

Francesco Bottino, Salvatore Cosentino, Salvatore Cunsolo and Sebastiano Pappalardo*

Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università di Catania,
Viale A. Doria 8, 95125 Catania, Italy
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The synthesis and spectral properties of the title compound are described.

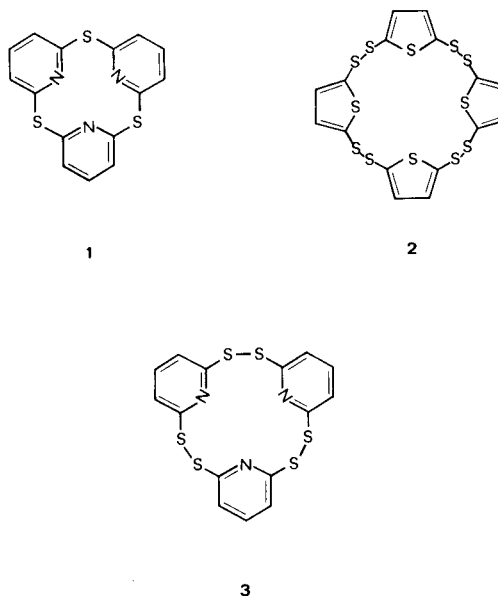
J. Heterocyclic Chem., **18**, 199 (1981).

Several efforts towards the synthesis of macrocyclic compounds possessing subheterocyclic rings have recently been carried out (1). However, occasional attention has been devoted to sulfur-bridged heterophanes (2-3). To date, 1,8,15-trithia[1.1.1](2,6)pyridinophane (1) and 1,2,8,9,15,16,22,23-octathia[2.2.2.2](2,5)thiophenophane (2) are the only known sulfur-bridged heterophanes (4). The first compound was obtained by an intermolecular condensation of 6-chloropyridine-2-thione in the presence of phosphorus pentasulfide at 130° (2), the second one was isolated in low yield from a mixture of oligomers formed in the polymerization of 5-thiocyanate-2-thienyl mercaptide in acetic acid (3). However, we believe that the procedures employed in the synthesis of (1) and (2) cannot be successfully applied to the attainment, in good yield, of sulfur-bridged macrocycles.

Recently, a facile synthesis of disulfide bridged cyclophanes by mild oxidation of dithioresorcinol derivatives under high-dilution conditions has been developed by us (5-6) and, in the present work, we wish to report such a method for the synthesis of 1,2,9,10,17,18-hexathia[2.2.2](2,6)pyridinophane (3), a novel 15-membered heterocyclic ring system.

Macrocycle 3 was obtained in a 45% overall yield through a two step synthesis starting from 2,6-dichloropyridine (4). Compound 4 was converted into 2,6-dimercaptopyridine (5) (90% yield) by treatment with sodium hydrogen sulfide in refluxing dimethylformamide (DMF). Subsequent oxidation of dithiol 5 to the macrocycle (3) was carried out in a 50% yield with iodine in benzene at room temperature in the presence of triethylamine, under high-dilution conditions. The use of solvents more polar than benzene, such as ethanol and tetrahydrofuran, greatly depressed the yield of 3, probably due to the resulting enhancement of the tautomeric thione form of 5, while the use of dimethylsulfoxide as oxidant (7) led to the formation of low-melting oligomers.

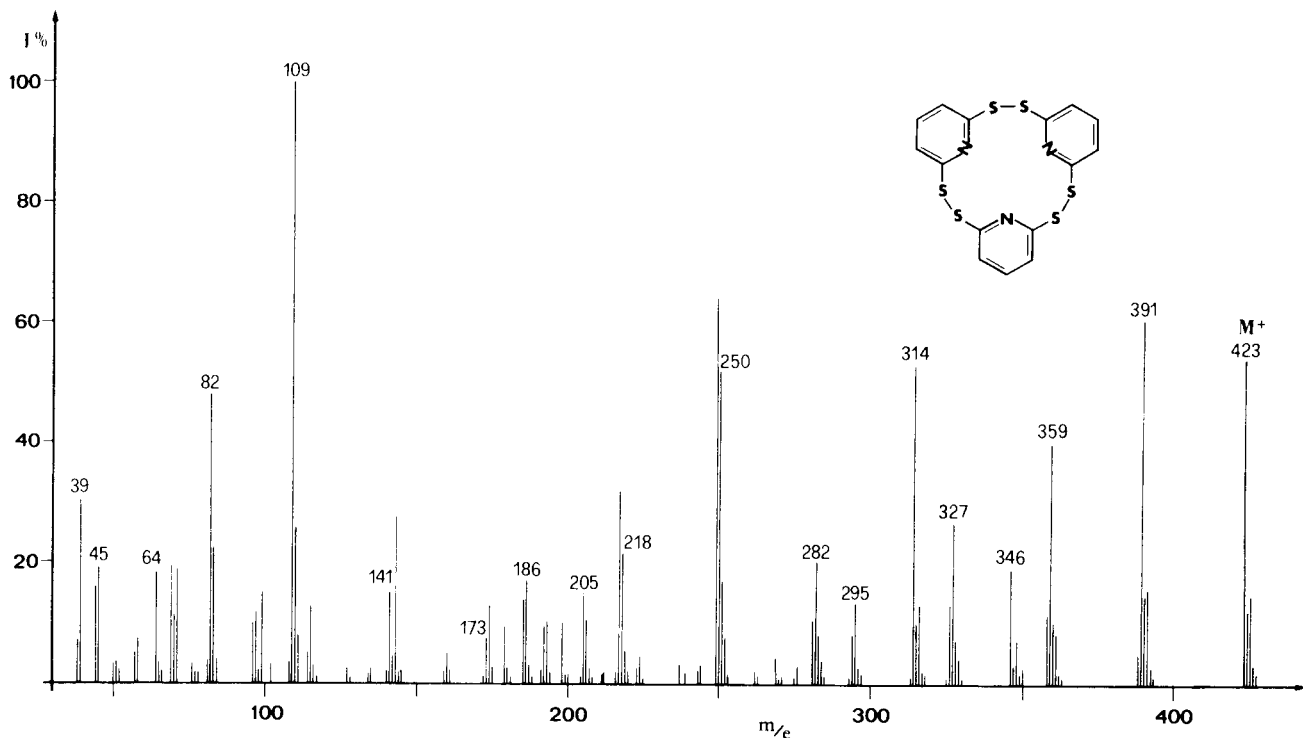
Remarkably, the reaction showed a great deal of selectivity, compound 3 being the only cyclic product formed. This fact is in agreement with the major role played by substituents ortho to the mercaptide groups present in the aromatic dithiols in determining the ring size of the form-



