A Synthetic and Structural Investigation of the Role of Hydrogen Bonding in Clathrate Formation

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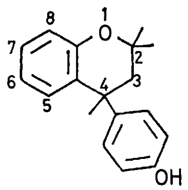
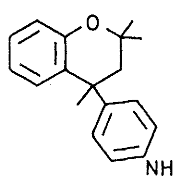
A study of molecules related to Dianin's compound (I) in which the hydroxy-function is replaced by another group capable of forming hydrogen bonds is described. The amine (II) crystallises with spontaneous resolution, without incorporation of solvent. The thiol (III) shows an interesting duality of behaviour, crystallising unsolvated with spontaneous resolution from cyclohexane, but forming a true clathrate with carbon tetrachloride. This clathrate crystallises in the trigonal space group $R\bar{3}$, with a = 27.063, c = 12.074 Å, with 18 host and 6 guest molecules in the unit cell. The structure was solved by direct methods, and refined to a final R value of 10.4% for 1 475 independent diffractometer data. Near planar hexagons of sulphur atoms, linked by SH · · · S hydrogen bonds, form the top and bottom of each closed cage in the clathrate structure.

A FASCINATING aspect of the chemistry of clathrates, or cage-type multimolecular inclusion compounds, is the possibility of defining the factors responsible for cage formation. The present study of inclusion behaviour is specifically concerned with the role of hydrogen bonding in clathrates.

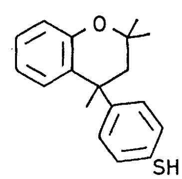
A common structural feature of the clathrates formed by Dianin's compound (I) [1-3] and a 2-nor-analogue,[4] 4-*p*-hydroxyphenyl-2,2,4-trimethylthiochroman (Va) [5-7] and its 8-methyl-analogue [8], phenol,[9] and hydroquinone [10] is the linking of the hydroxy-groups of six molecules by a network of OH · · · O hydrogen bonds such that the oxygen atoms form a hexagon.



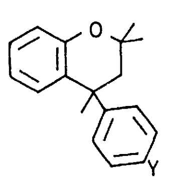
(I)



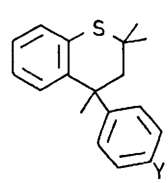
(II)



(III)



(IV)a; Y = O·CSNMe$_2$
b; Y = S·CONMe$_2$



(V)a; Y = OH
b; Y = O·CS·NMe$_2$
c; Y = S·CO·NMe$_2$
d; Y = NH$_2$
e; Y = SH

Following preliminary communications,[11,12] we now report the results of a detailed study which sought to determine if it is possible to replace such a key hydroxy-group by another hydrogen bonding function while still retaining the ability to form clathrates. We have prepared the amine (II) and the thiol (III), together with the related compounds (Vd) and (Ve). Compound (III) had indeed been found to form clathrates, and we have performed a single-crystal X-ray diffraction analysis of the CCl_4 clathrate of (III) to determine the detailed geometry of the hydrogen bonding and also to elucidate the nature of the voids available for guest accommodation. Also briefly considered is the effect of varying the size of the guest on the dimensions of the hydrogen-bonded hexagons of a given host.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on Varian T-60, HA-100, and XL-100 instruments with $CDCl_3$ as solvent and $SiMe_4$ as internal standard. Mass spectra were recorded on an A.E.I.–G.E.C. MS 12 instrument and i.r. spectra on Perkin-Elmer 225 and Unicam SP 1000 spectrometers. M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected.

O-[p-(2,2,4-*Trimethylchroman*-4-*yl*)*phenyl*] *Dimethylthiocarbamate* (IVa).—Dianin's compound (I) (11.33 g, 0.04 mol) [13] as the ethanol adduct was added under nitrogen to a solution of sodium metal (1.07 g, 0.05 g-atom) in absolute ethanol (40 ml), more ethanol being added until complete dissolution was achieved on heating. Removal of solvent under reduced pressure gave the sodium salt of (I). Dimethylthiocarbamoyl chloride (8.41 g, 0.07 mol) in dry dimethylformamide (56 ml) was added to this salt at 10 °C, and the reaction mixture stirred for 1.5 h at 40—45 °C, according to the method of Newman and Karnes.[14] On cooling the mixture was poured into water (120 ml) and extracted with benzene–n-hexane (4 : 1) (4 × 100 ml), the combined extracts being washed with water, 5% NaOH solution, and finally with NaCl solution (3 × 100 ml in each case). The dried solution ($MgSO_4$) was evaporated to give a yellow oil, which on recrystallisation (twice) from methanol yielded (IVa) (90%), m.p. 139—141 °C [Found: C, 70.75; H, 6.85; N, 4.0%; M (mass spec), 355. $C_{21}H_{25}NO_2S$ requires C, 70.96; H, 7.09; N, 3.94%; M, 355]; $\nu_{max.}$ (KBr) 1528, and 1 204 cm^{-1}; τ($CDCl_3$) 9.06, 8.65, and 8.27 (each 3 H, s, Me), 7.75 (2 H, AB, δ_{AB} = 0.28 p.p.m., J 14 Hz, methylene), 6.68, and 6.56 (each 3 H, s, NMe_2), and 2.6—3.3 (8 H, complex, aromatic ^{1}H).

