Crystal Structure of a Clathrate Formed by a Mercapto-analogue of Dianin's Compound

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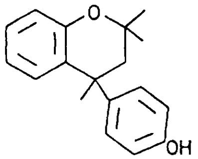
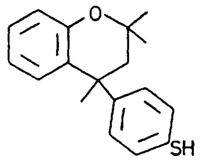
Summary An *X*-ray diffraction analysis of the CCl_4 clathrate of the mercapto-host (II) is described; a key feature of the host structure is the linking of the SH groups of six molecules of (II) by SH $\cdots$ S hydrogen bonds, such that the sulphur atoms form a near-planar hexagon.



(I)



(II)

In connection with a study of the part played by hydrogen bonding in clathrate formation,[1] we have recently prepared 4-*p*-mercaptophenyl-2,2,4-trimethylchroman (II), which corresponds to the replacement of the hydroxy function of Dianin's compound (I) by the thiol group. The new host (II) has been found to form inclusion compounds with CCl_4, CCl_3Br, and CCl_3Me, the host to guest ratio being 3 : 1 in each case.† We now report preliminary results of a single

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† Recrystallisation of (II) from cyclohexane gives unsolvated, spontaneously resolved, crystals of space group $P2_12_12_1$, with $Z = 4$. On occasion, unsolvated crystals have also been obtained from CCl_4.

crystal *X*-ray study of the CCl_4 complex of (II).[‡] The adduct, which is isomorphous with the clathrates of (I), crystallises in the trigonal system with lattice constants referred to a hexagonal unit cell containing 18 molecules of $C_{18}H_{20}OS$ and 6 molecules of CCl_4, $a = 27{\cdot}063$ and $c = 12{\cdot}074$ Å. The space group is $R\bar{3}$; the structure was solved by direct methods employing 1746 independent reflections measured with Mo-K_α radiation on a Hilger and Watts automatic diffractometer, and has been refined to a current R factor of 0·120. A Lindemann capillary was employed for crystal containment, as included solvent is lost on standing in air. During the course of the analysis all 20 host hydrogen atoms were located and allowed for; allowance has been made for the guest molecules in terms of two orientations.

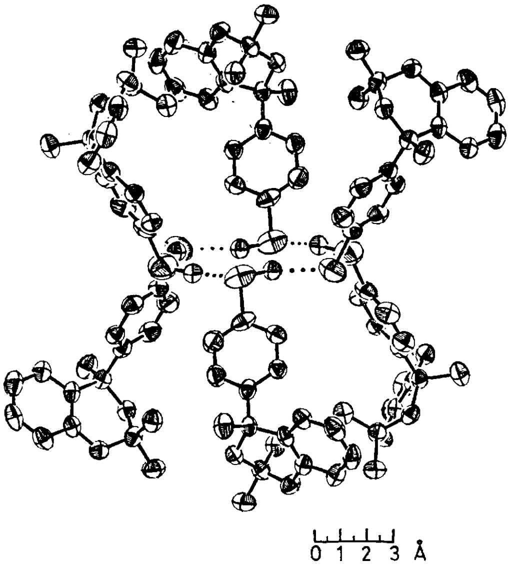

FIGURE. A general view of the hydrogen-bonded hexameric host unit of (II) in the CCl_4 clathrate.

The Figure illustrates the basic packing unit of the host structure of (II), the six thiol molecules shown being linked by a network of S–H ··· S hydrogen bonds such that the sulphur atoms form a near-planar hexagon. Two such hexameric units are stacked along the *c*-axis such that their bulkier parts interlock forming a cage which accommodates two CCl_4 molecules. Thus the top and bottom of a cage are formed by hexagons of sulphur atoms which are a unit translation in the *c*-axis direction apart, *i.e.* 12·07 Å. The cage is therefore significantly longer than that of Dianin's compound (I), where the cage length is 11·02 Å (for the chloroform clathrate[2]). The S–H ··· S hydrogen bond of (II) is characterised[3] by S ··· S and S ··· H distances of 3·75(1) and 2·41(11) Å, respectively, and an S–H ··· S angle of 168°. The oxygen-containing ring of (II) has a somewhat more distorted half-chair conformation than that found in clathrates of Dianin's compound.[2]

To our knowledge the present study provides the first structural information concerning a cyclic hydrogen-bonded hexameric unit not involving the hydroxy function.[4]

We thank the S.R.C. for support.

(*Received, 25th February* 1977; *Com.* 166.)

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] A. D. U. Hardy, D. D. MacNicol, J. J. McKendrick, and D. R. Wilson, *Tetrahedron Letters*, 1975, 4711.

[2] J. L. Flippen, J. Karle, and I. L. Karle, *J. Amer. Chem. Soc.*, 1970, **92**, 3749.

[3] For a review of the structural chemistry of the thiol group see, I. C. Paul in 'The Chemistry of the Thiol Group,' Part 1, ed. S. Patai, Wiley, 1974, ch. 2, p. 111.

[4] The hexameric unit involving OH groups is, of course, of central importance in many clathrates; see, for example, ref. 1 and references therein.