ed macrocycle(s). In fact, it is known that in the benzenophane series the smaller 10-membered ring system is formed, provided that electron-releasing substituents are present (5), while either neutral (8) and electron-withdrawing (9) substituents lead exclusively to the larger 15- or 20-membered ring systems.

The mass spectrum of 3 (Figure) shows the molecular ion (54% relative intensity) at m/e 423 and two intense peaks at m/e 391 and 359, due to the losses of one or two sulfur atoms, respectively, the last process arising directly from the molecular ion, as shown by the presence of a metastable peak at about m/e 304. A subsequent direct extrusion of two sulfur atoms from the fragment at m/e 359 gives the ion at m/e 295, as shown by the presence of a metastable peak at about m/e 242. Fragments at m/e 327 $[(C_{15}H_9N_3S_3)]^+$, and 295 $[(C_{15}H_9N_3S_2)]^+$ can also be rationalized by a multistep loss of sulfur atom one at the time from the molecular ion.

A second decomposition pathway derives from the cleavage of the S-S bonds to generate the fragments at m/e 282 $[(2/3 M)]^+$ and 141 $[(1/3 M)]^+$. Subsequent losses of one or two sulfur atoms from these ions give rise to the fragments at m/e 250, 218 and 109 (base peak), respectively.



Mass spectrum (70 eV) of macrocycle (**3**) at 230°.

Finally, a third fragmentation process is due to the loss of pyridyl units through the cleavage of C-S bonds to give the fragments at m/e 346 $[(C_{10}H_6N_2S_6)]^+$ and 205 $[(C_5H_3NS_4)]^+$ which can lose up to four sulfur atoms to generate the fragments at m/e 314, 282, 250, 218 and at m/e 173, 141, 109, respectively.

The 80 MHz 1H -nmr spectrum of **3** shows a pattern of eight lines (with lines 5 and 6 superimposed) peculiar of an AB_2 system ($\delta_A = 7.60$ ppm, $\delta_B = 7.40$ ppm; $J_{AB} = 8.06$ Hz). Unfortunately, these data are not conclusive enough to infer the stereochemistry in solution of this novel heterocyclic ring system.

EXPERIMENTAL

Melting points are uncorrected. Mass spectra were obtained at 70 eV by direct insertion into the ion source of a LKB 9000S instrument. 1H -Nmr spectra were recorded in DMSO- d_6 on a Bruker WP-80 instrument (TMS as the internal standard). Molecular weights were determined ($\pm 5\%$) by thermoelectric osmometry in *o*-dichlorobenzene solution at 130° with a Mechrolab 302 instrument.

2,6-Dimercaptopyrindine (**5**). A slightly modified Vögtle and Effler procedure (10).

Sodium hydrogen sulfide monohydrate (Fluka) (44.4 g., 0.6 mole) was dissolved in refluxing DMF (150 ml.). After cooling, a solution of 2,6-dichloropyridine (14.7 g., 0.1 mole) in DMF (40 ml.) was added dropwise with stirring. The resulting mixture was refluxed for 8 hours, cooled and the precipitated salt was filtered. The filtrate was diluted with an equal volume of water and acidified with dilute hydrochloric acid to give a precipitate. This was collected by filtration, dissolved in dilute alkali and recrystallized by slow addition of hydrochloric acid. Yellow needles of the desired dithiol were obtained (90% yield), m.p. 139-144° dec., (lit. (10) m.p. 136-139°); ms: m/e (% relative intensity) 143 (100, M^+).

Anal. Calcd. for $C_5H_5NS_2$: C, 41.93; H, 3.52; N, 9.78. Found: C, 41.75; H, 3.55; N, 9.72.

1,2,9,10,17,18-Hexathia[2.2.2](2,6)pyridinophane (**3**).

Benzene solutions of dithiol (**5**) (1.43 g., 0.01 mole) and iodine (2.54 g., 0.01 mole) were dropped separately but simultaneously from two dropping funnels into benzene (1 l.) containing triethylamine (3 ml.) under vigorous stirring. Overall addition took 8 hours. After the addition was over, stirring was continued overnight. The crystalline precipitate obtained was filtered, washed with a dilute solution of thiosulfate and with water, and dried. Recrystallization from pyridine afforded light yellow prisms of **3** (50% yield), m.p. 200-203° dec.

Anal. Calcd. for $C_{15}H_9N_3S_6$: C, 42.53; H, 2.14; N, 9.92. Found: C, 42.38; H, 2.10; N, 9.96.

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