S-[p-(2,2,4-*Trimethylchroman*-4-*yl*)*phenyl*] *Dimethylthiocarbamate* (IVb).—Pure, dry compound (IVa) (4.0 g, 0.11 mol) was heated [14] in an evacuated pyrolysis tube at 270 °C in a Wood's metal bath for 1.5 h. The resultant gummy glass was pure by ^{1}H n.m.r., but a sample recrystallised from ethanol–benzene formed clusters of glassy needles, m.p. 128—129 °C [Found: C, 71.1; H, 7.25; N, 3.65; S, 8.85%; M (mass spec.) 355. $C_{21}H_{25}NO_2S$ requires C, 70.98; H, 7.05;

N, 3.94; S, 9.02%; *M*, 355]; $\nu_{max.}$ (KBr) 1 665 cm^{-1} (C=O); τ($CDCl_3$) 9.06, 8.28, and 8.65 (each 3 H, s), 7.76 (2 H, AB, δ_{AB} = 0.31 p.p.m., J_{AB} = 14 Hz), 6.95 (6 H, s), and 2.5—3.3 (8 H, aromatic ^{1}H).

4-p-*Mercaptophenyl*-2,2,4-*trimethylchroman* (III).—A solution of the above pyrolysis product (IVb) in methanol (110 ml) was added to a 10% NaOH solution (56 ml) and the mixture refluxed under nitrogen for 20 h; a white solid was deposited as the mixture cooled. The product was extracted into benzene (3 × 150 ml) and the combined extracts were washed with water (100 ml) and dried ($MgSO_4$). Solvent evaporation left a pale yellow oil which solidified with time; recrystallisation from cyclohexane gave unsolvated material (90%), m.p. 137—138 °C (slight sublimation at *ca.* 107 °C) [Found (from benzene): C, 76.2; H, 7.25%; *M* (mass spec.) 284. $C_{18}H_{20}OS$ requires C, 76.03; H, 7.09%; *M* 284]; $\nu_{max.}$ (KBr) 2 546 cm^{-1} (SH); τ($CDCl_3$) 9.06, 8.64, and 8.32 (each 3 H, s, Me), 7.80 (2 H, AB, δ_{AB} = 0.27 p.p.m., J_{AB} = 14 Hz, methylene), 6.6 (1 H, s, S*H*), and 2.7—3.3 (8 H, complex, aromatic ^{1}H).

Clathrates with a 3 : 1 host : guest ratio were formed with (i) CCl_4 (Found: Cl, 15.0%. $3C_{18}H_{20}OS{\cdot}CCl_4$ requires Cl 15.67%); m.p. 45—90 °C; $\nu_{max.}$ (Nujol, crystals lightly ground) 2 506 cm^{-1}, $\Delta\nu_{\frac{1}{2}}{}^{a}$ *ca.* 70 cm^{-1}: (ii) CCl_3Br (Found: halogen, 18.85%. $3C_{18}H_{20}OS{\cdot}CCl_3Br$ requires halogen, 18.85%), m.p. 50—80 °C; (iii) CCl_3CH_3 (ratio by ^{1}H n.m.r. integration); m.p. 45—80 °C.

These three adducts appear to form only in the presence of minute amounts of Dianin's compound (I). Reproducible inclusion compound formation is ensured by deliberate addition of 2% by weight of (I). No inclusion behaviour has been found for the compounds (II), (Vd), and (Ve), even with the addition of small amount of (I).

O-[p-(2,2,4-*Trimethylthiochroman*-4-*yl*)*phenyl*] *Dimethylthiocarbamate* (Vb).—This compound was prepared analogously to (IVa), but using 4-*p*-hydroxyphenyl-2,2,4-trimethylthiochroman [7] (Va) (9.8 g, 0.033 mol). After work-up and recrystallisation from methanol (450 ml), 9.69 g (80%) of glistening white needles were obtained, m.p. 140—141 °C [Found: C, 67.95; H, 6.85; N, 3.7; S, 17.6%; *M* (mass spec.) 371. $C_{21}H_{25}NOS_2$ requires C, 67.85; H, 6.78; N, 3.77; S, 17.26%; *M* 371]; $\nu_{max.}$ (KBr) 1 538, 1 498, 1 206, 1 168, and 1 119 cm^{-1}; τ($CDCl_3$) 8.88, 8.57, and 8.17 (each 3 H, s), 7.68 (2 H, AB, δ_{AB} = 0.32 p.p.m., J_{AB} = 14 Hz), 6.67 and 6.54 (each 3 H, s, NC*H*$_3$), and 2.65—3.15 (8 H aromatic ^{1}H).

