Novel Polysulphur Bridged Metacyclophanes from the Iron-catalysed Reaction of Bis-(2,4-dimethoxyphenyl) Sulphide with Disulphur Dichloride. Evidence for the Cleavage of the Carbon–Sulphur Bond by Electrophilic Agents

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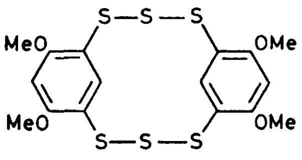
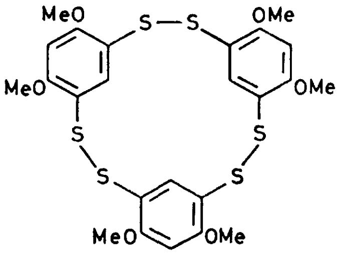
The iron-catalysed reaction of bis-(2,4-dimethoxyphenyl) sulphide (3) with disulphur dichloride(S_2Cl_2) in dilute chloroform solution has been investigated. Surprisingly, the reaction gives 4,6,11,13,18,20-hexamethoxy-1,2,9,16-tetrathia[2.1.1]metacyclophane (4) as the major product, accompanied by minor amounts of 3,5,10,12,17,19,24,26-octamethoxy-1,8,15,22-tetrathia[1.1.1.1]metacyclophane (5), 4,6,11,13,18,20,25,27-octamethoxy-1,2,9,16,23-pentathia[2.1.1.1]metacyclophane (6), and 5,7,14,16-tetramethoxy-1,2,3,10,11,12-hexathia[3.3]metacyclophane (1). The ^1H n.m.r. and mass spectra of compounds (4)—(6) are briefly discussed. The unexpected formation of compounds (1) and (4) suggests the occurrence of an unusual cleavage of carbon–sulphur bonds, operated by electrophilic species on sulphur-bridged oligomers, and subsequent rearrangement of the involved intermediates to the cyclic derivatives. This interpretation is supported by the successful chlorinolysis under mild conditions of the sulphide (3) by means of sulphuryl chloride, affording 1,3-dichloro-4,6-dimethoxybenzene (8) and bis-(5-chloro-2,4-dimethoxyphenyl) disulphide (9). A probable reaction pathway is proposed.

OUR earlier studies have been concerned with the chemistry of sulphur-bridged metacyclophanes. The syntheses of a number of polysulphur bridged ring systems have been accomplished by condensation of dithioresorcinol derivatives with sulphur chlorides,[1-2] and by mild oxidation of the appropriate dithiols.[3-5]



(1)



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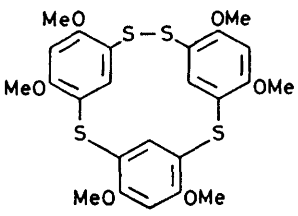

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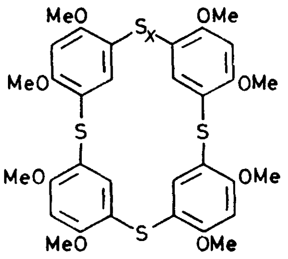


(5) X = 1

(6) X = 2

Furthermore, a variety of cyclic polysulphur derivatives have been obtained in a single-step reaction by sulphuration of activated substrates with sulphur chlorides under catalytic conditions.[6-8] Recently we obtained compounds (1) and (2) by treating *m*-dimethoxybenzene with disulphur dichloride (S_2Cl_2) in dilute solution, in chloroform, in the presence of iron powder as a catalyst.[8]

We have now investigated the iron-catalysed reaction of bis-(2,4-dimethoxyphenyl) sulphide (3) with S_2Cl_2, in order to detect the possible formation of cyclic polysulphur compounds. Apart from compound (1), three other macrocycles (4)—(6) were isolated, the structures of which were confirmed by ^1H n.m.r. and mass spectroscopy. Furthermore, the unexpected formation of compounds (1) and (4) from the reaction of (3) with S_2Cl_2 suggests the occurrence of an unusual cleavage of C_{Ar}–S bonds by means of electrophilic species; this is fully verified by the results of the reaction of the sulphide (3) with sulphuryl chloride.

RESULTS AND DISCUSSION

The required sulphide (3) was easily obtained free from linear polysulphides,[8] so as to avoid tedious procedures of purification, by treating *m*-dimethoxybenzene with thionyl chloride in the presence of iron powder.

