

Cyclic Polysulphur Compounds from the Iron-catalysed Reaction of *m*-Dimethoxybenzene with Disulphur Dichloride

By Francesco Bottino, * Salvatore Foti, and Sebastiano Pappalardo, Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

The iron-catalysed reaction of *m*-dimethoxybenzene with sulphur chlorides (SCl_2 and S_2Cl_2) has been investigated both neat and in dilute solution. Neat reaction gives linear polysulphides (3), bis-(2,4-dimethoxyphenyl) sulphide (4), and 1,3-dimethoxy-4,6-bis-(2,4-dimethoxyphenylthio)benzene (5), while in dilute solution the formation of 5,7,14,16-tetramethoxy-1,2,3,10,11,12-hexathia[3.3]metacyclophane (1) and 4,6,12,14,20,22-hexamethoxy-1,2,9,10,17,18-hexathia[2.2.2]metacyclophane (2) is observed. Compounds (1) and (2) were also obtained by independent synthetic routes. Their ^1H n.m.r. and mass spectra are discussed.

We are interested in the synthesis of polysulphur bridged metacyclophanes,¹⁻⁴ and have recently reported a series of novel double sulphur-bridged eighteen-membered ring systems, obtained by the iron-catalysed aromatic sulphuration with sulphur chlorides (SCl_2 or S_2Cl_2) of activated substrates, such as mesitylene, dimesityl sulphide and dimesitylmethane.^{2,3}

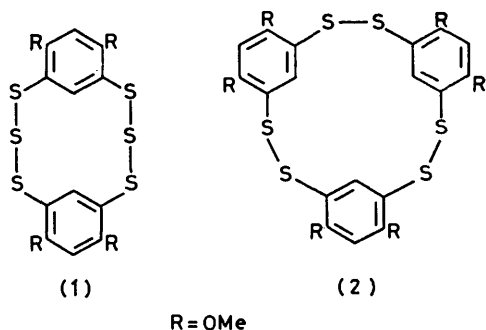
Here we report the results of the iron-catalysed sulphuration of *meta*-dimethoxybenzene with sulphur chlorides.

The action of sulphur monochloride on *meta*-dimethoxybenzene and its *ortho*- and *para*-isomers has been investigated by Ariyan *et al.*^{5,6} The uncatalysed reactions of the *ortho*- and *para*-isomers in inert solvents gave linear sulphides, while under catalytic conditions and in chlorinated solvents the *ortho*-isomer yielded a substituted thianthren, and the *para*-isomer a large ring polysulphide.

In particular, the uncatalysed reaction of *meta*-dimethoxybenzene with S_2Cl_2 gave an uncharacterized product, which was probably a polymer.

Because of the lack of information about the catalysed reaction of *meta*-dimethoxybenzene with sulphur chlorides, we have investigated this reaction using iron powder as catalyst, both neat and in dilute solution, in order to detect the possible formation of cyclic polysulphur derivatives.

As a result, two polysulphur compounds (1) and (2) were obtained, which were characterized by ^1H n.m.r. and mass spectroscopy.

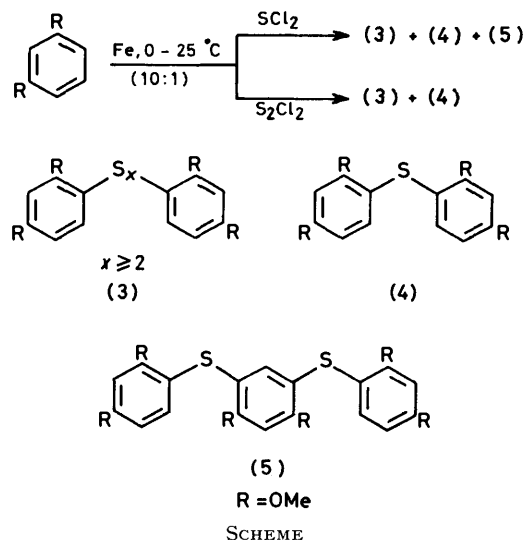


RESULTS AND DISCUSSION

The reaction of *meta*-dimethoxybenzene with sulphur chlorides in the absence of solvent was carried out at

room temperature in the presence of iron powder as catalyst, using a 10 : 1 *m*-dimethoxybenzene-sulphur chloride molecular ratio (see Scheme).