S-[p-(2,2,4-*Trimethylthiochroman*-4-*yl*)*phenyl*] *Dimethylthiocarbamate* (Vc).—Pyrolysis of (Vb) (7.5 g, 0.02 mol) as described for (IVa) gave a quantitative yield of the title compound, greater than 95% pure by n.m.r. A little material was recrystallised for analysis with difficulty from n-pentane–ethanol–benzene, m.p. 105.5—107.5 °C [Found: C, 68.2; H, 6.75; N, 3.75; S, 17.70%; *M* (mass spec.) 371. $C_{21}H_{25}NOS_2$ requires C, 67.85; H, 6.8; N, 3.75; S, 17.25%; *M*, 371]; $\nu_{max.}$ (KBr) 1 666 cm^{-1} (C=O); τ($CDCl_3$) 8.88, 8.57, and 8.19 (each 3 H, s), 7.69 (2 H, AB, δ_{AB} = 0.33 p.p.m. J_{AB} = 14 Hz), 6.93 (6 H, s, NC*H*$_3$), and 2.5—3.1 (8 H, aromatic ^{1}H).

4-p-*Mercaptophenyl*-2,2,4-*trimethylthiochroman* (Ve).—Hydrolysis of (Vc) (6.5 g, 0.018 mol) as described for (IVb) followed by benzene extraction and solvent removal afforded a white powder (4.9 g, 93%), pure by n.m.r. On recrystallisation from cyclohexane–ethanol, fine white needles were obtained, m.p. 137—138 °C [Found: C, 72.07; H, 6.79; S, 21.02%; *M* (mass spec.) 300. $C_{18}H_{20}S_2$ requires C, 71.96; H, 6.71; S, 21.34%; *M* 300]; $\nu_{max.}$ (KBr) 2 544 cm^{-1} (SH); τ($CDCl_3$) 8.90, 8.60, and 8.25 (each 3 H, s), 7.74, (2 H, AB, δ_{AB} = 0.32 p.p.m., J_{AB} = 14 Hz), 6.64 (1 H, S*H*), and 2.6—3.2 (8 H, aromatic ^{1}H).

4-p-*Aminophenyl*-2,2,4-*trimethylchroman* (II).—A mixture of 2-phenyl-3-*p*-(2,2,4-trimethylchroman-4-yl)phenylquinazolin-4(3*H*)-one (VIa) [15] (4.5 g, 0.009 5 mol) was stirred at 150 °C for 22 h in ethylene glycol (100 ml) with KOH pellets (6.5 g) under nitrogen. After ether extraction (3 × 100 ml), washing with brine, and removal of solvent, the amine (II) (2.37 g, 93%) was recrystallised from ethanol to give prisms, m.p. 136—137 °C (sealed tube) [Found: C, 80.6; H, 7.6; N, 5.5%; *M* (mass spec.) 267.162 04. $C_{18}H_{21}NO$ requires C, 80.86; H, 7.92; N, 5.24%; *M* 267.162 306]; $\nu_{max.}$ (KBr) 3 463 and 3 368 cm^{-1} (NH); τ($CDCl_3$) 9.03, 8.63, 8.32 (each 3 H, s), 7.81 (2 H, AB, δ_{AB} = 0.29 p.p.m., J_{AB} = 14 Hz), 6.2—6.7 (2 H, broad N*H*$_2$), and 2.6—3.6 (aromatic ^{1}H).

4-p-*Aminophenyl*-2,2,4-*trimethylthiochroman* (Vd).—This was prepared analogously to compound (II) from (VIb) [15] (6.7 g, 0.013 7 mol) which on hydrolysis yielded the crude amine (3.6 g, 92.5%), which was greater than 95% pure on the evidence of n.m.r. spectroscopy. Recrystallisation from ethanol after decolourisation with powdered animal charcoal gave colourless needles, m.p. 137—138 °C [Found: C, 76.15; H, 7.45; N, 4.65; S, 11.65%; *M* (mass spec.) 285. $C_{18}H_{21}NS$ requires C, 76.30; H, 7.47; N, 4.94; S, 11.31%; *M* 283]; $\nu_{max.}$ (KBr) 3 435 and 3 347 cm^{-1} (N–H); τ($CDCl_3$) 8.9, 8.61, and 8.27 (each 3 H, s), 7.73 (2 H, AB, δ_{AB} = 0.32 p.p.m., J_{AB} = 14 Hz), 6.49 (2 H, broad N*H*$_2$), and 2.7—3.4 (8 H, aromatic ^{1}H).

The amine (Vd) crystallised unsolvated from carbon tetrachloride, t-butyl alcohol, cyclohexane, acetone, and 1,1,1-trichloroethane.

X-*Ray Crystal Structure Analysis of the Carbon Tetrachloride Adduct of Compound* (III).—*Crystal data.* $C_{18}H_{20}OS{\cdot}\frac{1}{3}CCl_4$; *M* = 335.7; a host : guest ratio of 3 : 1 was found by microanalysis for chlorine; trigonal space group $R\bar{3}$ (or *R* 3), referred to a hexagonal unit cell with *a* = 27.063, *c* = 12.074 Å, *Z* = 18 (host, +6 molecules of CCl_4), *U* = 7 658.4 Å^3, D_c = 1.31 g cm^{-3}, *F* (000) = 3 180. Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 3.95 cm^{-1}. The crystal used was an initially colourless (some red colouration after data collection) extended hexagon of approximate dimensions 1.30 × 0.65 × 0.65 mm, the crystal being sealed in a Lindemann capillary, as included solvent is lost on standing in air.