The sulphide (3) was treated with S_2Cl_2 in a 1 : 1 molar ratio in dilute chloroform solution in the presence of traces of iron powder. On gradual concentration of the reaction mixture, a large amount of amorphous polymeric material deposited, which was removed by filtration. Further evaporation of the filtrate yielded a crystalline precipitate, extraction of which with boiling dioxan followed by recrystallization from the same solvent afforded yellow crystals, m.p. 208—210 °C, identical in all respects to an authentic sample of 5,7,14,16-tetramethoxy-1,2,3,10,11,12-hexathia[3.3]metacyclophane (1).[2,8]

After extraction of the crude mixture with dioxan a less soluble residue remained (5.6%) which was recrystallized from nitrobenzene to yield yellow microcrystals, infusible up to 340 °C. Analytical and mass spectral data suggested this compound to be 3,5,10,12,17,19,24,26-octamethoxy-1,8,15,22-tetrathia[1.1.1.1]metacyclophane (5). No ^1H n.m.r. spectra could be obtained for the compound owing to its low solubility.

By column chromatography of the mother-liquor on silica gel (1 : 1 ethyl acetate–light petroleum as eluant), besides an additional amount of compound (1) (total yield 1.5%) two other crystalline compounds were isolated; these were shown to be the 13-membered 4,6,11,13,18,20-hexamethoxy-1,2,9,16-tetrathia[2.1.1]-metacyclophane (4) (7%), m.p. 275—277 °C, and its higher 17-membered homologue 4,6,11,13,18,20,25,27-octamethoxy-1,2,9,16,23-pentathia[2.1.1.1]metacyclophane (6) (1.1%), m.p. 303—305 °C (decomp.). Convincing evidence for the suggested unsymmetrical structures (4) and (6) was provided by ^1H n.m.r. and mass spectroscopy. The mass spectra (70 eV) of compounds (4)—(6) are listed in the Table. These cyclic sulphur derivatives display a high stability to electron impact, as shown by very strong molecular ion intensities, by the presence of intense peaks corresponding to $(M/2)^+$ fragments (clearly attributable to double charged molecular ions), and by a negligible fragmentation pattern. These features are in agreement with the proposed structures, since it is well known that macrocyclic compounds of this type behave similarly.[3,9]

Mass spectra (70 eV) of compounds (4)—(6)

Compound	*m/e* (rel. intensity)
(4)	540 (3), 539 (7), 538 (25), 537 (32), 536 (100, M^+), 523 (5), 522 (7), 521 (20), 504 (2), 494 (2), 493 (5), 320 (2), 269 (3), 268.5 (4), 268 (10), 261 (2), 260.5 (1.5), 246.5 (1.5), 168 (3), 153 (2), 125 (2).
(5)	676 (3), 675 (8), 674 (23), 673 (37), 672 (100, M^+) 659 (2), 658 (4), 657 (6), 642 (2), 504 (2), 490 (2.5), 489 (2), 488 (4), 458 (2.5), 337 (5), 336.5 (7), 336 (19), 328.5 (2), 321 (3), 293 (3), 275 (2), 168 (3), 153 (3), 125 (2).
(6)	708 (4), 707 (11), 706 (38), 705 (39), 704 (100, M^+), 689 (2), 674 (3), 673 (2), 672 (4), 536 (6), 521 (3), 507 (2), 506 (8), 505 (11), 504 (42), 491 (3), 490 (7), 489 (8), 461 (3), 446 (3), 353 (7), 352.5 (8.5), 352 (27), 338 (3), 320 (2), 290 (3), 275 (2), 202 (2), 170 (5), 169 (2), 168 (3), 153 (4), 138 (2), 125 (2), 64 (3).

The loss of a methyl group from the molecular ion is common to compounds (4)—(6); moreover in compound (4) the subsequent loss of carbon monoxide, peculiar to dimethoxybenzene derivatives,[10] is also present (*m/e* 493). In compound (6) the intense fragment at *m/e* 504 arises from the cleavage of the disulphide bond and loss of a 4,6-dimethoxy-dithioresorcinol biradical.

