

## Synthesis of a New Eighteen-membered Ring Tetrathia[2.1.2.1]metacyclophane with Alternating Disulphide and Methylene Linkages

By Francesco Bottino,\* Salvatore Foti, and Sebastiano Pappalardo, Istituto di Chimica Organica, Università di Catania, Viale A. Doria, 6-95125, Catania, Italy

A single-step synthesis of 4,6,8,11,13,15,19,21,23,26,28,30-dodecamethyl-1,2,16,17-tetrathia[2.1.2.1]metacyclophane is reported. The structure of this compound was determined by reductive degradation to bis-(3-mercaptopomesityl)methane and reoxidation of the latter to the original macrocycle, and by mass spectrometry.

CONSIDERABLE attention has been devoted recently to the chemistry of macrocyclic polysulphur compounds.<sup>1</sup> The synthesis of bridged polysulphur ring systems by reactions of aromatic dithiols with bis(chlorodithio)benzenes<sup>2</sup> or chlorosulphanes,<sup>3,4</sup> and by mild oxidation of appropriate dithiols<sup>5,6</sup> has been reported.

Ariyan and Martin<sup>7</sup> obtained a set of crystalline large-ring tetrasulphide bridged macrocycles by treating *para*-dialkoxybenzenes with sulphur monochloride under catalytic conditions. Using a similar procedure we recently synthesised the 18-membered ring hexathia[2.1.2.1]metacyclophane (I) from mesitylene and

sulphur chlorides, and showed that its formation occurs through the intermediate dimesityl sulphide.<sup>8</sup> We now report the synthesis and characterization of 4,6,8,11,13,15,19,21,23,26,28,30-dodecamethyl-1,2,16,17-tetrathia[2.1.2.1]metacyclophane † (2), a new 18-membered ring system with alternating disulphide and methylene linkages.

Dimesitylmethane was treated with sulphur monochloride in 1 : 1 molar ratio in dilute solution in chloroform, under reflux, and in the presence of traces of iron powder (*cf.* ref. 8). A crystalline precipitate with high, sharp m.p. [*M* (osmometric in *o*-dichlorobenzene) 620], scarcely soluble in organic solvents, was obtained. The

† The nomenclature of F. Vogtle and P. Neumann, *Tetrahedron*, 1970, **26**, 5847, is employed.

<sup>1</sup> J. S. Bradshaw and J. Y. K. Hui, *J. Heterocyclic Chem.*, 1974, **11**, 649 and references therein.

<sup>2</sup> F. Fehér, K. Glinka, and F. Malcharek, *Angew. Chem. Internat. Edn.*, 1971, **10**, 413.

<sup>3</sup> F. Fehér and M. Langer, *Tetrahedron Letters*, 1971, 2125.

<sup>4</sup> D. W. Allen, P. N. Braunton, I. T. Millar, and J. C. Tebby, *J. Chem. Soc. (C)*, 1971, 3454.

<sup>5</sup> L. Field, W. D. Stephens, and E. L. Lippert, jun., *J. Org. Chem.*, 1961, **26**, 4782.

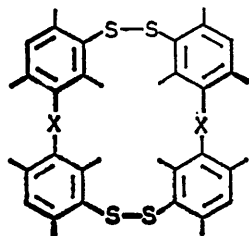
<sup>6</sup> F. Bottino, S. Foti, and S. Pappalardo, *Tetrahedron*, 1976, **32**, 2567.

<sup>7</sup> Z. S. Ariyan and R. L. Martin, *Chem. Comm.*, 1969, 847; *J.C.S. Perkin I*, 1972, 1687.

<sup>8</sup> F. Bottino, S. Foti, and S. Pappalardo, *Tetrahedron*, 1977, **33**, 337.

reaction of dimesitylmethane with sulphur dichloride gave the same product in lower yield.