Crystallographic Measurements.—Least-squares best-cell dimensions were obtained by a treatment of the θ, χ, and ϕ setting angles of 22 reflections measured on a Hilger and Watts automatic diffractometer. The intensities were measured by the θ—2θ step-scan procedure with Zr-filtered Mo-K_α radiation. Background counts were taken at each end of the scan range. The intensities of three reflections were monitored after every 60 intensity measurements, and the results used to place the reflections on a common scale; the changes in the standard intensities during data collection were small (<6%). Reflections were surveyed out to $\theta \leqslant 30°$, with an option whereby those intensities with $I \leqslant 2.\sigma(I)$ were not measured. The intensity values were corrected for Lorentz-polarisation effects, but not for absorption, and 1 475 independent reflections, with $I > 2.\sigma(I)$, were obtained.

Structure Analysis.—The structure was solved in the centrosymmetric space group $R\bar{3}$ (this choice was justified by the success of the analysis), by direct phase-determining methods using 'MULTAN'[16] and the 200 reflections having the largest $|E|$ magnitudes. An E-map computed with that set of phases which gave the highest figure of merit and the lowest residual revealed all 20 of the host non-hydrogen atom positions. These approximate atomic parameters were adjusted by several cycles of full-matrix least-squares calculations using the programme CRYLSQ from the '*X*-RAY '72' system,[17] and for anisotropic temperature factors the R value was 28.5%.

Subsequent difference electron-density distributions revealed the 20 hydrogen atoms of the host molecule and the position of the guest molecule CCl_4 in terms of two orientations (whose occupancies were later refined, and gave a host : guest value of 3 : 0.85). When these atoms were included in the least-squares calculations (with isotropic temperature factors, and with the co-ordinates of the four atoms which lie on the z axis being fixed) the R value converged to a final value of 10.4% ($R_w = 9.9\%$). The weighting scheme employed in the last cycles of the least-squares calculations was $w = (11.150 + 0.936.|F| - 0.003.|F|^2)^{-1}$.

Calculations were carried out on an IBM 370/168 computer at Newcastle. Observed and calculated structure factors, anisotropic temperature factors, and hydrogen atom co-ordinates and thermal parameters are listed in Supplementary Publication No. 22486 (15 pp).* The scattering factors employed for S, Cl, O, and C atoms are those listed in ref. 18, those for H in ref. 19. The anomalous dispersion was allowed for in the least-squares calculations, with values of $\Delta f'$ and $\Delta f''$ for sulphur and chlorine taken from ref. 20. Atomic fractional co-ordinates of the host molecule are listed in Table 1(a); guest atom co-ordinates, isotropic temperature factors, and occupancy factors are given in Table 1b; and various parameters connected with the clathrate's molecular geometry are listed in Tables 2—4.

TABLE 1

(a) Atomic co-ordinates (× 10^4) *

	X	Y	Z
O(1)	7 372(3)	8 231(3)	−1 282(5)
C(2)	7 732(4)	8 819(4)	−0 931(7)
C(3)	7 367(4)	9 009(3)	−0 286(7)
C(4)	7 054(3)	8 646(3)	0 728(7)
C(5)	6 443(4)	7 588(4)	1 136(8)
C(6)	6 222(4)	7 029(4)	0 897(10)
C(7)	6 387(4)	6 871(4)	−0 063(10)
C(8)	6 766(4)	7 283(4)	−0 762(9)
C(9)	7 004(3)	7 863(3)	−0 516(8)
C(10)	6 838(3)	8 022(3)	0 468(7)
C(11)	7 427(4)	8 842(3)	1 780(7)
C(12)	7 574(4)	8 496(4)	2 350(7)
C(13)	7 894(4)	8 674(4)	3 345(7)
C(14)	8 071(4)	9 219(5)	3 730(8)
C(15)	7 955(5)	9 580(4)	3 134(9)
C(16)	7 636(4)	9 387(4)	2 159(8)
C(17)	6 540(4)	8 738(4)	0 936(9)
C(18)	8 227(4)	8 863(4)	−0 281(8)
C(19)	7 936(4)	9 156(4)	−2 013(8)
S(20)	8 417(2)	9 436(2)	5 009(3)

(b) Atomic co-ordinates, thermal and population (P.P.) parameters for carbon tetrachloride molecules

Atom	X	Y	Z	U	P.P.
			Molecule I		
Cl(1)	0.929 8(2)	0.962 8(2)	0.223 8(5)	0.154(2)	0.85(1)
Cl(4)	1.0000	1.0000	0.407 0(20)	0.185(7)	0.48(4)
C(111)	1.0000	1.0000	0.266 2(45)	0.075(10)	0.48(4)
			Molecule II		
Cl(1)	0.929 8(2)	0.962 8(2)	0.223 8(5)	0.154(2)	0.85(1)
Cl(42)	1.0000	1.0000	0.055 0(20)	0.197(10)	0.37(3)
C(112)	1.0000	1.0000	0.195 0(45)	0.040(8)	0.37(3)

* These atoms have anisotropic thermal parameters of the form exp $[-2\pi^2(h^2a^{*2}U_{11} + \ldots 2hka^*b^*U_{12} + \ldots)]$.