The 80 MHz ^1H n.m.r. spectra of compounds (4) and (6) in $CDCl_3$ are consistent with the proposed unsymmetrical structures. Compound (4) shows three singlets for the aromatic protons at δ 7.23, 6.83, and 6.51, with an integrating ratio of 2 : 1 : 3, and three other singlets for methoxy-protons at δ 3.96, 3.92, and 3.88, in the ratio 6 : 6 : 6. The assignment of the aromatic signals to the respective protons was made by considering that a small long range coupling between the methoxy-groups and the *ortho*-protons occurs in these molecules, which causes broadening of the corresponding signals.[11,12] Thus, the downfield signals at δ 7.23 and 6.83 are assignable to the C-8,22 and C-15 intra-annular aryl protons, respectively, and the slightly broadened signal at δ 6.51 to the external aryl protons.

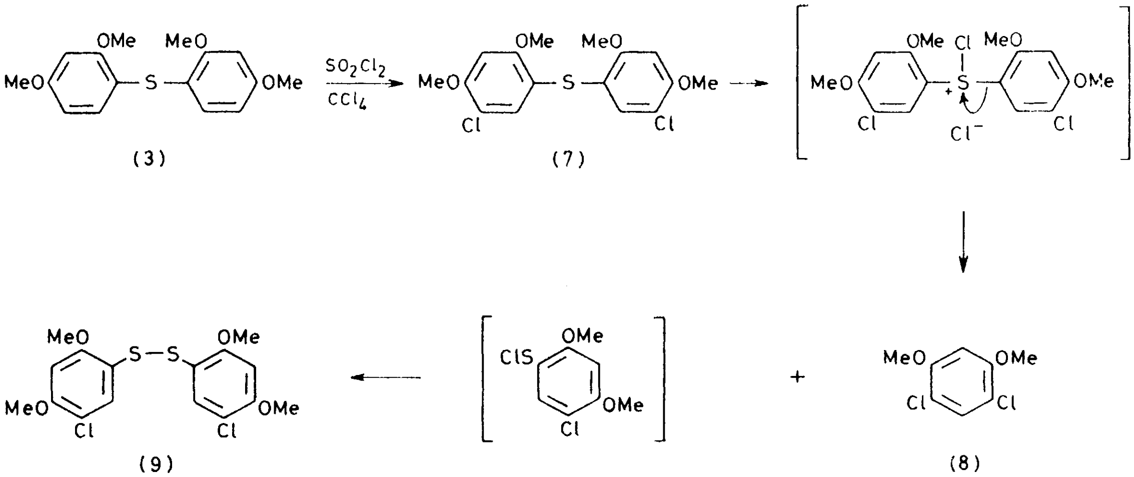
These spectral features differ from those of the corresponding hydrocarbon [2.1.1]metacyclophane,[13] since structural variation by replacement of methylene with sulphur linkages causes a downfield shift and inversion in the absorptions of the intra-annular aryl protons of (4) with respect to those of the hydrocarbon.

Compound (6) shows the expected four singlets for the aromatic protons at δ 7.00, 6.52, 6.46, and 6.39, with an integrating ratio of 1 : 1 : 1 : 1, and four singlets for the methoxy-protons at δ 3.95, 3.91, 3.86, and 3.82, integrating for 3 : 3 : 3 : 3. Also in this case the downfield signals at δ 7.00 and 6.52 are assignable to the C-8,29 and C-15,22 intra-annular aryl protons, respectively, and the upfield signals at δ 6.46 and 6.39 to the external protons. Compounds (4) and (6) appear to be very useful models for the elucidation of the stereochemistry of some related open-chain and/or cyclic sulphides and disulphides.

Previous studies on the iron-catalysed sulphuration of dimesityl sulphide and dimesitylmethane by means of sulphur chlorides have shown that the cyclization of these substrates to the corresponding 18-membered bis-disulphide derivatives is determined by steric factors.[6,7,14] In the absence of steric restraints, the reaction of the sulphide (3) with S_2Cl_2 yielded the smaller 16- and 17-membered ring systems (5) and (6); moreover, the reaction surprisingly produced also the cyclic 12-membered bis-trisulphide (1) and the 13-membered disulphide (4) (the major product). The formation of the latter two compounds could be explained on the assumption that the sulphide (3), or probably sulphur-bridged oligomers, undergo *inter alia* cleavage of carbon–sulphur bonds by electrophilic species present in the reaction mixture. However, a literature survey shows that only in alkyl–aryl sulphides does cleavage of the carbon–sulphur bond occur using electrophilic agents (*viz.* acid catalysts,[15] diazonium salt,[16] chlorine [17-21]);

to our knowledge such a phenomenon has passed unnoticed for diaryl sulphides.

