The Crystal and Molecular Structure of a New Clathrate-host Compound: 4-*p*-Hydroxyphenyl-2,2,4-trimethylthiachroman

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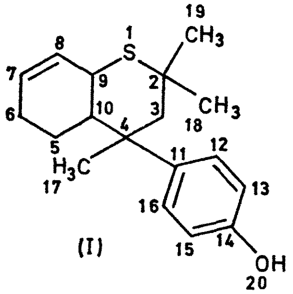
Summary The crystal structure of the clathrate-host compound, 4-*p*-hydroxyphenyl-2,2,4-trimethylthiachroman (I), is described.

X-RAY crystal-structure analysis provides a method for defining the atomic geometry and composition of clathrates,[1] molecular compounds having a regular cage structure of one component (the host compound), which physically encloses the other component or components [the guest compound(s)]. We now report the crystal structure of a new clathrate-host system, 4-*p*-hydroxyphenyl-2,2,4-trimethylthiachroman (I), which has been synthesised recently and found to form clathrates with all organic solvents from which it has been crystallised.[2] The crystals used in this analysis were recrystallised from ethanol and shown to have a host: guest ratio of 3 : 1.[2]



(I)

Fractional co-ordinates of the atoms of the host-molecule

	x	*y*	*z*
S(1)	0·2625	0·0770	0·6506
C(2)	0·2211	0·1066	0·5961
C(3)	0·2583	0·1577	0·5171
C(4)	0·2843	0·1489	0·3974
C(5)	0·3550	0·1217	0·3310
C(6)	0·3817	0·0890	0·3532
C(7)	0·3689	0·0562	0·4541
C(8)	0·3360	0·0535	0·5353
C(9)	0·3029	0·0827	0·5268
C(10)	0·3151	0·1173	0·4205
C(11)	0·2412	0·1250	0·2967
C(12)	0·2132	0·1507	0·2564
C(13)	0·1728	0·1302	0·1697
C(14)	0·1629	0·0830	0·1118
C(15)	0·1902	0·0519	0·1436
C(16)	0·2308	0·0746	0·2334
C(17)	0·3284	0·2112	0·3609
C(18)	0·2030	0·1251	0·7113
C(19)	0·1708	0·0630	0·5270
O(20)	0·1205	0·0563	0·0203

The ethanol clathrate of (I) crystallises in the trigonal system with lattice constants, referred to a hexagonal unit cell containing 18 molecules of $C_{18}H_{20}OS$, $a = 27{\cdot}81$ and $c = 10{\cdot}90$ Å.† The space group is either $R3$ or $R\bar{3}$;[6] the centrosymmetric space group ($R\bar{3}$) was chosen and this choice has been justified by the success of the analysis. Some 2272 intensity data were measured visually from equi-inclination Weissenberg photographs, *hki*0, . . . *hki*9, taken with Cu-K_α radiation. The position of the sulphur atom was deduced from a three-dimensional Patterson synthesis and the remainder of the structure obtained from an electron-density map phased on the sulphur atom. The structure was refined by Fourier and isotropic least-squares methods and the *R*-factor is presently 0·19. Further refinement is in progress.

