# Synthesis and Properties of the Inclusion Compound 2-Phenyl-3-p-(2,2,4-trimethylchroman-4-yl)phenylquinazolin-4(3H)-one; Use of Quartets in the Crystal Structure Determination of the Methylcyclohexane Clathrate

By **Christopher J. Gilmore, Andrew D. U. Hardy, David D. MacNicol,*** and **Derek R. Wilson,** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

The title compound (III) has been found to form stable adducts with a wide range of solvents. important classes of guest being cycloalkanes, cyclic ethers and ketones. alcohols. and aromatic molecules. An X-ray investigation of the inclusion compound formed with methylcyclohexane has been carried out. A key feature of the solution of this complex structure. which has 79 non-hydrogen atoms in the asymmetric unit. was the use of quartet relationships in the direct-method analysis. Crystals are triclinic. space group $P\bar{1}$. with a = 18.649(25). b = 19.443(25), c = 9.390(15) Å, α = 78.88(5). β = 98.97(5). γ = 118.16(10)°. with four host and two guest molecules in the unit cell. The structure was refined by least-squares methods to a final R of 0.098. employing 3 432 significant diffractometer data. The packing of host molecules of (III) is such that large closed cages are formed : in each of these clathrate voids two methylcyclohexane guest molecules are accommodated. Compound (V). a thio-analogue of (III), has also been prepared and found to exhibit inclusion behaviour.

In a preliminary communication [1] we have briefly described the unexpected ability of the title compound (III) to act as host in the formation of molecular inclusion compounds.[2] This property was discovered when (III) was characterised as a synthetic intermediate in the conversion [3] of Dianin's compound (Ia) into the

(I) a; Y = OH
b; Y = NH₂

(II) Z = O
(IV) Z = S

(III) Z = O
(V) Z = S
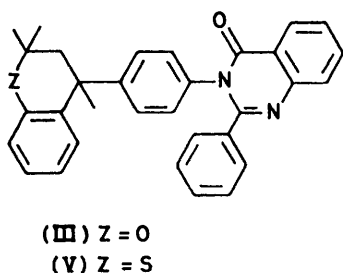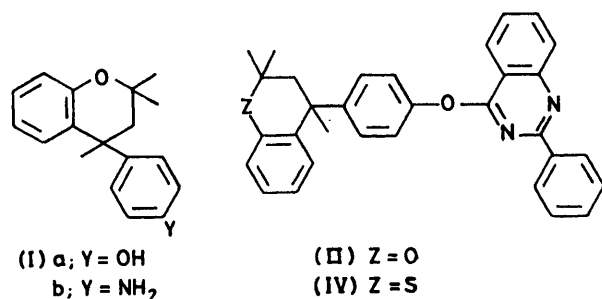
amino-analogue (Ib). Compound (II), the immediate precursor of (III), has been found to possess a much more limited ability to form adducts. We now report the results of a detailed study of the versatile host (III), for which thirty adducts have been prepared. In the

case of the inclusion compound with methylcyclohexane we have performed a single-crystal X-ray diffraction analysis in order to determine the molecular architecture of (III) and also to elucidate the geometry of the voids available for guest accommodation.

The inclusion properties of (V), a compound in which the ether oxygen of (III) is replaced by sulphur, are also discussed.

EXPERIMENTAL

M.p.s were determined as a Kofler hot-stage apparatus, i.r. spectra on a Perkin-Elmer 225 instrument, and ¹H n.m.r. spectra on a Varian HA 100 instrument with tetramethylsilane as internal standard and CDCl₃ as solvent. Mass spectra were obtained on an A.E.I.–G.E.C. MS12 spectrometer.

2-Phenyl-4-p-(2,2,4-trimethylchroman-4-yl)phenoxyquinazoline (II).—Dianin's compound (Ia) [4] (13.95 g, 0.05 mol) as the methanol adduct was added to a magnetically stirred suspension of 60% NaH (2.4 g, 0.06 mol) in dry bis-(2-methoxyethyl) ether (30 ml) under nitrogen. After heating until all the phenol had dissolved, 4-chloro-2-phenyl-quinazoline (12 g, 0.05 mol) was added [5] and the mixture stirred at 145 °C for 40 min, and then poured on to crushed ice (500 g). In order to remove traces of the extremely insoluble Dianin's compound (Ia), the crude product in toluene (750 ml) was extracted with aqueous KOH (5N, 4 × 100 ml). After evaporation of the toluene, the dense granular product was recrystallised from pentyl alcohol giving unsolvated crystals, m.p. 172—173 °C, 15.1 g (80%) (Found: C, 81.15; H, 6.06; N, 6.06. C₃₂H₂₈N₂O₂ requires C, 81.33; H, 5.97; N, 5.93%; *M*, 472); *m/e* 472; $\nu_{max.}$ (KBr) 1 572, 1 484, 1 201, and 710 cm⁻¹; τ (CDCl₃) 8.94, 8.58, 8.22 (each 3 H, s), 7.68 (2 H, ABq, δ_{AB} 0.32 p.p.m., J_{AB} 14 Hz), and 1.6—3.2 (17 H, aromatic H). Recrystallisation of unsolvated (II) from benzene gives a 1 : 1 adduct with this solvent;

[1] A. D. U. Hardy, D. D. MacNicol, and D. R. Wilson, *J.C.S. Chem. Comm.*, 1974, 783.

[2] 'Non-stoicheiometric Compounds,' ed. L. Mandelcorn, Academic Press, New York, 1964; S. M. Hagan, 'Clathrate Inclusion Compounds,' Reinhold, New York, 1962; F. Cramer, 'Einschlussverbindungen,' Springer–Verlag, Berlin, 1954; V. M. Bhatnagar, 'Clathrate Compounds,' Chemical Publishing Co., New York, 1970; S. G. Frank, *J. Pharm. Sci.*, 1975, **64**, 1585.

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

[4] W. Baker, A. J. Floyd, J. F. W. McOmie, G. Pope, A. S. Weaving, and J. H. Wilde, *J. Chem. Soc.*, 1956, 2010.

[5] R. A. Scherrer and H. R. Beatty, *J. Org. Chem.*, 1972, **37**, 1681.

melting starts at 89—93°, rearrangement of microcrystallites at 95°, and finally melting at 171—172 °C (Found: C, 82.97; H, 6.37. $C_{38}H_{34}N_2O_2$ requires C, 82.88; H, 6.22%); $\nu_{max.}$ (KBr) 683 cm^{-1}. The solvent 1,4-dioxan also forms a 1 : 1 adduct as shown by ^{1}H n.m.r. Compound (II) does not exhibit general inclusion properties, the solvents fluorobenzene, chlorobenzene, pyridine, pyrrole, furan, thiophen, tetrahydrofuran, and acetonitrile not being retained.

