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1,2,9,16,17,24-HEXATHIA[2.1.2.1]-4,6,8,11,13,15,19,21,23, 26,28,30-DODECAMETHYL-METACYCLOPHANE. A NOVEL MACROCYCLIC POLYSULPHUR COMPOUND BY DIRECT SULPHURATION OF MESITYLENE

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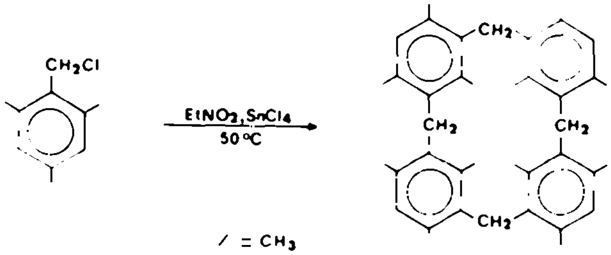
Abstract—The synthesis of 1,2,9,16,17,24 - hexathia[2.1.2.1] - 4,6,8,11,13,15,19,21,23,26,28,30 - dodecamethyl - metacyclophane by direct sulphuration of mesitylene, the first report of a single-step synthesis of an aromatic macrocycle with alternating sulphide and disulphide linkages, is reported. Structure determination of this compound was achieved by mass spectrometry, and by reductive degradation to 3,3'-dithio-dimesitylsulphide and reoxidation of the latter to the original macrocycle. Some evidence concerning the probable pathway to macrocycle formation is reported.

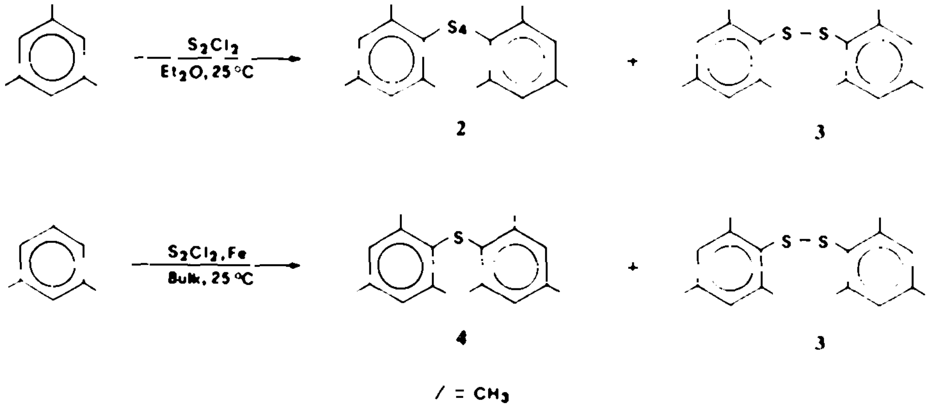
As part of our work concerning the investigation of bridged aromatic macrocycles,[1-6] we previously synthesized the methylene bridged mesitylenic macrocycle 1 by autocondensation of 2-chloromethylmesitylene in presence of $SnCl_4$ (Scheme 1). We report here the synthesis and structural characterization of the hexathiametacyclophane 7, with a regular alternation of sulphide and disulphide linkages. This compound was obtained during an attempt to synthesize an isomer of 1 in which methylene bridges are replaced by sulphur, by direct sulfuration of mesitylene with sulphur chlorides. The reaction of mesitylene with sulphur monochloride has been investigated by various authors.[7,8] Ariyan *et al.*[7] obtained dimesityl-tetrasulphide 2 (42%) and dimesityldisulphide 3 (19%) by reacting mesitylene and sulphur monochloride in molecular ratio 2:1 in ether at room temperature and in absence of catalyst, while Inamoto *et al.*[8] obtained mainly dimesityl sulphide 4 (64%), together with dimesityl disulphide 3 (15%), by reacting mesitylene and sulphur monochloride in molecular ratio 10:1 in presence of iron powder at 0–25°C (Scheme 2).