The reaction with S_2Cl_2 led to the formation of linear polysulphur compounds (3) as major products, together with a small amount of the sulphide (4) (12%). Although the polysulphur compounds were not isolated,



their presence was shown by reduction of the reaction mixture with zinc and hydrochloric acid, to give 2,4-dimethoxythiophenol (65%) and hydrogen sulphide; the sulphide (4) was left as a residue.

By treating *m*-dimethoxybenzene with SCl_2 , the main reaction product was the sulphide (4) (63%), accompanied by minor amounts of linear polysulphur compounds (3) (33%). In addition, compound (5) was obtained in very low yield (4%).

These results show that because of the high reactivity of *m*-dimethoxybenzene, both SCl_2 and S_2Cl_2 react easily with it, in spite of their different strengths as electrophilic agents.⁷ Further, S_2Cl_2 is shown to be the more effective reagent in obtaining polysulphur bridged derivatives, although the neat reaction led to the formation of only linear compounds.

In view of this, the reaction of S_2Cl_2 with *m*-dimethoxybenzene in dilute solution was thought to be more

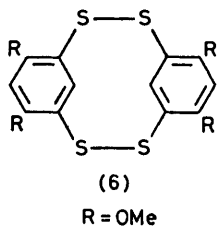
appropriate for the formation of cyclic polysulphur compounds. Chloroform was, therefore, chosen as solvent, and equimolecular amounts of the reactants were employed, in the presence of iron powder as catalyst.

The reaction yielded an amorphous polymeric material as precipitate, which was not further characterized. From the mother liquor a crystalline precipitate was recovered after some days. Extraction of this crude precipitate with dioxan and repeated recrystallization from the same solvent yielded yellow needles, m.p. 208–210 °C (5–6%) [M (osmometric in *o*-dichlorobenzene) 471]. Elemental analysis indicated a molecular composition, corresponding to $C_{16}H_{16}O_4S_6$.

Three isomeric hexathia-[3.3]-, [4.2]-, and [5.1]-metacyclophane structures are compatible with the analytical results although the last one can be excluded on the basis that the reductive degradation of the compound gave only 4,6-dimethoxydithioresorcinol. This result further supports the hypothesis that the compound with m.p. 208–210 °C is bridged at the 1,3-positions.

The compound corresponding to the [3.3] structure (1) was unequivocally synthesized according to Fehér's procedure,⁸ starting from 4,6-dimethoxydithioresorcinol and SCl_2 . The resulting product showed analytical and spectral data identical to those of the product obtained from the direct sulphuration of *m*-dimethoxybenzene. Thus, the structure of our compound could be unequivocally assigned.†

From dioxan extraction of the crude mixture a less soluble residue was left, which was repeatedly recrystallized from *o*-dichlorobenzene to yield yellow needles (1.5%), m.p. 242–245 °C [M (osmometric in *o*-dichlorobenzene) 594], to which the hexathia[2.2.2]-metacyclophane structure (2) could be assigned. This structure is substantiated by the fact that the mild oxidation of 4,6-dimethoxydithioresorcinol with iodine gave an identical product. From this reaction the tetrathia[2.2]metacyclophane (6), whose characterization has been previously reported,⁴ was also obtained.



An interesting feature connected with compound (2), also common to compound (6),⁴ is its ability to generate clathrates, trapping solvents such as *o*-dichlorobenzene in its crystal structure.

Compounds (1) and (2) were also characterized by their 1H n.m.r. and mass spectral properties.

The mass spectrum of compound (1) (Table) shows the molecular ion at m/e 464 (base peak). Other intense peaks are present at m/e 432 and 400, corresponding to loss of one and two sulphur atoms respectively from the molecular ion. A strong metastable peak at about m/e

345 shows that the ion at m/e 400 is formed directly from the molecular ion.