2-*Phenyl*-3-p-(2,2,4-*trimethylchroman*-4-*yl*)*phenylquinazo-lin*-4(3H)-*one* (III).—(II) (4.72 g, 0.01 mol) was heated [5] in an evacuated sealed tube in a Wood's metal bath at 337° for 5½ h. The resultant red glass was recrystallised from methanol (or nitromethane), giving unsolvated (III), m.p. 176.5—178.6 °C, 3.8 g (80%) (Found: C, 81.56; H, 6.24; N, 6.01. $C_{32}H_{28}N_2O_2$ requires C, 81.33; H, 5.97; N, 5.93%; M, 472); m/e 472; $\nu_{max.}$ (KBr) 1 688 cm^{-1} (C=O); τ (CDCl$_3$) 9.28, 8.63, 8.31 (each 3 H, s), 7.79 (2 H, ABq, δ_{AB} 0.27 p.p.m., J_{AB} 14 Hz), and 1.5—3.3 (17 H, aromatic H).

Unsolvated (III) was recrystallised from various pure dry solvents and in many cases stable adducts were formed (Table 1). Some thermal analysis data for cycloalkane adducts of (III) are given in Table 2. However, among

TABLE 1

Inclusion compounds formed by (III)

Guest	Mol ratio host : guest [a]	M.p./°C
Cyclopropane [b]	1 : 1	104—120
Cyclobutane [b,c]	2 : 1	110—126
Cyclopentane	2 : 1	120—136
Cyclohexane	2 : 1	120—136
Cycloheptane	2 : 1	110—134
Cyclo-octane	2 : 1	108—117
Cyclodecane	2 : 1	107—114
Methylcyclohexane	2 : 1	115—120
Fluorocyclohexane	2 : 1	119—135
Chlorocyclohexane	2 : 1	107—127
Bromocyclohexane	2 : 1	119—127
Cyclopentanone	1 : 1	109—116
Cyclohexanone	2 : 1	111—127
Benzene	1 : 1	122—134
o-Xylene	2 : 1	126—133
p-Xylene	2 : 1	110—120
Fluorobenzene	2 : 1	114—118
Anisole	2 : 1	105—112
Isobutyl alcohol	2 : 1	120—122
t-Butyl alcohol	1 : 1	90—100
t-Butylamine	2 : 1	114—135
Tetrahydrofuran	1 : 1	123—137
Tetrahydropyran	1 : 1	105—134
1,4-Dioxan	1 : 1	107—130
Tetrahydrothiophen	2 : 1	110—131
Acetic acid	1 : 1	118—138
Carbon tetrachloride	1 : 1	105—112
1,2-Dibromoethane	2 : 1	103—120
1,2-Dibromotetrafluoroethane	2 : 1	121—128
Nitromethane [d]	1 : 1	100—109

[a] Determined by multiple integration of ^{1}H n.m.r. spectrum (CDCl$_3$ solution), and/or microanalysis for halogen, and given as nearest integral ratio. [b] Recrystallisation performed in a sealed tube. [c] Prepared by the method of D. S. Connor and E. R. Wilson (*Tetrahedron Letters*, 1967, 4925). [d] This solvent often gives unsolvated crystals, occasional formation of adduct possibly being result of chance seeding.

solvents not included are: ethanol, acetone, ethyl acetate, toluene, chlorobenzene, iodobenzene, cyclohexyl iodide, di-isopropyl ether, and bis-(2-methoxyethyl) ether. An

attempt to include white phosphorus, P_4, (CS$_2$ solution) gave unsolvated (III).

2-*Phenyl*-4-p-(2,2,4-*trimethylthiochroman*-4-*yl*)*phenoxy-quinazoline* (IV).—This compound was prepared analogously to (III), using 4-p-hydroxyphenyl-2,2,4-trimethylthio-chroman.[6] The crude solid was collected on a sinter and

TABLE 2

Thermal analysis data for some cycloalkane adducts of (III)

Guest molecule	% Weight loss	T_{Th} (escape)/°C [a]	$T_{max.}$/°C [b]
Cyclopropane	7.0 (8.2) [c]	95	125
Cyclobutane	6.0 (5.6) [d]	116	130
Cyclopentane	6.0 (6.9) [d]	122	140
Cyclohexane	8.0 (8.2) [d]	129	141
Cycloheptane	9.5 (9.4) [d]	104	128

[a] Approximate onset of weight loss for heating rate of 3° min^{-1}. [b] Approximate temperature of maximum solvent loss as indicated by thermal volatilisation analysis. [c] Calc. for host : guest ratio 1 : 1. [d] Calc. for host : guest ratio 2 : 1.

washed with aqueous NaOH (5 N, 2 × 100 ml) and brine, giving a white solid (80%) which was found to be pure by ^{1}H n.m.r. Unsolvated crystals were obtained on re-crystallisation from pentyl alcohol, m.p. 188—189 °C (Found: C, 78.6; H, 5.91; N, 5.45; S, 6.80. $C_{32}H_{28}N_2OS$ requires C, 78.65; H, 5.77; N, 5.74; S, 6.56%; M, 488); m/e 488; $\nu_{max.}$ (KBr) 1 484, 1 380, 1 347, 1 209, and 703 cm^{-1}; τ (CDCl$_3$) 8.78, 8.52, 8.13 (each 3 H, s), 7.59 (2 H, ABq, δ_{AB} 0.35 p.p.m., J_{AB} 14 Hz), and 1.4—3.0 (17 H, aromatic H).

Unlike (II), no inclusion compounds were found for (IV), the solvents tried being benzene, dioxan, and cyclohexane.