Reductive degradation of this compound led to bis-(3-mercaptopmesityl)methane, identified from analytical



(1) X = S

(2) X = CH<sub>2</sub>

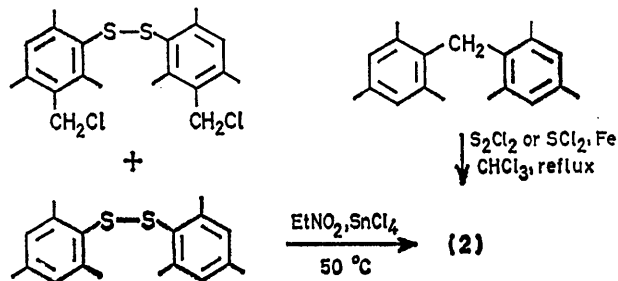
and spectral data. Mild oxidation of the latter provided the original compound (2) in high yield and suggested its cyclic nature.

Alternatively, the macrocycle (2) was conveniently prepared in higher yield by coupling in dilute solution in nitroethane equimolar amounts of bis-(3-chloromethylmesityl) disulphide and dimesityl disulphide in the presence of tin(IV) chloride.

The mass spectrum of the macrocycle (2) (Figure) shows the molecular ion at  $m/e$  628 (base peak) and an intense, diagnostically important peak at  $m/e$  313 [ $(M/2$

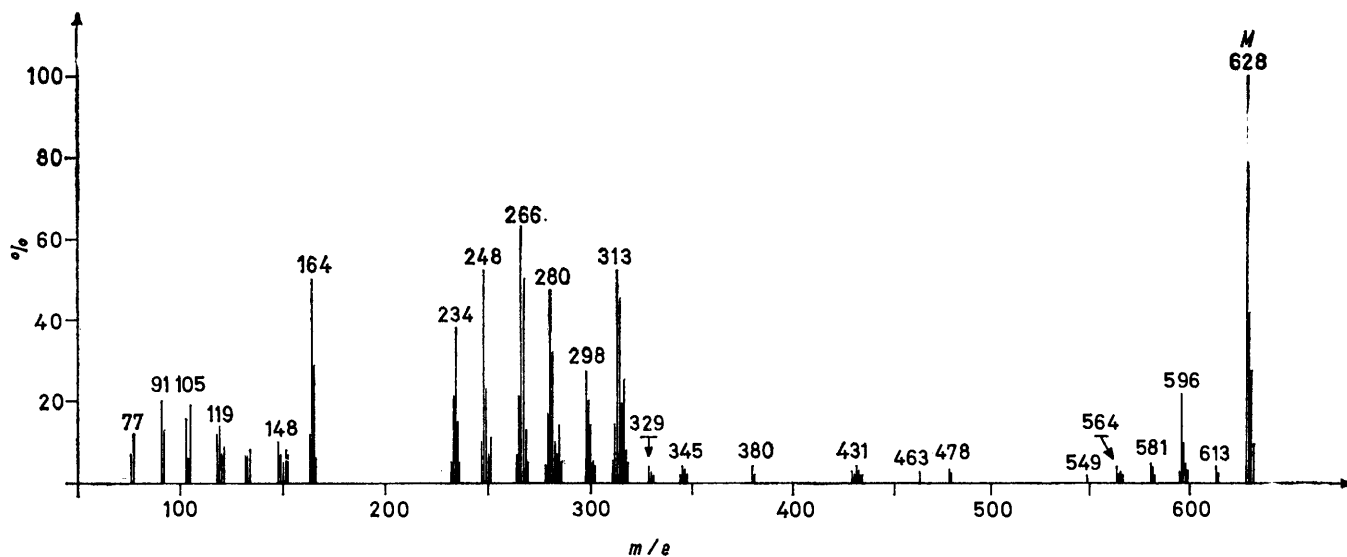
alized in terms of losses of methyl groups and/or sulphur from the molecular ion and from the fragment at  $m/e$  313.

Attempts to synthesize the analogous 18-membered dioxatetrathia[2.1.2.1]metacyclophane with alternating oxygen and disulphide linkages, from dimesityl ether and sulphur chlorides under similar conditions, yielded only polymeric materials.