Since the intermediate sulfuration products obtained did not undergo further reaction under the literature conditions, we chose conditions more appropriate to the direct formation of the macrocycle. Thus the reaction of mesitylene and sulphur chlorides in molecular ratio 1:1 was carried out in dilute solution of chloroform, under reflux, in presence of a trace amount of iron powder.[9] In this way a crystalline precipitate with high, sharp m.p. was obtained, which showed low solubility in organic solvents. Molecular weight determination (osmometry in o-dichlorobenzene) indicated a value of about 660, corres-



1

Scheme 1.



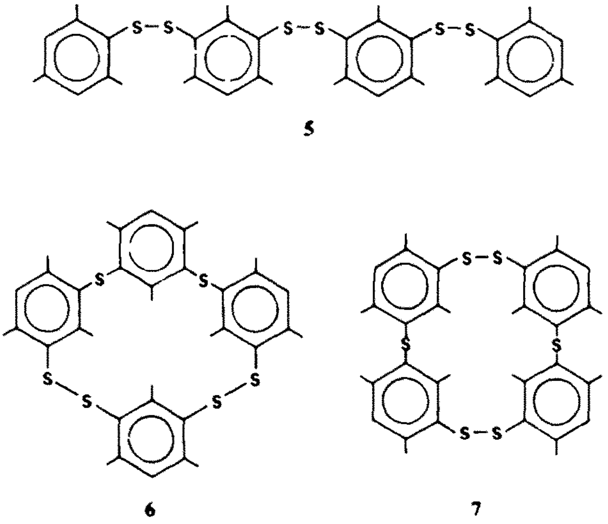
Scheme 2.

ponding roughly to a tetramer. Elemental analysis suggested the presence of six sulphur atoms in the molecule.

These data did not agree with a sulphur-bridged macrocycle isomeric with **1**, and the following tetrameric structures **5–7** can be considered (Scheme 3).

Reductive degradation of the compound obtained afforded in good yield exclusively **8**, whose structure was demonstrated by analytical and spectral data. This is strong evidence in favour of structure **7** with a regular alternation of sulphide and disulphide groups. Reoxidation of **8** gave in excellent yield the original compound **7** and indicated irrefutably its cyclic nature (Scheme 4).

Further proof of the structure **7** is given by the mass spectrum, reported in Fig. 1. It shows the molecular ion at *m/e* 664, corresponding to the base peak, and an intense, diagnostically important peak at *m/e* 331 $[(M/2-1)]^+$. These data are in agreement with the cyclic structure **7**, having alternate single and double sulphur bridges. In fact, it is well known[6,10] that macrocyclic compounds show very strong molecular ion intensities, and that for double bridged sulphur macrocycles the preferred fragmentation process is the homolytic cleavage of the S–S bond.[6] Other fragments present in the spectrum (*m/e* 649, 631, 617, 317, 299, 285) indicate losses of CH_3 and/or S from molecular ion and from the fragment at *m/e* 331.



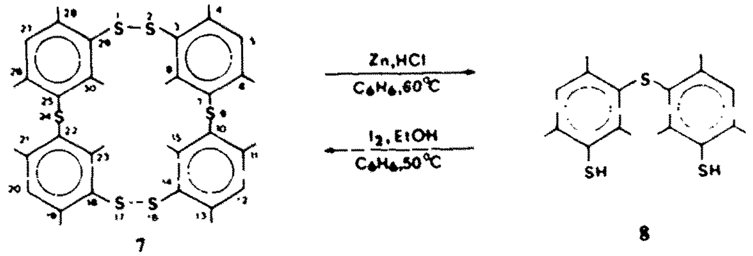
5

6

7

/ = CH_3

Scheme 3.



7

8

/ = CH_3

Scheme 4.