2-*Phenyl*-3-p-(2,2,4-*trimethylthiochroman*-4-*yl*)*phenyl-quinazolin*-4(3H)-*one* (V).—This was prepared by pyrolysis of (IV) under the conditions described for (III). Re-crystallisation from EtOH gave unsolvated material (80%),

TABLE 3

Inclusion compounds formed by (V)

Guest	Mol ratio host : guest [a]	M.p./°C
Cyclopentane	2 : 1	128—138
Cyclohexane	2 : 1	130—139
Cycloheptane	2 : 1	129—140
Tetrahydrofuran	1 : 1	97—123
1,4-Dioxan	2 : 3	129—147
Toluene	2 : 1	145—149
t-Butylamine	1 : 1	116—121
Carbon tetrachloride	1 : 1	112—115
1,1,1-Trichloroethane	3 : 2	105—109
Chloroform [b]	1 : 1	70—90

[a] Determined by multiple integration of ^{1}H n.m.r. spectrum (CDCl$_3$ solution), and/or microanalysis for halogen and given as nearest integral ratio. [b] Scavenged from a mixture of ca. 5% (v/v) CHCl$_3$ in hexamethyldisilane, the latter being included to only a slight extent.

melting initially at ca. 146.5—149 °C, followed by crystallis-ation, and final melting at 173.5—175 °C (Found: C, 78.91; H, 6.10; N, 5.46; S, 6.34. $C_{32}H_{28}N_2OS$ requires C, 78.65; H, 5.77; N, 5.74; S, 6.56%; M, 488); m/e 488; $\nu_{max.}$ (KBr) 1 686 cm^{-1} (C=O); τ (CDCl$_3$) 9.09, 8.61, 8.26 (each 3 H, s), 7.73 (2 H, ABq, δ_{AB} 0.28 p.p.m., J_{AB} 14 Hz), and 1.6—3.2 (17 H, aromatic H).

[6] D. D. MacNicol, *Chem. Comm.*, 1969, 836.

Several solvents gave stable crystalline adducts with (V) (Table 3), however, methanol, isobutyl alcohol, and s-butyl alcohol were not included.

Selectivity Experiments for Hosts (III) *and* (V).—Both (III) and (V) exhibit significant selective inclusion behaviour towards mixtures of hydrocarbon solvents. Thus on a single recrystallisation of (III) from an equimolar mixture of cyclopentane, cyclohexane, and cycloheptane, the relative % included were found by ^{1}H n.m.r. to be 38, 39, and 23% respectively; corresponding results for (V) employing the same mixture are 18, 47, and 35%. Recrystallisation of (III) from pure n-pentane gives unsolvated material; however, an equimolar mixture of n-pentane and cyclopentane gives inclusion in the ratio 1 : 7. The inclusion of n-pentane in these circumstances may be attributed to an auxiliary guest effect.[7]

Unsolvated (V) was recrystallised from an equimolar mixture of *o*- and *p*-xylene and an equimolar mixture of *o*- and *m*-xylene, In both cases, a marked preference was shown for the *ortho*-isomer, the *ortho–para* and *ortho–meta* ratios being 5 : 1 and 4 : 1.

X-*Ray Crystal Structure Analysis of the Methylcyclohexane Adduct of Compound* (III)

Crystal Data.—$(C_{32}H_{28}O_2N_2)_2 \cdot C_7H_{14}$, $M = 1 043.4$, host : guest ratio 2 : 1 found by integration of the ^{1}H n.m.r. spectrum ($CDCl_3$ solution) for the methylcyclohexane adduct, triclinic, with $a = 18.649(25)$, $b = 19.443(25)$, $c = 9.390(15)$ Å, $\alpha = 78.88(5)$, $\beta = 98.97(5)$, $\gamma = 118.16(10)°$, with four host and two guest molecules in the unit cell, $U = 2 937.2$ Å^3, $D_c = 1.18$ g cm^{-3}, $F(000) = 1 112$. Space group $P\bar{1}$, distinguished from $P1$ by the subsequent successful analysis. Mo-K_α radiation, $\lambda = 0.710 7$ Å; μ(Mo-K_α) = 0.72 cm^{-1}. The crystal used (m.p. 115—120 °C) was a thin colourless plate *ca.* $0.65 \times 0.45 \times 0.20$ mm.

Crystallographic Measurements.—Least-squares best cell dimensions were obtained by a treatment of the θ, χ, ϕ setting of 22 reflections measured on a Hilger and Watts automatic diffractometer. Intensities were measured by the θ—2θ scan procedure with Zr-filtered Mo-K_α radiation. Background counts were taken at each end of the scan range. The intensities of three standard reflections were monitored after every 40 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 (<10%). Reflections were surveyed out to $\theta \leqslant 25°$, with an option whereby those intensities with $I < 2\sigma(I)$ were not measured. Intensity values were corrected for Lorentz-polarisation effects, but not for absorption, and 3 432 independent reflections with $I/\sigma(I) > 2.0$ were obtained.

Structure Analysis.—Initial phasing attempts using the ' *X*-Ray ' System [8] and MULTAN [9] were unsuccessful. A subsequent MULTAN starting set, employing three origin-defining reflections and nine symbols, yielded 512 possible solutions, one of which gave possible positions for 49 of the 72 host atoms in the asymmetric unit, but it was not

---

* It would, perhaps, have been possible to derive the true position of this fragment *via* a translation function, but the ease of the subsequent quartet analysis vindicates the method described.

† Owing to the complexity of the $P_{13}{}^\pm$ formula, the explicit form is not given here.

---

possible to complete the structure from this information, and the atoms were clearly misplaced in the unit cell.* At this point the use of triple-phase invariants was abandoned in favour of quartets.

Quartets are four-phase structure invariants of the form :

$$\phi = \phi_h + \phi_k + \phi_l + \phi_m \quad (1)$$

where

$$h + k + l + m = 0 \quad (2)$$

Associated with each quartet is the variable B, where there

$$B = \frac{2}{N} |E_h E_k E_l E_m| \quad (3)$$

are N identical atoms in the unit cell. Recent work by Hauptman and Green has secured formulae which give, under certain conditions, accurate estimates of ϕ for space group $P\bar{1}$. The first of these is the $P_7{}^\pm$ formula,[10] in which the probability of the quartet (1) being positive, $P_7{}^+$ (ϕ 0°), or negative, $P_7{}^-$ (ϕ 180°), is given by (4), where $Z_7{}^\pm$

$$P_7{}^\pm = \frac{1}{k} Z_7{}^\pm \quad (4)$$

is defined (5) in terms of seven E-magnitudes and k is a

$$Z_7{}^\pm = e^{\mp}\{-\cosh\}(R_{12}/N^{\frac{1}{2}})(R_1R_2 \pm R_3R_4)\{\cosh\}(R_{23}/N^{\frac{1}{2}})(R_2R_3 \pm R_1R_4)\{\cosh\}(R_{31}/N^{\frac{1}{2}})(R_3R_1 \pm R_2R_4)^B \quad (5)$$

normalising constant, $k = Z^+ + Z^-$; $R_1 = |E_h|$, $R_2 = |E_k|$, $R_3 = |E_l|$, and $R_4 = |E_m|$, define the four-magnitude, first neighbourhood;[11] $R_{12} = |E_{h+k}|$, $R_{23} = |E_{k+l}|$, and $R_{31} = |E_{l+h}|$ the three-magnitude, second neighbourhood.[11] Associated with each probability estimate is the conditional standard deviation σ_7, where $\sigma_7 = 2\sqrt{P_7{}^+P_7{}^-}$.