In order to verify the above hypothesis, the action of electrophilic agents on the sulphide (3) was investigated. Sulphuryl chloride was chosen for our experiments, because it gave a cleaner reaction than the corresponding sulphur chlorides, and because the formation of by-products, such as oligomers, could be minimized.[22] Therefore, the sulphide (3) was treated with one equivalent of sulphuryl chloride at 0 °C in carbon tetrachloride. The reaction afforded bis-(5-chloro-2,4-dimethoxyphenyl) sulphide (7) in 35% yield; unchanged (3) was recovered, and no products from cleavage of the carbon–sulphur bond were detected. However, when the sulphide (3) was treated with an excess of sulphuryl chloride, besides uncharacterized amorphous material, 1,3-dichloro-4,6-dimethoxybenzene (8), and bis-(5-chloro-2,4-dimethoxyphenyl)disulphide (9) were formed in 34 and 15% yields respectively; neither (3) nor (7) were detected amongst the products. The reaction products were identified by ^{1}H n.m.r. and mass spectroscopy, and by comparison with authentic samples, synthesized by appropriate unequivocal sequences (see Experimental section).



SCHEME

In view of the isolation of these compounds, it appears highly probable that the sulphide (3) is first converted into (7), which through a chlorosulphonium intermediate undergoes quantitative cleavage to the sulphenyl chloride, which then disproportionates to the corresponding disulphide (9) (Scheme).

These results, while confirming the susceptibility of the bridged heteroatom to the action of electrophilic agents, can also account for the formation of compounds (1) and (4) from the reaction of the sulphide (3) with S_2Cl_2, through a similar mechanism.

We believe that the strong electron-releasing effect of methoxy-groups may play a role in the cleavage of carbon–sulphur bonds by electrophilic agents, and it will be of interest to examine to what extent the nature of the substituents and/or the strength of the electrophilic agents affect this unusual reaction in diaryl sulphides.

EXPERIMENTAL

All solvents and available organic materials were commercial products purified by standard procedures. 1-Chloro-2,4-dimethoxybenzene [22] was prepared according to the published procedure. All experiments were carried out in red glass flasks. Mass spectra were obtained at 70 eV by direct insertion into the ion source of a LKB 9000S instrument. Independent molecular weights were determined by thermoelectric osmometry for solutions in *o*-dichlorobenzene at 130 °C with a Mechrolab 302 instrument. ^{1}H N.m.r. spectra were recorded on a Bruker WP-80 instrument ($SiMe_4$ as internal reference).

Bis-(2,4-*dimethoxyphenyl*) *Sulphide* (3).—Thionyl chloride (8.85 g, 0.075 mol) in chloroform (20 ml) was added dropwise to a stirred mixture of *m*-dimethoxybenzene (69 g, 0.5 mol) and iron powder (*ca.* 50 mg), cooled in an ice-bath. The mixture was stirred under nitrogen until evolution of hydrogen chloride was judged complete. After pouring into water (100 ml), the mixture was extracted with diethyl ether, dried (Na_2SO_4), and the solvent evaporated off. Removal *in vacuo* of the excess of *m*-dimethoxybenzene left an oily residue, which was chromatographed on a column of silica gel [diethyl ether–light petroleum (1 : 1 v/v) as eluant] to afford the sulphide (3) (12 g), m.p. 109—110 °C (from methanol) (lit.,[8] 109—110 °C) (Found: C, 62.6; H, 5.8; S, 10.4. Calc. for $C_{16}H_{18}O_4S$: C, 62.7; H, 5.9; S, 10.5%).

Reaction of (3) ***with*** S_2Cl_2.—The sulphide (3) (3.06 g, 0.01 mol) and S_2Cl_2 (1.35 g, 0.01 mol) in chloroform (50 ml) were dropped separately but synchronously from two dropping funnels during 2 h into chloroform (400 ml) containing a trace amount of iron powder, with efficient stirring, under nitrogen. The mixture was allowed to react at room temperature for a week. Evaporation of the mixture to 150 ml gave amorphous material, which was removed by filtration. Further concentration of the filtrate to 50 ml gave a crystalline precipitate (240 mg). Extraction of the precipitate with boiling dioxan afforded yellow crystals of 5,7,14,16-tetramethoxy-1,2,3,10,11,12-hexathia[3.3]metacyclophane (1) (30 mg), m.p. 208—210 °C, leaving as a residue 3,5,10,-

12,17,19,24,26-*octamethoxy*-1,8,15,22-*tetrathia*[1.1.1.1]*metacyclophane* (5) (190 mg) (5.6%), m.p. >340 °C (from nitrobenzene) (Found: C, 57.4; H, 4.9; S, 18.9. $C_{32}H_{32}O_8S_4$ requires C, 57.1; H, 4.8; S, 19.1%).