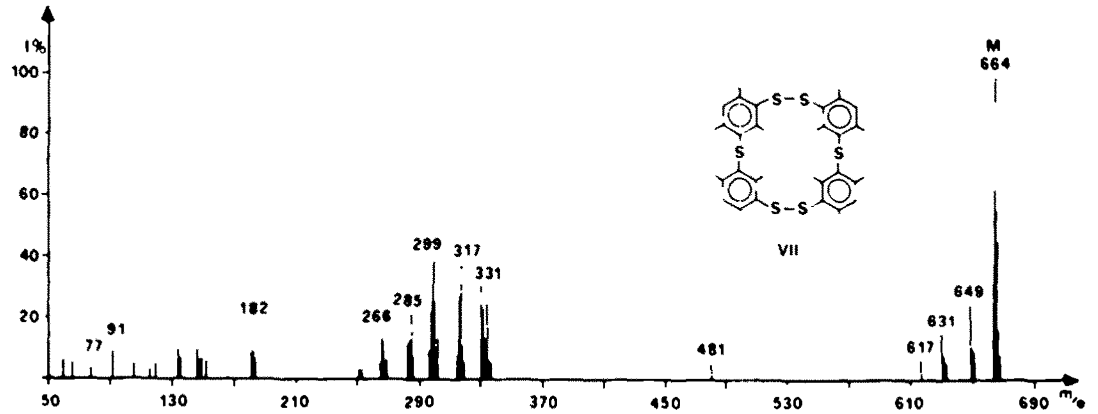
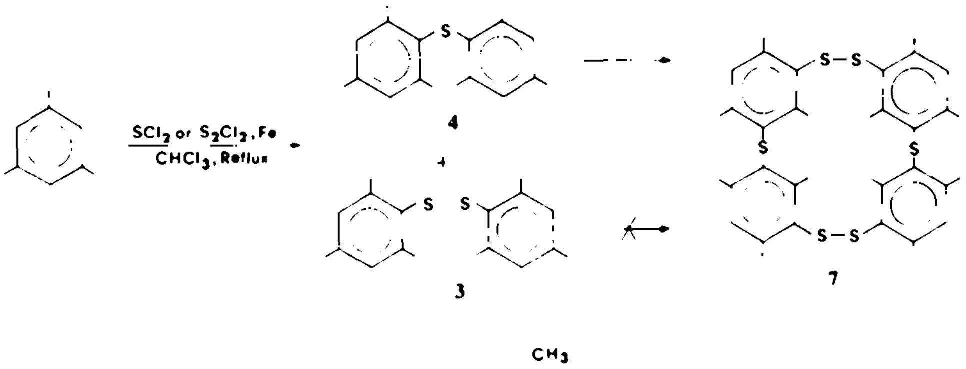


Fig. 1. Mass spectrum at 70 eV, 300°C, of 7.



Scheme 5.

In order to account for formation of the macrocycle 7 both dimesityl sulphide 4 and dimesityldisulphide 3 can be regarded as possible intermediates; moreover dimesityl disulphide 3 might also give the double sulphur bridged macrocycle, previously synthesized by us[6] by mild oxidation of 2,4-dithio-mesitylene.

However, the reactivity of the two substrates with respect to sulfuration with sulphur chlorides, tested under identical conditions of mesitylene, indicated that dimesityl sulphide 4 gives macrocycle 7 in identical yield to mesitylene, together with considerable amount of uncharacterized polymers, while dimesityl-disulphide 3 gives neither macrocycle 7 nor double sulfur bridged macrocycle, but only polymeric materials.

These results indicate that the macrocycle formation occurs through dimesityl sulphide 4, as summarized in Scheme 5.