A second, more powerful, formula for estimating ϕ involves a third neighbourhood of six E-magnitudes.[12] To derive this neighbourhood a second quartet is constructed (6) in which two of the reciprocal lattice vectors are co-

$$\phi' = \phi_h + \phi_k + \phi_p + \phi_q \quad (6)$$

incident with those of quartet (1) and in which $|E_p|$ and $|E_q|$ are large. The probability $P_{13}{}^\pm$ that ϕ is 0 or 180° is now a function of the seven magnitudes utilised by the $P_7{}^\pm$ formula, plus the six magnitudes $|E_p|$, $|E_q|$, $|E_{h+p}|$, $|E_{k+p}|$, $|E_{l-p}|$, and $|E_{m-p}|$.† A conditional standard deviation σ_{13} is derived *via* $\sigma_{13} = 2\sqrt{P_{13}{}^+P_{13}{}^-}$.

The use of quartets instead of triplets overcomes two problems normally associated with space group $P\bar{1}$: (1) the lack of translational symmetry, since it becomes possible to predict with accuracy those invariants in which $\phi = 180°$, and (2) the paucity of sign relationships necessitating large numbers of symbolic phases, since, for a given set of conditions, there are many more quartets than triplets.

The utilisation of weak reflections with low associated

[7] S. Brzozowski, *Roczniki Chem.*, 1973, **47**, 831.

[8] ' *X*-Ray '72,' J. M. Stewart, G. J. Kruger, M. L. Amon, C. Dickerson, and S. R. Hall, 1972, Technical Report TR 192, Computer Science Center, University of Maryland.

[9] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[10] H. Hauptman and E. A. Green, *Acta Cryst.*, 1976, **A32**, 45.

[11] H. Hauptman, *Acta Cryst.*, 1975, **A31**, 680.

[12] H. Hauptman, *Acta Cryst.*, in the press.

E-magnitudes is important in quartet analysis. In the $P_7{}^{\pm}$ formula, ϕ is 0 or 180° depending on whether the second-neighbourhood terms R_{12}, R_{23}, R_{31} are all large or all small respectively. The data set used here did not incorporate the weak reflections, and so to ensure sufficient negative quartets the missing reflections were generated and incorporated in the data set with E magnitudes of 0.3. Quartets were generated * for the 233 reflections having $|E_h|$, $|E_k|$, $|E_l|$, $|E_m| \geqslant 1.7$, by use of both the $P_7{}^{\pm}$ and $P_{13}{}^{\pm}$ formulae with the B limit of 0.5, and sorted on σ_{13}. For $P_{13}{}^{\pm}$, $|E_p|$ and $|E_q|$ were $\geqslant 1.7$. It should be noted that numerous third neighbourhoods exist which satisfy equations (1) and (6), and each such neighbourhood gives rise to its own probability estimate. The probability selected was the one with the lowest associated σ_{13}.

The incorporation of $P_{13}{}^{\pm}$ gave a spectacular improvement in the associated probabilities. By use of $P_7{}^{\pm}$ alone, only eight quartets out of a total of 889 had probabilities $P_7{}^{+} \geqslant 0.97$ or $P_7{}^{+} \leqslant 0.03$; whereas for $P_{13}{}^{\pm}$ this value increased to 160, enabling phases to be determined with greater reliability. A starting set of three origin-defining reflections plus six symbols was expanded *via* quartet symbolic addition to give 63 symbolic phases. New phases were only accepted if $P_{13}{}^{+} \geqslant 0.99$ or $\leqslant 0.01$ and $P_7{}^{+} \geqslant 0.90$ or $\leqslant 0.10$.

Each of the 64 possible solutions was expanded *via* the tangent formula to phase 499 E magnitudes $\geqslant 1.39$ by use of MULTAN. To select the correct solution the negative quartet figure of merit NQEST [equation (7)] was used,[13]

$$\text{NQEST} = \sum_{h,k,l,m} \omega_{hklm} \cos (\phi_h + \phi_k + \phi_l + \phi_m) / \sum_{h,k,l,m} \omega_{hklm} \quad (7)$$

where both summations are over those quartets predicted to be negative; ω_{hklm} is a weighting function. In the original formulation De Titta *et al.* used B for the weight, and included only those quartets for which the second-neighbourhood terms $|E_{h+k}|$, $|E_{k+l}|$, $|E_{l+h}|$ were less than a specified cut-off (usually ≈ 0.7). We have used an expression for ω_{hklm} of the form: $\omega_{hklm} = B|2P_{13}{}^{+} - 1|$, in which $P_{13}{}^{+} < 0.5$ and no cross-term limits are imposed in the summation. This tends to sharpen the discrimination of the formula. For the ideal case NQEST $= -1.0$; practice has shown, however, that the correct phase-set usually gives values in the range -0.6 to -0.3.

Utilising this and the conventional figures of merit, the correct solution was readily identified as having the highest combined-figure-of-merit, CFOM,[14] (2.29) and a NQEST of -0.22. There was one solution with a lower NQEST (-0.29) but the associated CFOM was only 1.33. The NQEST values are higher than expected, probably because the quartets were used *a priori* in the analysis, whereas the suggested values of -0.6 to -0.3 are only applicable to those cases where the quartets are used to select the best phase set after the conventional phase determinations have been completed.

The subsequent E map revealed 67 of the 72 host atoms correctly placed in the unit cell. All 63 phases derived *via* the quartets were subsequently shown to be correct.

* Program QGEN available from C. J. G. upon request.
† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.
[13] G. T. De Titta, J. W. Edmonds, D. A. Langs, and H. Hauptman, *Acta Cryst.*, 1975, **A31**, 472.

A structure-factor calculation using the 67 (host) atom positions found gave an R value of 34.2%. The five remaining host atoms were found from a subsequent electron-density distribution (where these five atoms, and the guest molecule, were later found to exhibit very large thermal motions and so would not be expected to be located in the initial E map). The approximate parameters for the 72 host atoms were adjusted by several cycles of full-matrix least-squares calculations, and with aniso-tropic temperature factors for all these atoms R was reduced to 15.9%.