* For details of supplementary publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1977, Index issue.

TABLE 2

Interatomic distances (Å) and valency angles (°), with standard deviations in parentheses

(a) Bond lengths

O(1)–C(2)	1.453(10)	C(6)–C(7)	1.384(16)
O(1)–C(9)	1.360(11)	C(7)–C(8)	1.366(14)
C(2)–C(3)	1.532(12)	C(8)–C(9)	1.396(13)
C(2)–C(18)	1.508(13)	C(9)–C(10)	1.413(12)
C(2)–C(19)	1.528(13)	C(11)–C(12)	1.371(12)
C(3)–C(4)	1.533(12)	C(11)–C(16)	1.367(13)
C(4)–C(10)	1.516(11)	C(12)–C(13)	1.417(12)
C(4)–C(11)	1.542(12)	C(13)–C(14)	1.385(14)
C(4)–C(17)	1.552(12)	C(14)–C(15)	1.371(14)
C(5)–C(6)	1.351(13)	C(14)–S(20)	1.748(10)
C(5)–C(10)	1.384(12)	C(15)–C(16)	1.397(14)
Cl(4)–C(111)	1.70(6)	Cl(1)–C(111)	1.72(2)
Cl(42)–C(112)	1.69(6)	Cl(1)–C(112)	1.68(1)
S(20)–H(21)	1.12(6)		

Means: $C(sp^3)$–H 0.93
$C(sp^2)$–H 0.95

(c) Valency angles

C(9)–O(1)–C(2)	116.6(7)	C(3)–C(2)–O(1)	109.0(7)
C(18)–C(2)–O(1)	108.6(7)	C(19)–C(2)–O(1)	104.4(7)
C(8)–C(9)–O(1)	115.8(8)	C(10)–C(9)–O(1)	125.2(7)
C(18)–C(2)–C(3)	113.9(7)	C(19)–C(2)–C(3)	109.7(7)
C(4)–C(3)–C(2)	115.7(7)	C(19)–C(2)–C(18)	110.8(7)
C(10)–C(4)–C(3)	109.3(7)	C(11)–C(4)–C(3)	112.3(7)
C(17)–C(4)–C(3)	106.2(7)	C(11)–C(4)–C(10)	112.1(7)
C(17)–C(4)–C(10)	109.5(7)	C(5)–C(10)–C(4)	122.0(8)
C(9)–C(10)–C(4)	120.6(7)	C(17)–C(4)–C(11)	107.2(7)
C(12)–C(11)–C(4)	122.7(7)	C(16)–C(11)–C(4)	119.6(8)
C(10)–C(5)–C(6)	123.3(9)	C(7)–C(6)–C(5)	119.5(9)
C(9)–C(10)–C(5)	117.2(7)	C(8)–C(7)–C(6)	119.5(9)
C(9)–C(8)–C(7)	121.5(9)	C(10)–C(9)–C(8)	118.9(8)
C(16)–C(11)–C(12)	117.6(8)	C(13)–C(12)–C(11)	122.1(8)
C(15)–C(16)–C(11)	122.0(9)	C(14)–C(13)–C(12)	118.2(8)
C(15)–C(14)–C(13)	120.1(9)	S(20)–C(14)–C(13)	119.7(7)
S(20)–C(14)–C(15)	120.0(8)	C(16)–C(15)–C(14)	119.7(9)
C(14)–S(20)–H(21)	103.1(33)	Cl(1)–C(111)–Cl(1^{I})	111.6(16)
Cl(1)–C(111)–Cl(4)	107.3(17)	Cl(1)–C(112)–Cl(1^{I})	115.8(12)
Cl(1)–C(112)–Cl(42)	101.9(18)		

Means: $C(sp^3)$–$C(sp^3)$–H 108.6
$C(sp^2)$–$C(sp^2)$–H 119.4
H–$C(sp^3)$–H 109.6

The superscripts refer to the following transformations of atomic co-ordinates: I $-y, x - y, z$.

DISCUSSION

When the amino-analogue (II) of Dianin's compound (I) was recrystallised from ethanol it was found that spontaneous resolution had occurred.[21] These unsolvated crystals are orthorhombic, space group $P2_12_12_1$, and exhibit a closer-packed molecular arrangement than that found[1] for the host molecules of (I) (Table 5). Interestingly the unit cell dimensions of (II) correspond closely to those of resolved $S(-)$-Dianin's compound.[22]

In contrast, the thiol 4-*p*-mercaptophenyl-2,2,4-trimethylchroman (III) forms both solvated and unsolvated crystals. Spontaneously resolved, unsolvated crystals are formed from cyclohexane (lattice parameters are given in Table 5); while inclusion com-

