves. After 10 min stirring at r.t. the alkylating reagent (8 mmol for **6a–c** or 4 mmol for **6d–e**) is added. The mixture is stirred for 10 min and then cooled with dry ice. The precipitated dithiolethiones **6** are filtered off and recrystallized (Table).

Pyridinium salt of 7-Mercapto-2,5-dithioxobenzo[1,2-*d*:3,4-*d'*]bis[1,3]dithiole-8-thiolate (8):

Benzenehexathiol (**7**;[2] 2.7 g, 10 mmol) is suspended in pyridine (100 mL). CS_2 (18 mL, 300 mmol) is added and the mixture is stirred for 15 min at r.t. The pyridinium salt **8** is precipitated by addition of Et_2O (450 mL) and filtered off. For purification, the product is dissolved in pyridine, precipitated by Et_2O and dried *in vacuo*; yield: 4.21 g (97%); yellow orange crystals; mp > 360 °C.

$C_{13}H_7NS_8$	calc.	C 36.04	H 1.63	N 3.23	S 59.09
(433.2)	found	35.75	1.71	3.41	59.05

UV (CH_3OH): λ_{max} (log ε) = 394 nm (4.37)

IR (KBr): $\bar{\nu}$ = 1060 cm^{-1} (C=S).

7,8-Bis(alkylthio)-2,5-dithioxobenzo[1,2-*d*:3,4-*d'*]bis[1,3]dithiole 9; General Procedure:

The solution of benzenehexathiol (**7**;[2] 2.7 g, 10 mmol) in a mixture of pyridine (75 mL) and CS_2 (6 mL, 100 mmol) is stirred at r.t. for 15 min. Then the alkylating reagent (22 mmol for **9a–c**, 11 mmol for **9d**) is added. After 10 min the precipitate is filtered off, washed with MeOH and recrystallized (Table).

2,5,8-Trithioxobenzotris[1,3]dithiole (2) from the Pyridinium Salt 8:

To a suspension of the pyridinium salt **8** (0.75 g, 1.73 mmol) in MeOH (20 mL) a 1 M $NaOCH_3$-solution in MeOH (10 mmol) is added, whereby the solid dissolves. To the red-brown mixture CS_2 (20 mL) is added. After 3 h stirring the yellow crystals are filtered off under reduced pressure, washed with MeOH and Et_2O and recrystallized from *o*-dichlorobenzene; yield: 0.51 g (74%); mp 310 °C (Lit.[5] mp 310 °C).

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