At this stage in the refinement the atoms C(5)—(10) had their positions fixed, as these six atoms exhibit very high thermal motion and did not refine smoothly. Also, the 56 host hydrogen atoms were generated in their idealised positions and given isotropic temperature factors equal to those of the atoms to which they are attached.

A difference electron-density distribution done at this point revealed atomic positions for the seven guest carbon atoms, and these were included in subsequent least-squares calculations with large isotropic temperature factors. After further cycles of least-squares adjustment, with parameters of the guest, host hydrogen, and six host carbon atoms all being fixed, the final R value was 9.80% (R' 13.4%). The weighting scheme employed in the last cycles of the least-squares calculations was $\omega = (1.368 + 0.210|F| - 0.002|F|^2)^{-1}$.

Calculations were carried out on an IBM 370/158 computer at Edinburgh and an IBM 370/168 at Newcastle. Observed and calculated structure factors, anisotropic thermal parameters, and co-ordinates and temperature factors of the hydrogen atoms, are listed in Supplementary Publication No. SUP 22024 (21 pp., 1 microfiche).† Scattering factors for non-hydrogen atoms were taken from ref. 15 and for hydrogen from ref. 16. Atomic fractional co-ordinates of non-hydrogen atoms are listed in Table 4, and various parameters connected with the adduct's molecular geometry in Tables 5—10.

DISCUSSION

Inclusion Properties of Compounds (III) *and* (V).— Table 1 gives the host : guest ratios of 30 adducts of (III) which were prepared by recrystallisation of the unsolvated host from the appropriate pure dry solvent. Apart from cyclopropane, which has a ratio of 1 : 1, the other cycloalkanes, ranging in size from cyclobutane to cyclodecane, have a ratio of 2 : 1. Thermal analysis data for the first five members of this series are given in Table 2; the temperature of maximum solvent loss, $T_{\text{max.}}$, appears to parallel the observed melting behaviour of the adducts (see Table 1).

The commonly encountered host : guest ratio of 2 : 1 is found for methylcyclohexane, and fluoro-, chloro-, and bromo-cyclohexane, though the larger iodocyclohexane is not included. Differences are found for the isomeric butanols, t-butyl and isobutyl alcohol forming inclusion compounds, whereas no complexes are found with the n- and s-isomers.

[14] S. A. Arora, R. B. Bates, R. A. Grady, G. Germain, and J. P. Declercq, *J. Org. Chem.*, 1975, **40**, 28.
[15] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[16] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

TABLE 4

Atomic co-ordinates (× 10⁴) and isotropic thermal parameters (× 10⁴) *

	x	y	z	U
Molecule (1)				
O(1)	161(8)	3 968(9)	−5 270(14)	
C(2)	−248(11)	3 148(10)	−5 033(17)	
C(3)	187(7)	2 822(8)	−5 567(12)	
C(4)	1 072(6)	3 040(6)	−4 935(10)	
C(5)	2 411(21)	4 379(17)	−5 000(26)	
C(6)	2 773(22)	5 261(17)	−5 018(24)	
C(7)	2 218(27)	5 512(18)	−5 118(30)	
C(8)	1 446(24)	5 164(25)	−5 253(36)	
C(9)	964(25)	4 276(14)	−5 071(26)	
C(10)	1 534(18)	3 933(15)	−4 945(22)	
C(11)	1 095(6)	2 588(6)	−3 420(10)	
C(12)	607(6)	1 787(6)	−3 149(10)	
C(13)	616(5)	1 332(5)	−1 807(10)	
C(14)	1 141(6)	1 723(6)	−683(10)	
C(15)	1 653(6)	2 503(6)	−876(10)	
C(16)	1 623(6)	2 941(5)	−2 259(11)	
C(17)	1 444(7)	2 791(6)	−5 969(11)	
C(18)	−1 071(9)	3 003(13)	−5 939(16)	
C(19)	−379(10)	2 968(12)	−3 349(16)	
N(20)	465(4)	572(4)	2 887(8)	
C(21)	509(5)	992(5)	1 657(11)	
N(22)	1 142(4)	1 257(4)	742(7)	
C(23)	1 779(6)	1 049(5)	1 131(11)	
C(24)	2 317(5)	295(5)	3 043(10)	
C(25)	2 249(6)	−172(6)	4 354(11)	
C(26)	1 614(6)	−364(5)	5 219(10)	
C(27)	1 029(5)	−103(5)	4 731(10)	
C(28)	1 077(5)	346(5)	3 347(10)	
C(29)	1 723(5)	553(5)	2 542(9)	
C(30)	−172(6)	1 205(6)	1 129(9)	
C(31)	−61(6)	1 972(6)	799(11)	
C(32)	−747(9)	2 108(8)	402(13)	
C(33)	−1 507(8)	1 496(10)	297(13)	
C(34)	−1 622(6)	728(9)	547(14)	
C(35)	−946(6)	585(6)	1 013(11)	
O(36)	2 335(4)	1 289(4)	329(7)	
Molecule (2)				
O(1)	4 545(4)	13 882(3)	6 267(7)	
C(2)	4 548(7)	13 396(6)	7 637(10)	
C(3)	3 716(6)	12 690(6)	7 776(9)	
C(4)	3 425(5)	12 173(5)	6 545(9)	
C(5)	3 282(5)	12 455(5)	3 793(11)	
C(6)	3 442(7)	12 956(8)	2 469(11)	
C(7)	3 947(8)	13 742(7)	2 468(11)	
C(8)	4 300(7)	14 021(5)	3 765(11)	
C(9)	4 145(6)	13 502(6)	5 073(10)	
C(10)	3 630(5)	12 718(5)	5 104(9)	
C(11)	3 759(5)	11 566(5)	6 779(10)	
C(12)	3 605(5)	11 022(5)	8 051(9)	
C(13)	3 825(5)	10 438(5)	8 252(9)	
C(14)	4 248(5)	10 396(5)	7 210(10)	
C(15)	4 416(5)	10 913(5)	5 951(9)	
C(16)	4 177(5)	11 508(5)	5 739(8)	
C(17)	2 481(5)	11 690(5)	6 578(11)	
C(18)	4 718(8)	13 941(6)	8 770(11)	
C(19)	5 245(6)	13 180(6)	7 689(11)	
N(20)	5 590(5)	9 429(5)	7 936(7)	
C(21)	5 332(6)	9 953(6)	7 751(8)	
N(22)	4 501(5)	9 776(4)	7 438(7)	
C(23)	3 892(7)	9 016(6)	7 229(10)	
C(24)	3 673(7)	7 673(7)	7 216(12)	
C(25)	3 939(9)	7 094(7)	7 349(14)	
C(26)	4 755(10)	7 325(8)	7 736(11)	
C(27)	5 308(7)	8 091(8)	7 954(10)	
C(28)	5 026(7)	8 667(7)	7 790(9)	
C(29)	4 208(7)	8 436(6)	7 445(9)	
C(30)	5 932(6)	10 787(6)	7 823(10)	
C(31)	5 915(5)	11 229(6)	8 752(11)	
C(32)	6 492(8)	11 992(8)	8 790(13)	
C(33)	7 113(8)	12 336(7)	7 797(19)	
C(34)	7 090(8)	11 850(12)	6 849(15)	
C(35)	6 518(8)	11 101(8)	6 864(13)	
O(36)	3 185(4)	8 877(4)	6 922(8)	