TABLE 3

Torsion angles (°), with standard deviations in parentheses

C(9)–O(1)–C(2)–C(3)	−44.4(9)
C(9)–O(1)–C(2)–C(19)	−161.5(7)
C(2)–O(1)–C(9)–C(10)	17.2(12)
C(18)–C(2)–C(3)–C(4)	−64.4(10)
C(2)–C(3)–C(4)–C(10)	−38.5(9)
C(2)–C(3)–C(4)–C(17)	−156.6(7)
C(3)–C(4)–C(10)–C(9)	9.0(10)
C(11)–C(4)–C(10)–C(9)	−116.3(8)
C(17)–C(4)–C(10)–C(9)	124.9(8)
C(3)–C(4)–C(11)–C(16)	59.3(10)
C(10)–C(4)–C(11)–C(16)	−177.1(8)
C(17)–C(4)–C(11)–C(16)	−56.9(10)
C(6)–C(5)–C(10)–C(4)	176.7(9)
C(5)–C(6)–C(7)–C(8)	−0.8(15)
C(7)–C(8)–C(9)–O(1)	−179.5(9)
O(1)–C(9)–C(10)–C(4)	2.1(13)
C(8)–C(9)–C(10)–C(4)	−175.7(8)
C(4)–C(11)–C(12)–C(13)	−177.0(8)
C(4)–C(11)–C(16)–C(15)	177.1(9)
C(11)–C(12)–C(13)–C(14)	−1.3(13)
C(12)–C(13)–C(14)–S(20)	174.9(7)
S(20)–C(14)–C(15)–C(16)	−174.7(8)
C(9)–O(1)–C(2)–C(18)	80.2(9)
C(2)–O(1)–C(9)–C(8)	−164.9(8)
O(1)–C(2)–C(3)–C(4)	57.1(9)
C(19)–C(2)–C(3)–C(4)	170.8(7)
C(2)–C(3)–C(4)–C(11)	86.6(9)
C(3)–C(4)–C(10)–C(5)	−166.6(8)
C(11)–C(4)–C(10)–C(5)	68.2(10)
C(17)–C(4)–C(10)–C(5)	−50.7(11)
C(3)–C(4)–C(11)–C(12)	−119.0(9)
C(10)–C(4)–C(11)–C(12)	4.5(11)
C(17)–C(4)–C(11)–C(12)	124.7(9)
C(10)–C(5)–C(6)–C(7)	−0.6(15)
C(6)–C(5)–C(10)–C(9)	1.0(13)
C(6)–C(7)–C(8)–C(9)	1.8(15)
C(7)–C(8)–C(9)–C(10)	−1.4(14)
O(1)–C(9)–C(10)–C(5)	177.9(8)
C(8)–C(9)–C(10)–C(5)	0.1(12)
C(16)–C(11)–C(12)–C(13)	4.7(13)
C(12)–C(11)–C(16)–C(15)	−4.5(14)
C(12)–C(13)–C(14)–C(15)	−2.3(14)
C(13)–C(14)–C(15)–C(16)	2.5(15)
C(14)–C(15)–C(16)–C(11)	0.9(15)

pounds have been obtained from the solvents CCl_4, CCl_3Br, and CCl_3CH_3 (see Experimental section).

A comparison of the lattice parameters for the CCl_4 clathrate of (III) and the $CHCl_3$ clathrate of Dianin's compound (I) is given in Table 5. The similarity in axial lengths, allowing for the longer C–S bond in (III), suggested analogous host packing in the two structures.

A general view of the molecular structure of (III) (for clarity all hydrogen atoms have been omitted) is shown in Figure 1; the oxygen-containing ring has a distorted half-chair conformation with atoms C(2) and C(3)

TABLE 4

Displacements (Å) of atoms from planes through various sets of atoms

Plane (A): C(5)—(10)

C(5) −0.007, C(6) 0.002, C(7) 0.008, C(8) −0.010, C(9) 0.002, C(10) 0.004, O(1) −0.029, C(4) −0.080

Plane (B): C(11)—(16)

C(11) 0.026, C(12) −0.016, C(13) −0.005, C(14) 0.022, C(15) −0.011, C(16) −0.018, C(4) 0.083, S(20) 0.173

Plane (C): O(1), C(4), C(9), C(10)

O(1) −0.002, C(4) 0.004, C(9) 0.010, C(10) −0.008, C(2) −0.418, C(3) 0.262

displaced from the mean-plane of the atoms O(1), C(9), C(10), and C(4) by −0.42 and 0.26 Å respectively. This contrasts with the more symmetrical half-chair conformation found for (I), with displacements of

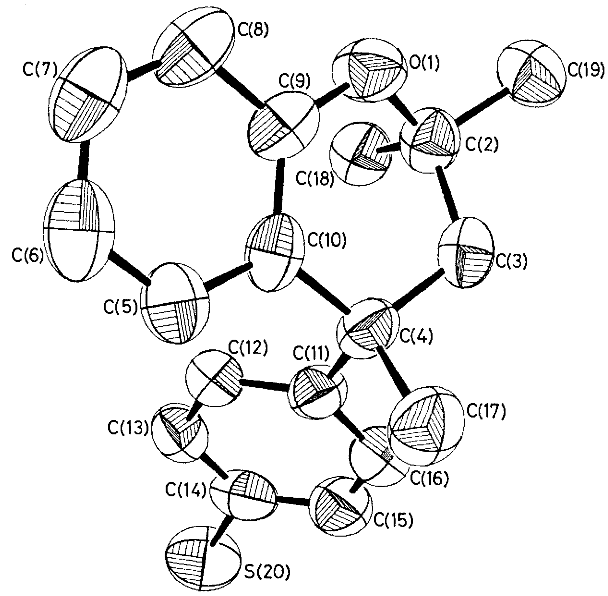


FIGURE 1 An ORTEP drawing showing a general view of the molecular structure of compound (III)

−0.32 and 0.36 Å calculated from the available data [1] for the chloroform clathrate.