#### EXPERIMENTAL

All solvents and available organic materials were commercial products purified by standard procedures. Sulphur dichloride and disulphur dichloride were commercial products used without purification. Dimesitylmethane<sup>11</sup> and dimesityl disulphide<sup>12</sup> were prepared according to literature procedures. Molecular weights were determined by thermoelectric osmometry in *o*-dichlorobenzene solution at 130 °C with a Mechrolab 302 instrument. Elemental analyses were obtained commercially. Mass spectra were



Mass spectrum at 70 eV (300 °C) of the macrocycle (2)

— 1)<sup>+</sup>]. These data agree with the proposed structure, having two sets of disulphide linkages. Whereas aromatic macrocycles display very strong molecular ion peaks,<sup>6,9,10</sup> the preferred fragmentation process for dithio-bridged macrocycles is homolytic cleavage of the S—S bond.<sup>6,8</sup> Other abundant fragments ( $m/e$  613, 596, 581, 564, 549, 298, 280, 266, 248, and 234) can be ration-

taken with an A.E.I. MS-9 spectrometer (probe temperature 300 °C). <sup>1</sup>H N.m.r. spectra were recorded with a Varian EM 360 instrument (Me<sub>4</sub>Si as internal standard).

*Bis-(3-chloromethylmesityl) Disulphide.*—To a solution of dimesityl disulphide (12 g, 0.04 mol) and chloromethyl methyl ether (9.66 g, 0.12 mol) in carbon disulphide (200 ml), cooled to -30 °C, tin(IV) chloride (10.42 g, 0.04 mol) in

<sup>11</sup> C. M. Welch and H. A. Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 4391.

<sup>12</sup> C. H. Wang and S. G. Cohen, *J. Amer. Chem. Soc.*, 1957, **79**, 1924.

<sup>9</sup> H. Herdtman, F. Haglid, and R. Ryhage, *Acta Chem. Scand.*, 1964, **18**, 1249.

<sup>10</sup> R. Paioni and W. Jenny, *Helv. Chim. Acta*, 1969, **52**, 2041.

carbon disulphide (20 ml) was added dropwise with rapid stirring, with the temperature kept below  $-15^{\circ}\text{C}$ . The mixture was then stirred for 1 h at  $-15^{\circ}\text{C}$ , and for 2 h at room temperature. After pouring into acidulated water (250 ml), the carbon disulphide layer was separated and the water layer extracted twice with carbon disulphide. The combined organic extracts were washed (5%  $\text{NaHCO}_3$  then  $\text{H}_2\text{O}$ ) and dried ( $\text{CaCl}_2$ ). Removal of carbon disulphide *in vacuo* left a dense yellow oil, which slowly crystallized. The crude product was washed several times with diethyl ether. Extractive crystallization of the residue from light petroleum (b.p.  $40-70^{\circ}\text{C}$ ) yielded pale yellow needles (48%), m.p.  $121-122^{\circ}\text{C}$  (Found: C, 60.25; H, 6.1; Cl, 17.45; S, 16.4.  $\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{S}_2$  requires C, 60.15; H, 6.05; Cl, 17.75; S, 16.05%),  $\delta(\text{CS}_2)$  6.87 (2 H, s, ArH), 4.45 (4 H, s,  $\text{CH}_2$ ), 2.34 (6 H, s,  $\text{CH}_3$ ), 2.23 (6 H, s,  $\text{CH}_3$ ), and 2.14 (6 H, s,  $\text{CH}_3$ ).

*Dimesityl Ether*.—2-Bromomesitylene (19.9 g, 0.1 mol), 2,4,6-trimethylphenol (13.6 g, 0.1 mol), potassium hydroxide (2.8 g, 0.05 mol) and potassium carbonate (6.91 g, 0.05 mol) were heated in autoclave at  $240-260^{\circ}\text{C}$  for 8 h, in the presence of activated copper (1 g). After cooling, the mixture was poured into aqueous 5% potassium hydroxide (400 ml) and extracted twice with diethyl ether; the extracts were washed several times with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated. Distillation of the residual oil under high vacuum afforded a white dense oil, b.p.  $130-140^{\circ}\text{C}$  at 1 mmHg, which crystallized. Recrystallization twice from methanol afforded white crystals (8–10%), m.p.  $95-96^{\circ}\text{C}$  (Found: C, 85.05; H, 8.9.  $\text{C}_{18}\text{H}_{22}\text{O}$  requires C, 85.0; H, 8.7%),  $\delta(\text{CCl}_4)$  6.74 (4 H, s, ArH), 2.23 (6 H, s,  $\text{CH}_3$ ), and 1.99 (12 H, s,  $\text{CH}_3$ ).

