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SYNTHESIS AND REACTIONS OF NEW CYCLIC POLYSULFIDES.
6,10-DISUBSTITUTED[1,2,3]TRITHIOLO[5,4-H]BENZOPENTATHIEPINS

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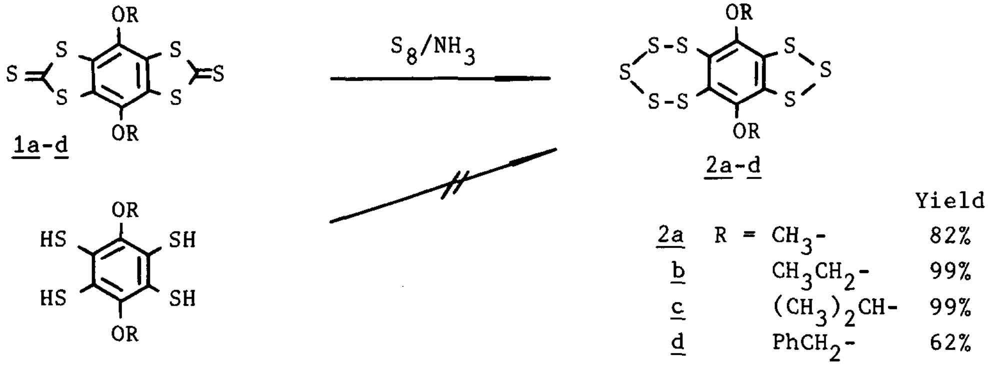
Abstract: New four 6,10-disubstituted[1,2,3]trithiolo[5,4-h]benzopentathiepins (2) were synthesized by reaction of 4,8-disubstituted benzo[1,2-d:4,5-d']bis [1,3]dithiole-2,6-dithione (1) with elemental sulfur in liquid ammonia. 2 was treated with sodium borohydride and then alkylated with alkyl halides to give some interesting benzopentathiepin derivatives and related compounds.

Recently, some interesting reports on the synthesis and chemistry of many cyclic polysulfides such as benzopentathiepins[1] and the related compounds[2] have appeared. We also reported a new synthesis[3] of benzopentathiepins and other cyclic polysulfides by the reactions of corresponding thiols or its derivatives with elemental sulfur in liquid ammonia and confirmed the reactivity.[4] However, there have never been, to our knowledge, any reports on the synthesis of certain cyclic polysulfides which have both pentathiepin and trithiole rings on benzene ring. Therefore, based on our previous results, we have studied the synthesis and reaction of such new benzopentathiepin derivatives. Here, we wish to report a first synthesis and reactions of some novel aromatic cyclic polysulfides, 6,10-disubstituted[1,2,3]trithiolo[5,4-h]benzopentathiepins (2), from the corresponding 4,8-disubstituted benzo[1,2-d:4,5-d']bis[1,3]dithiole- 2,6-dithione (1)[5] with elemental sulfur in liquid ammonia (Scheme 1). In addition, 2 was found to give some benzopentathiepin derivatives, 3 and 5, in good yields by selective reduction of trithiole ring with sodium borohydride followed by alkylation with alkyl halides.



1a-d

2a-d

			Yield
2a	R =	CH_3-	82%
b		CH_3CH_2-	99%
c		$(CH_3)_2CH$-	99%
d		$PhCH_2$-	62%

Scheme 1.

A typical synthesis of 2b is as follows. 1b[5] (0.5 mmol) and elemental sulfur (25 mg-atom) were taken into an all titanium autoclave (volume, 50 ml). After evacuation, liquid ammonia (20 ml) was charged into the autoclave. The mixture was stirred at room temperature for 5 h and then added dropwise to benzene (200 ml) through needle valve attached on the autoclave. Then the residure obtained by evaporation of ammonia and solvent was chromatographed on silica gel using CCl_4 as an eluent giving 2b as reddish yellow crystals (207 mg, 99%).