TABLE 4 (Continued)

Guest	x	y	z	U
C(50)	2 411	4 655	284	2 850
C(51)	1 482	4 396	−108	2 850
C(52)	2 429	5 793	248	2 850
C(53)	1 607	5 793	−430	2 850
C(54)	3 040	5 517	71	2 850
C(55)	1 089	4 914	141	2 850
C(56)	732	4 827	−1 429	2 850

* Anisotropic temperature factors of the form $\exp[-2\pi^2(h^2a^{*2}\cdot U_{11} + \ldots 2hka^*b^*U_{12} + \ldots)]$ were assigned to other atoms, and are listed in a Supplementary Publication (see text).

TABLE 5

Interatomic distances (Å) with standard deviations in parentheses

	Molecule (1)	Molecule (2)
O(1)−C(2)	1.39(2)	1.44(1)
O(1)−C(9)	1.32(4)	1.38(1)
C(2)−C(3)	1.43(3)	1.51(1)
C(2)−C(18)	1.56(2)	1.54(2)
C(2)−C(19)	1.58(2)	1.53(2)
C(3)−C(4)	1.55(2)	1.54(1)
C(4)−C(10)	1.53(3)	1.52(1)
C(4)−C(11)	1.53(1)	1.54(2)
C(4)−C(17)	1.54(2)	1.56(1)
C(5)−C(6)	1.51(4)	1.40(1)
C(5)−C(10)	1.45(4)	1.37(1)
C(6)−C(7)	1.32(7)	1.37(2)
C(7)−C(8)	1.27(6)	1.37(1)
C(8)−C(9)	1.51(5)	1.40(1)
C(9)−C(10)	1.48(6)	1.36(1)
C(11)−C(12)	1.38(1)	1.40(1)
C(11)−C(16)	1.39(1)	1.39(1)
C(12)−C(13)	1.40(1)	1.35(2)
C(13)−C(14)	1.39(1)	1.39(1)
C(14)−C(15)	1.35(1)	1.37(1)
C(14)−N(22)	1.46(1)	1.46(1)
C(15)−C(16)	1.42(1)	1.39(2)
N(20)−C(21)	1.27(1)	1.29(2)
N(20)−C(28)	1.39(1)	1.37(1)
C(21)−N(22)	1.40(1)	1.41(1)
C(21)−C(30)	1.50(2)	1.48(1)
N(22)−C(23)	1.40(1)	1.40(1)
C(23)−C(29)	1.47(1)	1.47(2)
C(23)−O(36)	1.23(1)	1.21(2)
C(24)−C(25)	1.37(1)	1.41(2)
C(24)−C(29)	1.40(2)	1.38(1)
C(25)−C(26)	1.40(2)	1.38(2)
C(26)−C(27)	1.39(2)	1.39(2)
C(27)−C(28)	1.41(1)	1.42(2)
C(28)−C(29)	1.38(1)	1.37(2)
C(30)−C(31)	1.38(2)	1.35(2)
C(30)−C(35)	1.38(1)	1.36(2)
C(31)−C(32)	1.41(2)	1.36(1)
C(32)−C(33)	1.36(2)	1.42(2)
C(33)−C(34)	1.38(3)	1.40(3)
C(34)−C(35)	1.40(2)	1.34(2)

Guest

C(50)−C(51)	1.56	C(50)−C(54)	1.52
C(51)−C(55)	1.56	C(52)−C(53)	1.57
C(52)−C(54)	1.51	C(53)−C(55)	1.55
C(55)−C(56)	1.53			

That factors other than guest size may be relevant to complex formation is implied by the behaviour encountered for aromatic solvents. For example, toluene, which is intermediate in bulk between benzene and p-xylene, does not form an inclusion compound even when seeded with the (1 : 1) benzene or the (2 : 1) p-xylene adduct.