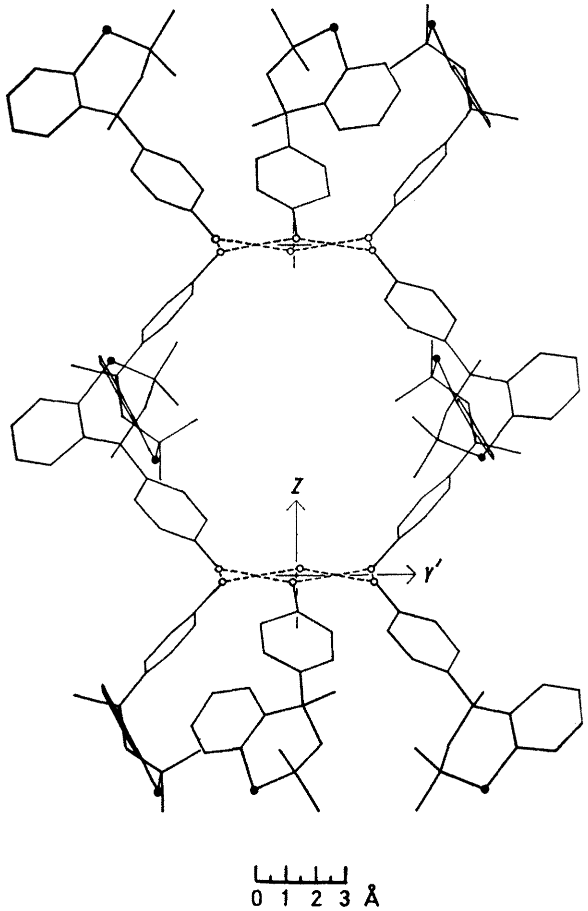


FIGURE. *The structure projected along the* a-*axis, showing the cavity. Two molecules of* (I), *which lie directly above and below the cavity as viewed in this direction, have been excluded apart from their hydroxyl oxygen atoms.* Y′ *is perpendicular to the* a- *and* c-*axes.*

The Table contains the atomic co-ordinates of the host molecule at this stage of the analysis.

The basic feature of the structure is the linking of the hydroxy-groups of six molecules by a network of hydrogen bonds such that the oxygen atoms form a distorted hexagon

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† The crystals of the ethanol clathrate of (I) are isomorphous with the guest-free form of (I)[3] and with clathrates formed by Dianin's compound, 4-*p*-hydroxyphenyl-2,2,4-trimethylchroman.[4,5]

of radius 2·9 Å. Three of the oxygen atoms come from molecules of (I) of one configuration which lie below the hexagon and three from molecules of (I) of the opposite configuration which lie above the hexagon. Two such groups of six molecules are stacked along the *c*-axis forming a cage capable of entrapping two ethanol molecules. Thus the top and bottom of a cage are formed by hexagons of oxygen atoms which are a unit translation in the *c*-axis direction apart, *i.e.* 10·90 Å. The walls of each cage are formed by six molecules; three are of one configuration and are involved in hydrogen bonding at the lower end of the cage and the remaining three of the other configuration are involved in hydrogen bonding at the upper end of the cage.

In the diagram, ten of the twelve molecules of (I) are shown which form the hexagon of oxygen atoms round (0, 0, 0) and (0, 0, 1)‡ with six molecules, three from each set, forming a cage with centre (0, 0, $\frac{1}{2}$). (Two of the six molecules forming the cage are represented by their oxygen atoms alone, so that the cavity will be seen more clearly.) The points (0, 0, 0), (0, 0, 1), and (0, 0, $\frac{1}{2}$) all possess $\bar{3}$ symmetry.[6] The complete structure consists of columns of molecules similar to the one illustrated packed along the *c*-axis forming cages round the points (0, 0, $\frac{1}{2}$), ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{6}$), and ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{5}{6}$).

The other interesting feature of the cage is that the *gem*-dimethyl groups of the six molecules of the cage point into the cavity and form a waist at approximately $Z = \frac{1}{2}$ in the section of the structure shown. Six methyl groups, one from each molecule, form a distorted hexagon of carbon atoms at the waist with a radius of 4·16 Å.

The contents of the cage will exhibit the symmetry of the cage, namely $\bar{3}$. As the ethanol molecule does not possess this symmetry, it is likely that the two molecules will be disordered. Attempts are under way to locate the ethanol molecules in this clathrate and other guest molecules in related clathrates.

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‡ The co-ordinates given in the text and in the Table are in fractional units of the hexagonal unit cell edge.[6]

[1] H. M. Powell, "Clathrates", in "Non-stoichiometric Compounds", ed. L. Mandelcorn, Academic Press, New York, 1964, p. 438.
[2] D. D. MacNicol, *Chem. Comm.*, 1969, 836.
[3] F. B. Wilson and H. H. Mills, unpublished work.
[4] H. M. Powell and B. D. P. Wetters, *Chem. and Ind.*, 1955, 256.
[5] J. L. Flippen and J. Karle, *Acta Cryst.*, 1969, **25**, *A*, S91.
[6] "International Tables for X-ray Crystallography", Kynoch Press, Birmingham, 1965, p. 253.