2b: Mp 146 °C (from CH_2Cl_2/Et_2O, 1/1: v/v); IR (KBr) 1025, 1338, and 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ =1.43 (t, 6H, CH_3) and 4.16 (q, 4H, CH_2); MS (70 eV) m/z 418 (M^+). Found: C, 28.64; H, 2.52; S, 61.5%. Calcd for $C_{10}H_{10}O_2S_8$: C, 28.69; H, 2.41; S, 61.3%. X-Ray analysis of the crystal of 2b was shown in Figure 1. Crystal data for 2b:[6] M = 418.6, monoclinic, space group $P2_1/a$, a=19.004(3) Å, b=9.299(4) Å, c=9.280(2) Å, γ=90.09(2)°, V=1639.9(8) Å^3, T=294 K, Z=4, Dx=1.70 gcm^{-3}, F(000) = 1672, $\mu(\text{Mo-K}_\alpha)$ = 10.4 cm^{-1}. Final R = 0.0614 for 3075 unique, observed [F $3.0\sigma(F)$].

New four cyclic polysulfides 2a-d having both pentathiepin and trithiole rings on benzene ring were first obtained in good to excellent yields from the corresponding thiones 1a-d as shown in Scheme 1. It should be noted that four benzopentathiepins 2 bearing trithiole ring were obtained by present procedure, since benzotrithiole is well known to be very labile and only two compounds have been hitherto isolated.[7] On the other hand, treatment of 1,2,4,5-benzenetetrathiol[8] and benzo[1,2-d:4,5-d']bis[1,3]dithiole-2,6-dithione,[9] which have no alkoxyl substituents, with elemental sulfur in liquid ammonia under the same conditions gave no desired cyclic polysulfides but unidentified polymer. Benzene as a solvent used at quenching of the reaction gave a preferable results for the yields of 2. The quantity in equivalents of elemental sulfur used affected enormously the yield of 2, for example, a use of 25 mg-atom (50 equivalents) resulted in an improvement of the the yields of 2b up to 99% from 86%, compared with the case of 15 mg-atom (30 equivalents). The structure of pentathiepin and trithiole ring of 2b was nearly compatible with known benzopentathiepin and benzotrithiole[1] and the whole structure was found to be a like butterfly conformation as shown in Fig 1.

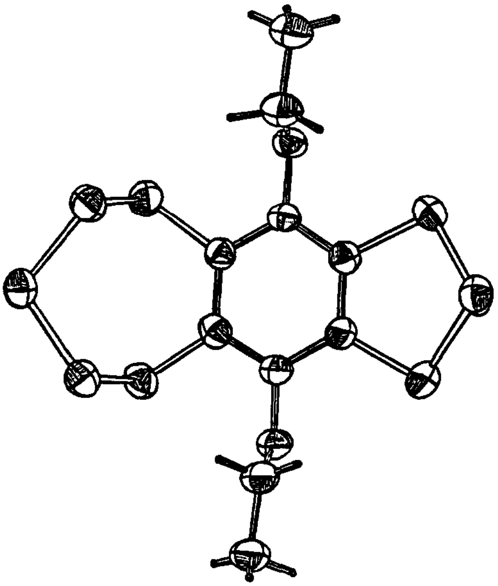
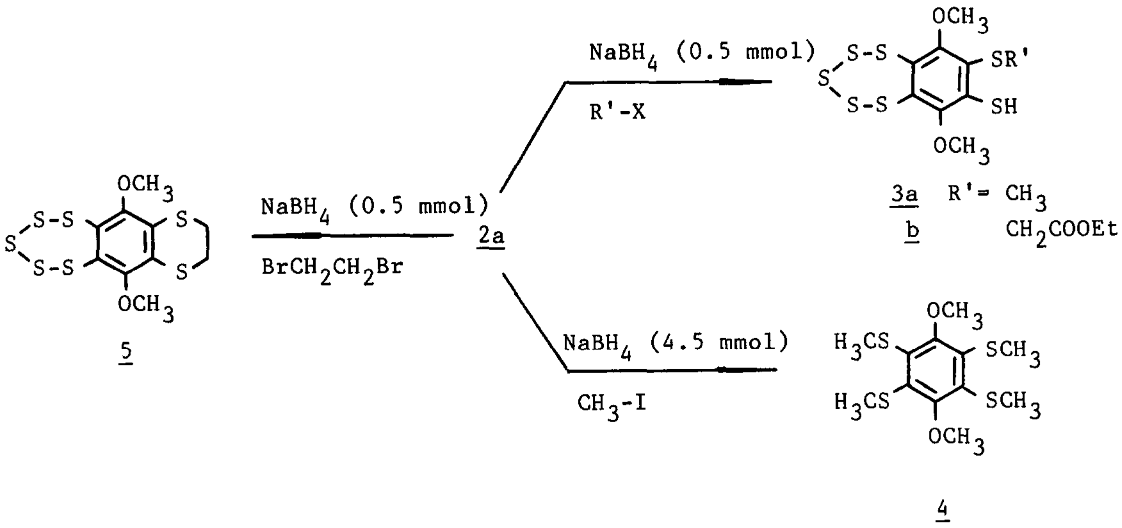