Figure 2 illustrates the basic packing unit of the host structure of (III), 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.

TABLE 5

Some selected crystal data for Dianin's compound (I) and related molecules

Compound	Space group *	Lattice parameters	Guest	Host : Guest ratio	Ref.
(I)	$R\bar{3}$	$a = 27.116\ (3)$, $c = 11.023(2)$ Å	$CHCl_3$	6 : 1	1
(III)	$R\bar{3}$	$a = 27.063$, $c = 12.074$ Å	CCl_4	3 : 1	This work, 11, 12
	$P2_12_12_1$	$a = 10.66(2)$, $b = 13.55(3)$, $c = 10.50(1)$ Å			This work, 11, 12
(II)	$P2_12_12_1$	$a = 10.42(2)$, $b = 13.69(1)$, $c = 10.37(2)$ Å			11
Resolved Dianin's compound	$P2_12_12_1$	$a = 10.60(1)$, $b = 13.30(2)$, $c = 10.08(1)$ Å			†

* For $R\bar{3}$ the cell dimensions refer to a hexagonal unit cell containing 18 host molecules. † Crystals kindly provided by Professor J. Jacques (see ref. 22).

The sulphur atoms deviate from planarity by only ±0.01 Å, which can be compared with ±0.21 Å for the oxygen atoms in the hydrogen-bonded hexamer of the $CHCl_3$ clathrate of (I). The i.r. spectrum displays a broad ν(S–H) band at 2 506 cm^{-1}, $\Delta\nu_{\frac{1}{2}}{}^{a}$ *ca.* 70 cm^{-1}, whose position is compatible with unusually short S–H · · · S hydrogen bonding.[23] This interaction is substantiated by the S · · · S and S · · · H distances * of 3.76(1) Å and 2.67(9) Å respectively, and by the S–H · · · S angle of 164(5)°.[24]

Figure 3 shows the molecular packing of the host structure as viewed onto the *ac* plane. The two hexameric units shown are stacked along the *c*-axis such that their bulkier parts interlock forming a cage. The top and bottom of each cage are formed by hexagons of sulphur atoms one *c*-spacing apart, that is, 12.07 Å. The two disordered carbon tetrachloride guest molecules present in each cage are not shown.

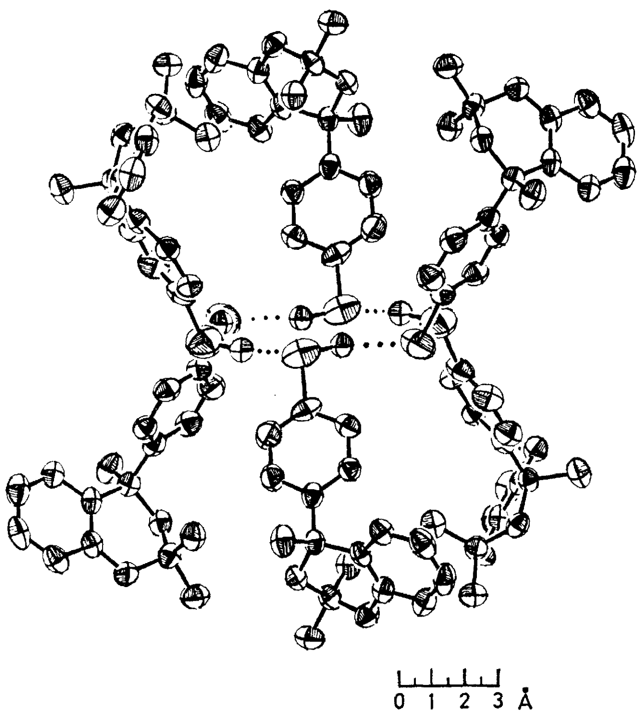


FIGURE 2 A general view of the hydrogen-bonded hexameric host unit of (III) in the CCl_4 clathrate

Allowance has been made for the CCl_4 guest molecules in terms of two orientations, both with a C–Cl bond collinear with the *c*-axis, and having common non-axial chlorine atoms (see Table 1a). In one orientation (molecule 1) the axial chlorine atom projects partially through the sulphur hexagon, and in the second orientation (molecule 2) the axial chlorine points into the waist region of the cavity. A section through the van der Waals' surface of the cavity for (III) is shown in Figure 4(a); this section is not dissimilar to that of the $CHCl_3$ clathrate of (I), given in Figure 4(b). Estimates of the 'free space' available in (III) and (I) are 264 and 181 $Å^3$ respectively. Calculation[25] of the molecular volume of the two CCl_4 guest species, 169 $Å^3$, indicates only moderate filling of the free-space available in the cage of (III). The shortest host to guest contact found is between Cl(1) and C(13), which is 3.44(1) Å; this value

* The above S · · · H distance is almost certainly unrealistically long owing to an artificial shortening of the S–H bond which occurred during refinement: the final S–H distance of 1.12 Å is significantly less than the expected value of *ca.* 1.35 Å. A possible secondary orientation of the thiol hydrogen atom was revealed in the final electron-density difference map; if real, this hydrogen atom is involved in only very weak hydrogen bonding.