EXPERIMENTAL

Materials and analytical procedures

All solvents and available organic materials were commercial products purified by standard procedures. SCl_2 and S_2Cl_2 were commercial products used without purification. Dimesityl sulphide[8] and dimesityl disulphide[11] were prepared according to literature. Molecular weights were determined by thermoelectric osmometry in solution of o-dichlorobenzene at 130°C with a Mechrolab 302. Elemental analyses were obtained commercially. Mass spectra were obtained at 70 eV by direct insertion into the source of a Varian MAT CH 711 double focusing mass spectrometer. The evaporation temperature was 300°C. NMR spectra were recorded with a Varian EM 360 instrument with tetramethylsilane as internal standard.

Reaction of mesitylene with sulphur monochloride and sulphur dichloride

In a red glass flask, fitted with a magnetic stirring bar, a dropping funnel and a condenser, were placed 12 g (0.1 mole) of mesitylene in 100 ml of $CHCl_3$ and *ca.* 5 mg of iron powder. The flask was flushed with N_2 and then a solution of 13.5 g (0.1 mole) of sulphur monochloride in 100 ml of $CHCl_3$ was added dropwise in two portions over a period of 6 h. The mixture was refluxed under stirring until the evolution of HCl was complete. The light yellow precipitate obtained was filtered from the hot solution, washed with $CHCl_3$ and dried. Recrystallization from 1,2-dichlorobenzene gave 2.98 g (18%) of 7 as light yellow microcrystals, m.p. 321–22°C. The same product was obtained in a smaller yield (3%) by reacting mesitylene with sulphur dichloride under identical conditions. Calc. for $C_{36}H_{40}S_6$: C, 65.02; H, 6.06; S, 28.92. Found: C, 65.18; H, 6.12; S, 28.65%.

Reduction of 7

To a well-stirred mixture of 1.33 g (0.002 mole) of 7 and 4 g of zinc-powder suspended in 40 ml of benzene, in ice bath, were added dropwise 40 ml of aq HCl (37%). When the addition was accomplished, the mixture was kept warm for 30 min. The benzene layer was separated from the water layer, and dried with Na_2SO_4. After concentration *in vacuo* the residue was chromatographed on silica gel. Elution with petroleum ether (b.p. 40–60°C) gave white crystals of 8, 0.92 g (70%), m.p. 98–100°C. Calc. for $C_{18}H_{22}S_3$: C, 64.63; H, 6.63; S, 28.75. Found: C, 64.45; H, 6.68; S, 28.56%. NMR (CCl_4): δ 6.48 (1 H Ar), 2.98 (1 H SH), 2.23 (9 H CH_3).

Reoxidization of 8 to 7

To a hot solution of 0.92 g (0.0027 mole) of 8 in 50 ml of benzene, was added dropwise with stirring I_2 in EtOH until the brown colour of I_2 persisted. The yellowish precipitate obtained was filtered, washed with a dilute solution of thiosulphate, then with water, ethanol and dried. The crude product recrystallized from 1,2-dichlorobenzene gave 0.55 g (60%) of light yellow microcrystals, m.p. 321–22°C, whose analytical and spectral data were identical to those of 7.

Reaction of dimesityl sulphide 4 with sulphur monochloride and sulphur dichloride

To a well-stirred solution of 2.7 g (0.01 mole) of dimesityl sulphide in 50 ml $CHCl_3$, containing a trace amount of iron powder, were added dropwise 1.35 g (0.01 mole) of S_2Cl_2 in 20 ml $CHCl_3$ in two portions over a period of 5 h, using the same equipment as above. After *ca.* 5 h 0.60 g (18%) of crystalline precipitate, m.p. 321–2°C, were obtained, which showed analytical and spectral data identical to those of 7. The same product was obtained in a smaller yield (3%) by reacting dimesityl sulphide with sulphur dichloride under identical conditions.

Reaction of dimesityl disulphide 3 with sulphur monochloride and sulphur dichloride

Dimesityl disulphide was treated in the same way as dimesityl sulphide, but formation of precipitate was not observed. By concentration of reaction mixture, polymeric materials, together with unreacted dimesityl disulphide (10%), were recovered.

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