The thio-analogue of (III), compound (V), forms

TABLE 6

Valency angles (°) with standard deviations in parentheses

	Molecule (1)	Molecule (2)
C(9)–O(1)–C(2)	115(2)	117(1)
C(18)–C(2)–O(1)	110(2)	103(1)
C(8)–C(9)–O(1)	118(3)	112(1)
C(18)–C(2)–C(3)	113(1)	111(1)
C(4)–C(3)–C(2)	118(1)	115(1)
C(10)–C(4)–C(3)	108(2)	108(1)
C(17)–C(4)–C(3)	106(1)	106(1)
C(17)–C(4)–C(10)	110(1)	109(1)
C(9)–C(10)–C(4)	111(2)	121(1)
C(12)–C(11)–C(4)	121(1)	119(1)
C(10)–C(5)–C(6)	117(3)	123(1)
C(9)–C(10)–C(5)	125(3)	117(1)
C(9)–C(8)–C(7)	122(4)	120(1)
C(16)–C(11)–C(12)	116(1)	118(1)
C(15)–C(16)–C(11)	122(1)	121(1)
C(15)–C(14)–C(13)	122(1)	121(1)
N(22)–C(14)–C(15)	120(1)	119(1)
C(21)–N(22)–C(14)	121(1)	121(1)
C(28)–N(20)–C(21)	118(1)	118(1)
C(30)–C(21)–N(20)	118(1)	119(1)
C(29)–C(28)–N(20)	124(1)	124(1)
C(23)–N(22)–C(21)	121(1)	122(1)
C(35)–C(30)–C(21)	116(1)	115(1)
O(36)–C(23)–N(22)	120(1)	121(1)
C(24)–C(29)–C(23)	120(1)	118(1)
C(29)–C(24)–C(25)	119(1)	121(1)
C(28)–C(29)–C(24)	121(1)	121(1)
C(28)–C(27)–C(26)	119(1)	119(1)
C(35)–C(30)–C(31)	120(1)	120(1)
C(34)–C(35)–C(30)	120(1)	120(1)
C(34)–C(33)–C(32)	121(2)	116(1)
C(3)–C(2)–O(1)	111(2)	109(1)
C(19)–C(2)–O(1)	103(1)	108(1)
C(10)–C(9)–O(1)	132(2)	126(1)
C(19)–C(2)–C(3)	119(2)	114(1)
C(19)–C(2)–C(18)	110(2)	111(1)
C(11)–C(4)–C(3)	111(1)	113(1)
C(11)–C(4)–C(10)	112(1)	113(1)
C(5)–C(10)–C(4)	123(3)	122(1)
C(17)–C(4)–C(11)	109(1)	106(1)
C(16)–C(11)–C(4)	123(1)	123(1)
C(7)–C(6)–C(5)	113(3)	119(1)
C(8)–C(7)–C(6)	133(4)	119(1)
C(10)–C(9)–C(8)	109(3)	122(1)
C(13)–C(12)–C(11)	124(1)	122(1)
C(14)–C(13)–C(12)	117(1)	119(1)
N(22)–C(14)–C(13)	118(1)	120(1)
C(16)–C(15)–C(14)	118(1)	119(1)
C(23)–N(22)–C(14)	118(1)	117(1)
N(22)–C(21)–N(20)	125(1)	123(1)
C(27)–C(28)–N(20)	117(1)	118(1)
C(30)–C(21)–N(22)	118(1)	118(1)
C(31)–C(30)–C(21)	124(1)	124(1)
C(29)–C(23)–N(22)	115(1)	113(1)
O(36)–C(23)–C(29)	125(1)	126(1)
C(28)–C(29)–C(23)	118(1)	120(1)
C(26)–C(25)–C(24)	120(1)	117(1)
C(27)–C(26)–C(25)	120(1)	123(2)
C(29)–C(28)–C(27)	119(1)	118(1)
C(32)–C(31)–C(30)	119(1)	122(1)
C(33)–C(32)–C(31)	121(1)	119(1)
C(35)–C(34)–C(33)	119(1)	122(2)

Guest

C(55)–C(51)–C(50)	121	C(52)–C(54)–C(50)	93
C(54)–C(50)–C(51)	121	C(53)–C(55)–C(51)	112
C(56)–C(55)–C(51)	85	C(55)–C(53)–C(52)	93
C(54)–C(52)–C(53)	143	C(56)–C(55)–C(53)	86

adducts with host : guest ratios (Table 3) similar to those found for compound (III). Both hosts (III) and (V) exhibit some selective inclusion behaviour (see Experimental section).

Structural Properties of the Methylcyclohexane Adduct

TABLE 7

Host torsion angles (°) with standard deviations in parentheses

	Molecule (1)	Molecule (2)
C(9)–O(1)–C(2)–C(3)	–39(2)	–40(1)
C(9)–O(1)–C(2)–C(19)	89(2)	83(1)
C(2)–O(1)–C(9)–C(10)	15(4)	13(1)
C(18)–C(2)–C(3)–C(4)	170(1)	171(1)
C(2)–C(3)–C(4)–C(10)	–48(2)	–43(1)
C(2)–C(3)–C(4)–C(17)	–166(1)	–160(1)
C(3)–C(4)–C(10)–C(9)	19(3)	13(1)
C(11)–C(4)–C(10)–C(9)	–105(2)	–113(1)
C(17)–C(4)–C(10)–C(9)	134(2)	128(1)
C(3)–C(4)–C(11)–C(16)	–135(1)	–126(1)
C(10)–C(4)–C(11)–C(16)	–13(2)	–2(1)
C(17)–C(4)–C(11)–C(16)	108(1)	118(1)
C(6)–C(5)–C(10)–C(4)	179(2)	177(1)
C(5)–C(6)–C(7)–C(8)	–3(6)	1(2)
C(7)–C(8)–C(9)–O(1)	–178(4)	–180(1)
O(1)–C(9)–C(10)–C(4)	–5(5)	2(2)
C(8)–C(9)–C(10)–C(4)	–173(2)	–176(1)
C(4)–C(11)–C(12)–C(13)	178(1)	174(1)
C(4)–C(11)–C(16)–C(15)	–178(1)	–175(1)
C(11)–C(12)–C(13)–C(14)	1(2)	3(1)
C(12)–C(13)–C(14)–N(22)	178(1)	179(1)
N(22)–C(14)–C(15)–C(16)	–179(1)	–180(1)
C(13)–C(14)–N(22)–C(23)	101(1)	76(1)
C(15)–C(14)–N(22)–C(23)	–77(1)	–103(1)
C(28)–N(20)–C(21)–N(22)	–1(1)	1(1)
C(21)–N(20)–C(28)–C(27)	178(1)	178(1)
N(20)–C(21)–N(22)–C(14)	178(1)	–179(1)
C(30)–C(21)–N(22)–C(14)	0(1)	–1(1)
N(20)–C(21)–C(30)–C(31)	121(1)	–123(1)
N(22)–C(21)–C(30)–C(31)	–60(1)	59(1)
C(14)–N(22)–C(23)–C(29)	–177(1)	178(1)
C(21)–N(22)–C(23)–C(29)	–1(1)	3(1)
N(22)–C(23)–C(29)–C(24)	179(1)	–178(1)
O(36)–C(23)–C(29)–C(24)	–2(2)	3(2)
C(29)–C(24)–C(25)–C(26)	–3(2)	1(2)
C(25)–C(24)–C(29)–C(28)	0(1)	1(2)
C(25)–C(26)–C(27)–C(28)	1(1)	1(2)
C(26)–C(27)–C(28)–C(29)	–3(1)	1(2)
N(20)–C(28)–C(29)–C(24)	–178(1)	176(1)
C(27)–C(28)–C(29)–C(24)	3(1)	–2(2)
C(35)–C(30)–C(31)–C(32)	2(2)	–2(2)
C(31)–C(30)–C(35)–C(34)	1(2)	1(2)
C(31)–C(32)–C(33)–C(34)	–1(2)	–1(2)
C(33)–C(34)–C(35)–C(30)	–4(2)	0(2)
C(9)–O(1)–C(2)–C(18)	–158(2)	–158(1)
C(2)–O(1)–C(9)–C(8)	–178(3)	–169(1)
O(1)–C(2)–C(3)–C(4)	59(2)	58(1)
C(19)–C(2)–C(3)–C(4)	–59(2)	–63(1)
C(2)–C(3)–C(4)–C(11)	76(1)	83(1)
C(3)–C(4)–C(10)–C(5)	–154(2)	–164(1)
C(11)–C(4)–C(10)–C(5)	82(3)	70(1)
C(17)–C(4)–C(10)–C(5)	–39(3)	–48(1)
C(3)–C(4)–C(11)–C(12)	47(1)	57(1)
C(10)–C(4)–C(11)–C(12)	169(1)	–179(1)
C(17)–C(4)–C(11)–C(12)	–69(1)	–59(1)
C(10)–C(5)–C(6)–C(7)	–6(4)	–2(2)
C(6)–C(5)–C(10)–C(9)	7(5)	0(2)
C(6)–C(7)–C(8)–C(9)	11(7)	0(2)
C(7)–C(8)–C(9)–C(10)	–8(5)	–2(2)
O(1)–C(9)–C(10)–C(5)	168(3)	179(1)
C(8)–C(9)–C(10)–C(5)	0(4)	1(2)
C(16)–C(11)–C(12)–C(13)	0(2)	–2(1)
C(12)–C(11)–C(16)–C(15)	–1(1)	1(1)
C(12)–C(13)–C(14)–C(15)	–3(2)	–3(1)
C(13)–C(14)–C(15)–C(16)	3(2)	2(1)
C(13)–C(14)–N(22)–C(21)	–75(1)	–109(1)
C(15)–C(14)–N(22)–C(21)	106(1)	73(1)
C(14)–C(15)–C(16)–C(11)	–1(2)	–1(1)
C(28)–N(20)–C(21)–C(30)	177(1)	–177(1)
C(21)–N(20)–C(28)–C(29)	0(1)	1(2)
N(20)–C(21)–N(22)–C(23)	2(1)	–3(1)
C(30)–C(21)–N(22)–C(23)	–177(1)	175(1)
N(20)–C(21)–C(30)–C(35)	–58(1)	58(1)
N(22)–C(21)–C(30)–C(35)	121(1)	–120(1)
C(14)–N(22)–C(23)–O(36)	4(1)	–2(1)