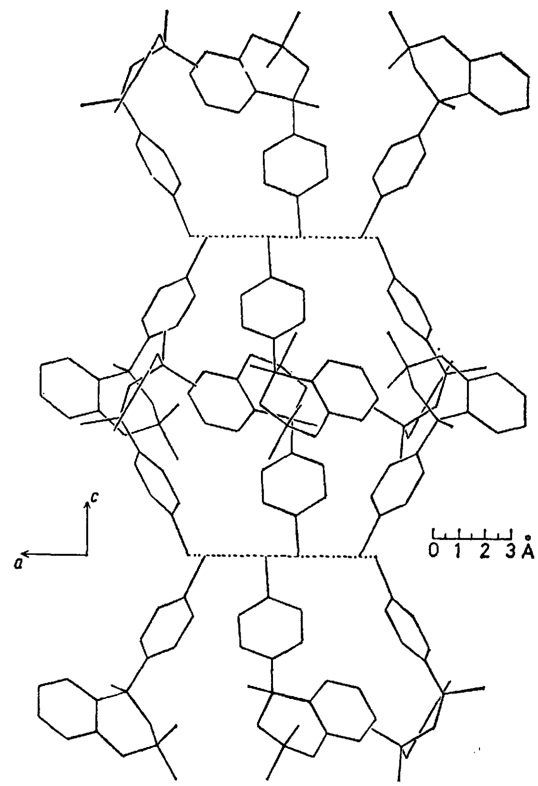


FIGURE 3 Structure of compound (III) looking onto the *ac* plane; the two disordered guest molecules (CCl_4) are not shown

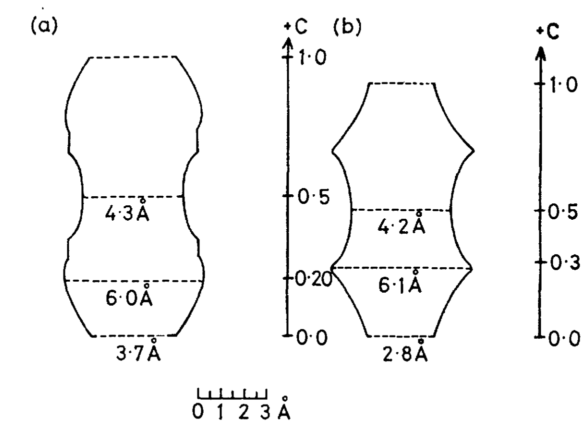


FIGURE 4 Section through the van der Waals surface of the cavity for: (a) compound (III) as the CCl_4 clathrate, (b) Dianin's compound (I) as the $CHCl_3$ clathrate, replotted from data of ref. 1

TABLE 6

Variation of lattice parameters, ν(OH), and O · · · O distance with guest size for clathrates of (Va)

Guest molecule	Host : Guest ratio	Lattice parameters	ν(OH) *	O · · · O distance	Ref.
Ethanol	3 : 1	$a = 27.81$, $c = 10.90$ Å	3 345 cm^{-1}	2.96(1) Å	5
2,5,5-Trimethylhex-3-yn-2-ol	6 : 1	$a = 27.91$, $c = 10.99$ Å	3 400 cm^{-1}	3.03(1) Å	6
Di-t-butylacetylene	6 : 1 †	$a = 28.00$, $c = 11.08$ Å	3 435 cm^{-1}	3.07(1) Å	‡

* Approximate band maxima. † In subsequent recrystallisations lower incorporations of di-t-butylacetylene were found. The i.r. value quoted was measured (microdisc) using the actual crystal employed for *X*-ray data collection. ‡ A. D. U. Hardy and D. D. MacNicol, unpublished results.

being shorter than the sum of the appropriate van der Waals radii (3.50 Å). This suggests the possibility of some charge-transfer [26] stabilisation of the cage structure. Although the cages of (III) are of closed nature, when the clathrate crystals are left in air they rapidly lose solvent, with apparent complete disruption of the crystal lattice.

Finally, Table 6 shows the effect of varying the guest molecule on lattice and other parameters for clathrates of the phenolic host 4-*p*-hydroxyphenyl-2,2,4-trimethylthiochroman (Va). As the bulk of the guest component increases slight increases in the *a* and *c* axial dimensions are observed. Significant increases in the O · · · O distance are found with increasing guest size, corresponding to a weakening of the hydrogen bonding in the hexameric unit [5-7] of (Va), which is paralled by the change in hydroxy-stretching frequency.

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