The mother-liquor was evaporated and the residue chromatographed through a silica gel column (1 : 1 ethyl acetate–light petroleum as eluant). The first fraction provided a crystalline solid, which after recrystallization from dioxan gave a further 45 mg of (1) (total yield 1.5%). The second fraction gave 4,6,11,13,18,20-*hexamethoxy*-1,2,-9,16-*tetrathia*[2.1.1]*metacyclophane* (4), as light yellow prisms (250 mg, 7%), m.p. 275—277 °C (from benzene) (Found: C, 53.8; H, 4.6; S, 23.7. $C_{24}H_{24}O_6S_4$ requires C, 53.7; H, 4.5; S, 23.9%). The third fraction afforded of 4,6,11,-13,18,20,25,27-*octamethoxy*-1,2,9,16,23-*pentathia*[2.1.1.1]-*metacyclophane* (6) (40 mg, 1.1%), m.p. 303—305 °C (decomp.) (from benzene–dichloromethane) (Found: C, 54.2; H, 4.65; S, 22.9. $C_{32}H_{32}O_8S_5$ requires C, 54.5; H, 4.6; S, 22.7%).

Reaction of (3) *with* 1 *Mol. Equiv. of* SO_2Cl_2.—To a solution of (3) (0.76 g, 2.5 mmol) in carbon tetrachloride (10 ml), cooled in an ice-bath, was added dropwise during 15 min a solution of SO_2Cl_2 (0.38 g, 2.5 mmol) in carbon tetrachloride (10 ml). The mixture was stirred for 2 h, then concentrated under reduced pressure and chromatographed on silica gel using diethyl ether–light petroleum (1 : 1 v/v) as an eluant. The first fraction gave unchanged (3). Further elution afforded *bis*-(5-*chloro*-2,4-*dimethoxyphenyl*) *sulphide* (7) (35%) as prisms, m.p. 171—173 °C (from ethanol) (Found: C, 51.5; H, 4.3; Cl, 18.7; S, 8.4. $C_{16}H_{16}Cl_2O_4S$ requires: C, 51.2; H, 4.3; Cl, 18.9; S, 8.5%); *m/e* 378 (14%), 377 (12), 376 (66), 375 (19), 374 (100, M^+), 361 (8), 359 (13), 340 (6), 330 (5), 328 (7), 326 (7), 324 (19), 202 (6), 187 (8, M^{2+}), and 152 (6); δ($CDCl_3$) 7.08 (2 H, s, ArH), 6.53 (2 H, s, ArH), 3.92 (6 H, s, OMe), and 3.87 (6 H, s, OMe).

Reaction of (3) *with an Excess of* SO_2Cl_2.—The sulphide (3) (0.76 g, 2.5 mmol) in carbon tetrachloride (40 ml) was treated with a solution of SO_2Cl_2 (1.55 g, 0.01 mol) in carbon tetrachloride (10 ml), using the above procedure. The mixture was stirred for 2 h at room temperature, then decanted from an oily polymeric material, and evaporated to dryness under reduced pressure. The crystalline residue was chromatographed on silica gel, using light petroleum–diethyl ether (3 : 1 v/v) as an eluant. The first fraction gave 350 mg (34%) of 1,3-dichloro-4,6-dimethoxybenzene (8), m.p. 117.5—118.5 °C (from ethanol) (lit.,[22] 118 °C) (Found: C, 46.4; H, 3.8; Cl, 34.1. Calc. for $C_8H_8Cl_2O_2$: C, 46.4; H, 3.9; Cl, 34.2%); *m/e* 210 (11%), 209 (6), 208 (70), 207 (9), 206 (100, M^+), 193 (10), 191 (15), 167 (4), 165 (26), 163 (40), 150 (6), and 148 (8); δ($CDCl_3$) 7.35 (1 H, s, ArH), 6.54 (1 H, s, ArH), and 3.91 (6 H, s, OMe).