In the mass spectrum of compound (2) (Table) the molecular ion appears with very low intensity, and the

Mass spectra (70 eV) of compounds (1) and (2)

| Compound | m/e (I%) |
|----------|---|
| (1) | 468 (3), 467 (5), 466 (30), 465 (21), 464 (100), 434 (6), 433 (5), 432 (27), 403 (3), 402 (20), 401 (21), 400 (97), 336 (5), 335 (12), 321 (4), 289 (8), 232 (5), 200 (10), 199 (22), 187 (5), 185 (9), 169 (9), 168 (26), 153 (42), 138 (12), 127 (6), 125 (7), 69 (13), 64 (22) |
| (2) | 602 (2), 601 (2), 600 (6), 570 (6), 569 (7), 568 (25), 553 (3), 538 (3), 537 (4), 536 (11), 521 (4), 469 (9), 434 (8), 433 (7), 432 (27), 404 (3), 403 (5), 402 (22), 401 (21), 400 (100), 368 (3), 336 (6), 335 (17), 320 (5), 289 (12), 202 (15), 201 (18), 200 (20), 199 (44), 187 (12), 185 (22), 170 (12), 169 (19), 168 (37), 155 (46), 153 (86), 140 (21), 138 (42), 127 (31), 125 (27), 109 (21), 101 (33), 97 (29), 96 (28), 95 (20), 85 (30), 69 (71) |

preferred fragmentation process of the macroring is the cleavage of the double sulphur bridge. This type of fragmentation leads to the formation of fragments at m/e 400 and 199 $[(M/3 - H)^+]$. Other peaks at m/e 568, 536, 368, 335, and 168 can be rationalized in terms of losses of one or two sulphur atoms, respectively, from the molecular ion and from the fragments at m/e 400 and 200. Less intense peaks at m/e 553, 521, and 320 are formed by loss of methyl groups. In the low mass range, the loss of a methyl group from the fragment at m/e 168 gives the strong peak at m/e 153, from which by a subsequent loss of CO the peak at m/e 127 is generated.

The 1H n.m.r. spectrum of compound (1) shows that the aromatic protons resonate as singlets at δ 8.40 and 6.74.

Previous work on structurally related compounds⁴ allows us to assign the upperfield signal to the protons between the methoxy-groups, and the downfield signal to the protons between the sulphur atoms.

It is interesting to note that the intra-annular protons resonate at very low field strength (δ 8.40) with respect to [3.3]metacyclophane (δ 6.58–7.0).⁹

Comparing the chemical shifts of these protons with the corresponding protons in the tetrathia[2.2]metacyclophane (6) (δ 7.85) and in the 1,3-dithiomethoxy-4,6-dimethoxybenzene (δ 7.37), it seems clear that the observed chemical shifts for the internal protons in these sulphur cyclic compounds are strongly affected by the magnetic anisotropy of the neighbouring sulphur atoms.

The 1H n.m.r. spectrum of compound (2) shows four singlets for the aromatic protons at δ 7.80, 7.27, 6.86, and 6.70, with an integration ratio of 1 : 2 : 1 : 2, respectively. Also in this compound the two downfield signals at δ 7.80 and 7.27 are assignable to the intra-annular aryl protons, and the two upfield signals at δ 6.86 and 6.70 to the external aryl protons.

† Further proof was provided by structural analysis, which shows that the molecule exists in the *syn* conformation (N. Bresciani-Pahor, M. Calligari, and L. Randaccio, to be published).

The presence of two sets of signals both for the intra-annular and external aryl protons could be explained taking into account that the molecular models show that compound (2) can exist in several conformations which, although rapidly interconverting, never result in an averaging of the chemical shifts of each set of the aromatic protons.

In fact, in each conformation, only two of the three aromatic rings are related by symmetry.

It should be noted also that this compound shows a downfield shift for the intra-annular protons with respect to the corresponding [2.2.2]metacyclopentane (δ 6.14).¹⁰

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. 4,6-Dimethoxydithioresorcinol and 4,6-dimethoxy-1,3-dimethylthiobenzene were prepared according to literature procedures.¹¹ 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 obtained at 70 eV by direct insertion into the ion source of a LKB 9000 S instrument. ¹H N.m.r. spectra were recorded on a Varian EM 360 instrument (SiMe₄ as internal standard).

Neat Reaction of m-Dimethoxybenzene with Sulphur Dichloride and Disulphur Dichloride.—In a red glass flask, equipped with a magnetic stirring bar, a dropping funnel, and a condenser, were placed *m*-dimethoxybenzene (69 g, 0.5 mol) and iron powder (*ca.* 5 mg). The flask was flushed with nitrogen and then a solution of sulphur dichloride (5.15 g, 0.05 mol) in CS₂ (20 ml) was added dropwise. The mixture, kept at 0 °C, was stirred until evolution of hydrogen chloride was judged complete. After removing by steam-distillation the excess of *m*-dimethoxybenzene, the residue was extracted with benzene and reduced with zinc (60 g) and hydrochloric acid (100 ml). Steam-distillation of the mixture gave 2,4-dimethoxythiophenol, b.p. 158–160 °C at 20 mmHg (lit.,¹² 159–160 °C at 20 mmHg); δ (CDCl₃) 7.23 (1 H, d, ³J_{HH} \approx 8 Hz, Ar-H), 6.53 (2 H, m, Ar-H), 3.86 (3 H, s, OCH₃), and 3.58 (1 H, s, SH).

