

## Formation and Structure of a Four-co-ordinate Organo-sulphur(IV) Compound

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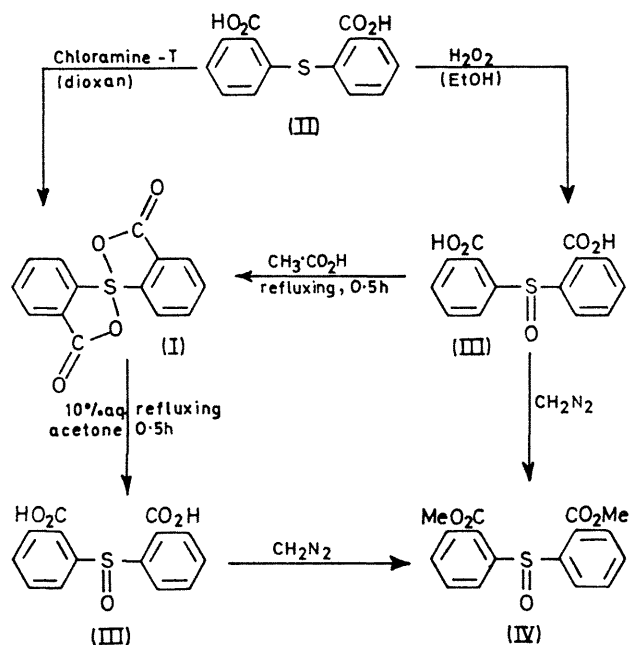
*Summary* Bis-(2-carboxyphenyl)sulphur dihydroxide dilactone was prepared from 2,2'-thiodibenzoic acid and from 2,2'-sulphinylidibenzoic acid; the structure of this stable dilactone containing a four-co-ordinated sulphur(IV) atom was investigated by chemical, spectroscopic, and X-ray methods.

ONLY a few stable organo-sulphur compounds containing four-co-ordinated sulphur(IV) atoms are known. We report now the synthesis and investigation of bis-(2-carboxyphenyl)sulphur dihydroxide dilactone (I) which belongs to such a class.

2,2'-Thiodibenzoic acid<sup>1</sup> (II) reacts with dry chloramine-T in dioxan (for 3 days at 20 °C), yielding (I) (45%) after evaporation at 20 °C and recrystallization from dry acetone. Alternatively, (I) can be obtained in 55% yield from 2,2'-sulphinylidibenzoic acid (III) on heating in acetic acid for 30 min; (I) crystallizes out on cooling. Compound (I) was also formed when (III) was sublimed (at 230 °C and 10<sup>-2</sup> Torr). Compound (III) was prepared from (II) by a known method,<sup>2</sup>  $\nu(\text{OH})$  3300—2300,  $\nu(\text{C}=\text{O})$  1720, and  $\nu(\text{S}=\text{O})$  988 cm<sup>-1</sup>.

As expected, (I), unlike (III), does not dissolve in cold KHCO<sub>3</sub> solution but can be hydrolysed (30 min) to (III) in

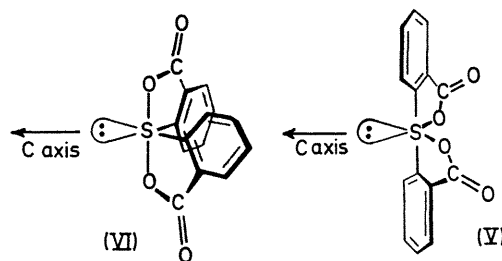
hot acetone-water (9:1). Compound (III) was methylated by diazomethane to the known dimethyl 2,2'-sulphonyldibenzoate (IV).<sup>3</sup>



The lactone (I) forms long, thin needles, m.p. 303–307 °C (sealed tube). Elemental analyses and X-ray data were consistent with the calculated formula for the dilactone. Lactone titration of (I) gave the expected value of  $136 \pm 2$ . The  $\nu(\text{C}=\text{O})$  band at  $1745 \text{ cm}^{-1}$  is in agreement with the dilactone structure. The lack of characteristic absorptions of sulphoxides, carboxylic acids, or carboxylic anhydrides excludes the possibility of such structures. In the n.m.r. spectrum the signals for the aromatic protons appear at 7.71 p.p.m. (solvent dimethyl sulphoxide, internal standard tetramethylsilane).

Crystal data [ $\text{C}_{14}\text{H}_8\text{O}_4\text{S}$ ,  $M = 272.28$ , orthorhombic,  $a = 27.830$ ,  $b = 20.089$ ,  $c = 4.224 \text{ \AA}$ ,  $D_m = 1.526 \text{ g cm}^{-3}$  (by flotation),  $Z = 8$ ,  $D_c = 1.531$ . Space group,  $Fdd2$

(No. 43)] were determined from Weissenberg and precession photographs. It follows from this that the sulphur atom must occupy the eight-fold position at  $00z$ , while the  $\text{C}_6\text{H}_4\cdot\text{CO}_2$  groups (two for each molecule), related by a two-fold axis, are in the sixteen-fold general position. These facts can be correlated only with structures (V) and (VI) if the unshared electron pair and  $sp^3d$  hybridization of sulphur(IV) are taken into account.



The structure of 2,2'-sulphonyldibenzoic acid (III) with a three-co-ordinated sulphur(IV) atom may be excluded. In this case not only the sulphur atom, but also the  $\text{S}=\text{O}$  bond ought to be on the two-fold axis. This is, however, incompatible with the well-known trigonal pyramidal form of sulphoxides.<sup>4</sup> Similarly, the bridging oxygen of a dicarboxylic anhydride group cannot be on the same two-fold axis, and the two-fold symmetry of the molecule does not allow an apical-equatorial phenyl-phenyl (or oxygen-oxygen) position.

Both structures (V) and (VI) resemble the trigonal bipyramidal form of the  $\text{SF}_4$  molecule<sup>5</sup> as well as the  $\text{Te}^{\text{IV}}\text{O}_4$  groups found in some tellurites.<sup>6</sup> In these compounds the apical bonds affected by the repulsion of the unshared electron pair,<sup>7</sup> are inclined toward the equatorial ones. As is generally accepted, most electronegative ligands assume apical positions in the trigonal bipyramidal structures,<sup>8</sup> so we may presume that (I) possesses structure (VI). This question will be settled by a full X-ray structure analysis which is now in progress.

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