Fig. 1. Molecular structure of 2b

In order to confirm the reactivity of new compounds 2, 2a was treated with sodium borohydride in THF/EtOH and then alkylated by alkyl halides. Some interesting products were consequently obtained (Scheme 2). Thus, 4,7-dimethoxy-6-mercapto-5-methylthio-1,2,3,4,5-benzopentathiepin (3a)[10] was obtained in 38% yield by the reaction of 2a with 0.5 mmol of NaBH$_4$ followed by methylation with methyl iodide as a mixture of two conformational isomers which were distinguishable by ^{1}H NMR. 3b was also given in 35% yield by alkylation with ethyl bromoacetate. The use of excess NaBH$_4$ gave 2,3,5,6-tetrakis(methylthio)-1,4-dimethoxybenzene (4) in 93% yield. When 1,2-dibromoethane was employed as an alkylating agent, 6,11-dimethoxy-1,4-dithiano[6,5-h]benzopentathiepin(5),[11] was formed in 45% yield (Scheme 2).



Scheme 2.

It is noteworthy that benzopentathiepin derivatives 3 and 5 were obtained by the reaction of 2a, since the pentathiepin ring of 2a remained intact and only trithiole ring reacted. Accordingly, the results obtained by the first reaction comparing the reactivity of pentathiepin ring with trithiole ring suggest that trithiole ring is rather more reactive than pentathiepin ring in this system. Further investigations on the versatility of trithiolopentathiepin 2 in organosulfur chemistry and biological chemistry are now in progress in our laboratory.

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10. 3a: Yellow crystals (from hexane-ether); mp 43 °C; IR (KBr) 1015, 1350, 1445, 2470, and 2920 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 2.37$ (s, 0.6H, SCH_3), 2.43 (s, 2.4H, SCH_3), 3.83 (s, 0.6H, OCH_3), 3.85 (s, 2.4H, OCH_3), 3.88 (s, 0.6H, OCH_3), 3.90 (s, 2.4H, OCH_3), 4.87 (s, 0.2H, SH), and 5.20 (s, 0.8H, SH); MS (20 eV) m/z 374 (M^+). Found: C, 28.45; H, 2.74; S, 59.7%. Calcd for $C_9H_{10}O_2S_7$: C, 28.85; H, 2.69; S, 59.9%.
11. 5: Yellow crystals (from CH_2Cl_2); mp 182 °C; IR (KBr) 1015, 1345, 1440, and 2910 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 3.24$ (s, 4H, CH_2) and 3.85 (s, 6H, CH_3); MS (20 eV) m/z 386 (M^+). Found: C, 30.89; H, 2.57; S, 58.2%. Calcd for $C_{10}H_{10}O_2S_7$: C, 31.07; H, 2.61; S, 58.0%.

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