The residue was extracted with benzene, washed with dilute NaOH and water, dried (Na₂SO₄), and chromatographed through a silica-gel column (1:1 diethyl ether-light petroleum as eluant).

The first fraction of eluate gave *bis*-(2,4-dimethoxyphenyl) sulphide (4) (63%) as colourless crystals, m.p. 109–110 °C (from methanol) (Found: C, 62.8; H, 5.9; S, 10.35. C₁₆H₁₈O₄S requires C, 62.72; H, 5.92; S, 10.46%); mass spectrum *m/e* (rel. intensity) 306 (100, M⁺), 291 (15), 276 (7), 260 (18), 231 (7), 217 (9), 205 (7), 168 (21), 153 (8), and 95 (15); δ (CDCl₃) 7.10 (2 H, d, ³J_{HH} \approx 8 Hz, Ar-H), 6.53 (4 H, m, Ar-H), 3.90 (6 H, s, OCH₃), and 3.85 (6 H, s, OCH₃).

The second fraction of eluate gave 1,3-dimethoxy-4,6-bis-(2,4-dimethoxyphenylthio)benzene (5) (4%) as light yellow crystals, m.p. 122–124 °C (from ethanol) (Found: C, 60.65; H, 5.5; S, 13.45. C₂₄H₂₆O₆S₂ requires C, 60.74; H, 5.52; S, 13.51%); mass spectrum *m/e* (rel. intensity) 474 (100, M⁺), 459 (5), 428 (8), 305 (5), 290 (10), and 237,

(23, M²⁺); δ (CDCl₃) 7.19 (2 H, d, ³J_{HH} \approx 10 Hz, Ar-H), 6.50 (6 H, m, Ar-H), 3.93 (6 H, s, OCH₃), 3.86 (6 H, s, OCH₃), and 3.73 (6 H, s, OCH₃).

From the reaction of *m*-dimethoxybenzene with disulphur dichloride using the above procedure, 2,4-dimethoxythiophenol (65%) and the sulphide (4) (12%) were obtained.

Reaction of m-Dimethoxybenzene with Disulphur Dichloride in Dilute Solution.—To a stirred mixture of *m*-dimethoxybenzene (13.8 g, 0.1 mol) and iron powder (*ca.* 5 mg) in chloroform (200 ml) a solution of disulphur dichloride (13.5 g, 0.1 mol) in chloroform (200 ml) was added dropwise during 4 h. The mixture was flushed with nitrogen and refluxed until evolution of hydrogen chloride was judged complete. The amorphous polymeric material formed was filtered from the hot solution, and the filtrate was allowed to evaporate. After some days the solution deposited yellow crystals. Soxhlet extraction of the crude precipitate with dioxan, and repeated recrystallizations from the same solvent, afforded yellow needles of 5,7,14,16-tetramethoxy-1,2,3,10,11,12-hexathia[3.3]metacyclopentane (1) (5–6%), m.p. 208–210 °C (Found: C, 41.8; H, 3.3; S, 41.3. C₁₆H₁₆O₄S₆ requires C, 41.36; H, 3.47; S, 41.40%); δ [(CD₃)₂SO] 8.40 (2 H, s, Ar-H), 6.74 (2 H, s, Ar-H), and 3.93 (12 H, s, OCH₃).

The less-soluble residue was recrystallized several times from *o*-dichlorobenzene to yield yellow needles of 4,6,12,14,20,22-hexamethoxy-1,2,9,10,17,18-hexathia[2.2.2]-metacyclopentane (2) (1.5%). ¹H N.m.r. analysis of the recrystallized material showed that compound (2) included 1 mol. equiv. of *o*-dichlorobenzene for each mol. equiv. of host (2). The unsolvated compound was obtained by recrystallization from mesitylene, m.p. 238–240 °C (Found: C, 48.05; H, 3.95; S, 31.95. C₂₄H₂₄O₆S₆ requires C, 47.98; H, 4.02; S, 32.02%); δ [(CD₃)₂SO] 7.80 (1 H, s, Ar-H), 7.27 (2 H, s, Ar-H), 6.86 (1 H, s, Ar-H), 6.70 (2 H, s, Ar-H), and 3.98 (18 H, s, OCH₃).