*Reactions of Dimesitylmethane with Sulphur Chlorides*.—In a red glass flask were placed dimesitylmethane (2.52 g, 0.01 mol) in chloroform (100 ml) and iron powder (*ca.* 5 mg). The flask was flushed with nitrogen and then a solution of disulphur dichloride (1.35 g, 0.01 mol) in chloroform (50 ml) was added dropwise. The mixture was refluxed with stirring until evolution of hydrogen chloride was complete (8 h). The precipitate was filtered from the hot solution, washed with carbon disulphide and ether, and dried. Recrystallization from *o*-dichlorobenzene afforded light yellow microcrystals of 4,6,8,11,13,15,19,21,23,26,28,30-

*dodecamethyl-1,2,16,17-tetrathia[2.1.2.1]metacyclophane* (2) (15%), m.p.  $310-311^{\circ}\text{C}$  (Found: C, 72.75; H, 7.1; S, 20.5.  $\text{C}_{38}\text{H}_{44}\text{S}_4$  requires C, 72.55; H, 7.05; S, 20.4%). From the reaction of dimesitylmethane with sulphur dichloride, the macrocycle (2) was obtained in 3% yield.

*Reduction of the Macrocycle* (2).—To a stirred mixture of compound (2) (0.44 g, 0.7 mmol) and zinc powder (2 g) suspended in benzene (40 ml), in an ice-bath, 37% hydrochloric acid (20 ml) was added dropwise. The mixture was kept warm for 30 min. The benzene layer was separated, washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated *in vacuo*. The residue was recrystallized from light petroleum (b.p.  $60-80^{\circ}\text{C}$ ) to give white crystals (65%) of *bis*-(3-mercaptomesityl)methane, m.p.  $125-127^{\circ}\text{C}$  (Found: C, 72.45; H, 7.55; S, 20.35.  $\text{C}_{19}\text{H}_{24}\text{S}_2$  requires C, 72.1; H, 7.65; S, 20.25%),  $\delta(\text{CCl}_4)$  6.85 (2 H, s, ArH), 4.03 (2 H, s,  $\text{CH}_2$ ), 3.01 (2 H, s, SH), 2.32 (6 H, s,  $\text{CH}_3$ ), and 2.12 (12 H, s,  $\text{CH}_3$ ).

*Reoxidation of Bis*-(3-mercaptomesityl)methane.—To a hot solution of *bis*-(3-mercaptomesityl)methane (0.28 g, 0.9 mmol) in benzene (40 ml), ethanolic iodine was added dropwise with stirring until a brown colour persisted. The yellowish precipitate was filtered off, washed with dilute thiosulphate, then water, and ethanol, and dried. The crude product, recrystallized from *o*-dichlorobenzene, gave light yellow microcrystals (52%), whose analytical and spectral data were identical with those of the macrocycle (2).

*Coupling of Bis*-(3-chloromethylmesityl) Disulphide with Dimesityl Disulphide.—To a hot solution of dimesityl disulphide (0.75 g, 2.5 mmol) in nitroethane (50 ml) containing traces of tin(IV) chloride, a solution of *bis*-(3-chloromethylmesityl) disulphide (1 g, 2.5 mmol) in nitroethane (50 ml) was added dropwise with stirring. The flask was flushed with nitrogen, and the mixture was kept warm until evolution of hydrogen chloride was complete. The yellowish crystalline precipitate was filtered from the hot solution, treated with ethanol–hydrochloric acid (4 : 1), washed with water and ethanol, and dried. Purification as above afforded light yellow microcrystals (63%), whose analytical and spectral data were identical with those of the macrocycle (2).

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