Further elution with increasing amounts of diethyl ether provided 150 mg (15%) of light yellow crystals, m.p. 180—182 °C, identical in all respect to an authentic sample of bis-(5-chloro-2,4-dimethoxyphenyl)disulphide (9), synthesized by appropriate unequivocal sequences (see below).

5-*Chloro*-2,4-*dimethoxybenzenesulphonyl Chloride*.—Chlorosulphonic acid (14.56 g, 0.125 mol) was added dropwise under stirring to 1-chloro-2,4-dimethoxybenzene (8.6 g, 0.05 mol), cooled in an ice-bath. After the addition was complete (15 min), the mixture was poured immediately onto ice. The precipitate obtained was extracted with chloroform and dried ($CaCl_2$). Evaporation left the crude desired compound (66%), recrystallization (decolourizing with charcoal) of which from chloroform afforded *prisms*, m.p. 154—155.5 °C (Found: C, 35.2; H, 3.1; Cl, 26.0; S, 11.7. $C_8H_8Cl_2O_4S$ requires C, 35.4; H, 3.0; Cl, 26.15; S, 11.8%); *m/e* 274 (9%), 273 (5), 272 (45), 271 (6), 270 (66, M^+), 237 (39), 236 (10), 235 (100), 189 (22), 188 (6), 187 (57), 174 (15), 173 (6), 172 (48), 158 (20), 157 (10), 156 (55), 143 (21), 142 (8), 141 (37), 128 (10), 127 (5), 126 (16), 113 (23), 97 (10), and 64 (22); δ($CDCl_3$) 7.93 (1 H, s, ArH), 6.60 (1 H, s, ArH), 4.08 (3 H, s, OMe), and 4.03 (3 H, s, OMe).

5-*Chloro*-2,4-*dimethoxythiophenol*.—To a well stirred mixture of 5-chloro-2,4-dimethoxybenzenesulphonyl chloride (8.91 g, 0.04 mol) and zinc dust (35 g) in benzene (100 ml), cooled in an ice-bath, was added dropwise 37% HCl (60 ml). When the addition was accomplished, the mixture was warmed (50 °C) for 30 min, and then steam-distilled. The thiol was extracted with chloroform, washed with water, and dried (Na_2SO_4). Removal of the solvent *in vacuo* left pale yellow crystals (71%), m.p. 99—101 °C (lit.,[23] b.p. 118 °C at 8 mmHg) (Found: C, 46.8; H, 4.5; Cl, 17.2; S, 15.6. Calc. for $C_8H_9ClO_2S$ C, 46.9; H, 4.4; Cl, 17.3; S, 15.7%); *m/e* 206 (38%), 205 (11), 204 (100, M^+), 191 (19), 190 (5), 189 (50), 169 (15), 163 (14), 161 (39), 141 (9), 129 (8), and 97 (8); δ($CDCl_3$) 7.26 (1 H, s, ArH), 6.49 (1 H, s, ArH), 3.89 (6 H, s, OMe), and 3.59 (1 H, s, SH).

Bis-(5-*chloro*-2,4-*dimethoxyphenyl*) *Disulphide* (9).—5-Chloro-2,4-dimethoxythiophenol (0.5 g, 2.5 mmol), dissolved in dimethyl sulphoxide (4 ml), was stirred for 24 h at room temperature. On pouring the mixture into brine, the *disulphide* precipitated in essentially quantitative yield. It was collected by filtration, washed with water, dried, and recrystallized from acetic acid, m.p. 180—182 °C (Found: C, 47.35; H, 4.1; Cl, 17.5; S, 15.6. $C_{16}H_{16}Cl_2O_4S_2$ requires C, 47.2; H, 4.0; Cl, 17.4; S, 15.7%); *m/e* 410 (14%), 409 (11), 408 (60), 407 (16), 406 (76, M^+), 376 (5), 374 (7), 206 (26), 205 (42), 204 (72), 203 (100), 191 (12), 189 (29), 169 (20), 168 (84), 163 (7), 161 (19), 159 (14), 157 (27), 142 (11), 131 (8), and 129 (18); δ($CDCl_3$) 7.58 (2 H, s, ArH), 6.47 (2 H, s, ArH), 3.91 (6 H, s, OMe), and 3.86 (6 H, s, OMe).

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