Reduction of Compound (1).—To a stirred mixture of compound (1) (0.46 g, 1 mmol) and zinc powder (2 g) suspended in benzene (40 ml) in an ice-bath, 37% hydrochloric acid (20 ml) was added dropwise. When the addition was complete, the mixture was warmed (60 °C) for 30 min. The benzene layer was separated, washed with water, dried (Na₂SO₄), and concentrated under reduced pressure. The residue, recrystallized from ethanol, afforded light yellow crystals of 4,6-dimethoxydithioresorcinol (65%), m.p. 90–92 °C (lit.,¹¹ 89–92 °C); δ (CDCl₃) 7.16 (1 H, s, Ar-H), 6.48 (1 H, s, Ar-H), 3.95 (6 H, s, OCH₃), and 3.62 (2 H, s, SH).

Reaction of 4,6-Dimethoxydithioresorcinol with Sulphur Dichloride.—4,6-Dimethoxydithioresorcinol (1.01 g, 5 mmol) and sulphur dichloride (0.51 g, 5 mmol) in diethyl ether (200 ml) were dropped separately but synchronously from two dropping funnels into diethyl ether (1.6 l) during 3 h, with vigorous stirring under nitrogen. When the evolution of hydrogen chloride was complete, the mixture was filtered and the solvent removed under reduced pressure to leave a yellow powder. The crude product was extracted with dioxan and recrystallized from the same solvent to yield yellow crystals (15%), whose analytical and spectral data were identical with those of compound (1).

Oxidation of 4,6-Dimethoxydithioresorcinol with Iodine.—4,6-Dimethoxydithioresorcinol (2.02 g, 0.01 mol) in benzene (500 ml) and iodine (2.54 g, 0.01 mol) in 9:1 benzene-ethanol (500 ml) were added simultaneously and dropwise to benzene (1 l) with vigorous stirring. When the addition

was complete (10 h), the reaction mixture was set aside overnight. The yellow crystalline precipitate formed was filtered off, washed with dilute thiosulphate and dried. The crude product was treated several times with boiling ethyl acetate, which extracted 4,6,12,14-tetramethoxy-1,2,9,10-tetrathia[2.2]metacyclophane (6). The residue recrystallized from *o*-dichlorobenzene afforded yellow needles (40—45%), whose analytical and spectral data were identical to those of macrocycle (2).

[8/1357 Received, 21st July, 1978]

REFERENCES

- ¹ F. Bottino, S. Foti, and S. Pappalardo, *Tetrahedron*, 1976, **32**, 2567.
- ² F. Bottino, S. Foti, and S. Pappalardo, *Tetrahedron*, 1977, **33**, 337.
- ³ F. Bottino, S. Foti, and S. Pappalardo, *J.C.S. Perkin I*, 1977, 1653.
- ⁴ F. Bottino, S. Foti, S. Pappalardo, P. Finocchiaro, and M. Ferrugia, *J.C.S. Perkin I*, 1979, 198.
- ⁵ Z. S. Ariyan and L. A. Wiles, *J. Chem. Soc.*, 1962, 4709.
- ⁶ Z. S. Ariyan and R. L. Martin, *Chem. Comm.*, 1969, 847; *J.C.S. Perkin I*, 1972, 1687.
- ⁷ T. Fujisawa, N. Ohtsuka, T. Kobori, and T. Tsuchihashi, *Tetrahedron Letters*, 1968, 4533.
- ⁸ F. Fehér, K. Glinka, and F. Malcharek, *Angew. Chem. Internat. Edn.*, 1971, **10**, 413.
- ⁹ L. Rossa and F. Vögtle, *J. Chem. Research* 1977, (M) 3010.
- ¹⁰ R. Flammang, H. P. Figeys, and R. H. Martin, *Tetrahedron*, 1968, **24**, 1171.
- ¹¹ J. Pollak and A. Wienerberger, *Monatsh.*, 1914, **35**, 1467.
- ¹² H. Burton and W. A. Davy, *J. Chem. Soc.*, 1948, 525.