TABLE 7 (*Continued*)

C(21)–N(22)–C(23)–O(36)	−179(1)	−178(1)
N(22)–C(23)–C(29)–C(28)	−1(1)	−1(2)
O(36)–C(23)–C(29)–C(28)	178(1)	180(1)
C(25)–C(24)–C(29)–C(23)	−179(1)	178(1)
C(24)–C(25)–C(26)–C(27)	2(2)	−2(1)
C(26)–C(27)–C(28)–N(20)	178(1)	−177(1)
N(20)–C(28)–C(29)–C(23)	1(1)	−1(2)
C(27)–C(28)–C(29)–C(23)	−177(1)	−178(1)
C(21)–C(30)–C(31)–C(32)	−176(1)	179(1)
C(21)–C(30)–C(35)–C(34)	179(1)	−180(1)
C(30)–C(31)–C(32)–C(33)	−2(2)	2(2)
C(32)–C(33)–C(34)–C(35)	4(2)	0(2)

TABLE 8

Displacements (Å) of atoms from planes through various sets of atoms; values for molecule (2) follow those for molecule (1)

Plane (*A*): N(22), C(21), N(20), C(28), C(29), C(23)

[N(22) 0.006, 0.017; C(21) −0.009, −0.012; N(20) 0.003, −0.002; C(28) 0.005, 0.009; C(29) −0.007, −0.002; C(23) 0.001, −0.010; O(36) 0.025, −0.021; C(14) −0.045, −0.024; C(30) −0.073, −0.098]

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

[O(1) −0.012, 0.004; C(4) 0.008, −0.003; C(9) 0.023, −0.008; C(10) −0.019, 0.008; C(2) 0.220, 0.318; C(3) −0.402, −0.364]

of (III) —The independent host molecules of (III) (Figure 1) have appreciably different conformations. These two molecules have the same configuration at C(4), but the phenylquinazolinone moieties have an approximately mirror image relationship to one another. Significant conformational differences occur at the ' backbone ' bonds C(4)–C(11) and C(14)–N(22). This is illustrated by the values of the two pairs of torsion angles C(3)–C(4)–C(11)–C(12) and C(13)–C(14)–N(22)–C(21) which are 47 and 57, and −75 and −109°.

The packing of the host molecules is shown in Figure 2, and is such that closed voids are formed. Two guest molecules of methylcyclohexane, approximately centred at the centrosymmetrically related points G and G', are accommodated in each cage. However, it was not found possible to interpret the results of the electron-density maps in terms of a single conformation for the guest molecule. An arbitrary allowance for the guest molecule was in fact made, and corresponding bond lengths and angles are listed in Tables 5 and 6.

TABLE 9

Some short intramolecular separations (Å)

Molecule (1)		Molecule (2)	
C(10) · · · C(19)	3.57	C(10) · · · C(19)	3.43
C(11) · · · H(192)	2.51	C(11) · · · H(192)	2.64
C(11) · · · C(19)	3.18	C(11) · · · C(19)	3.22
C(12) · · · C(19)	3.52	C(16) · · · C(19)	3.60
C(13) · · · C(30)	3.24	C(15) · · · C(30)	3.18
C(14) · · · C(31)	3.07	C(14) · · · C(31)	3.02
C(19) · · · C(32)	3.62		

TABLE 10

Some intermolecular separations (Å)

C(54) · · · C(19ᴵ)	3.66	C(54) · · · H(193ᴵ)	2.88
C(54) · · · C(25ᴵᴵ)	3.49	C(56) · · · C(19)	3.86
C(17) · · · H(172ᴵᴵᴵ)	2.89	C(17) · · · C(17ᴵⱽ)	3.81
C(12) · · · C(17ᴵⱽ)	3.64		

Roman numeral superscripts refer to the following transformations of the atomic co-ordinates of molecule (2):

I 1 − x, 2 − y, 1 − z   III x, 1 + y, 1 + z
II x, y, z − 1   IV x, y − 1, z − 1

* C(19) of molecule (1).

Both molecules have a distorted half-chair conformation for the oxygen containing ring. The atoms C(2) and C(3) are displaced from the mean-plane of the atoms
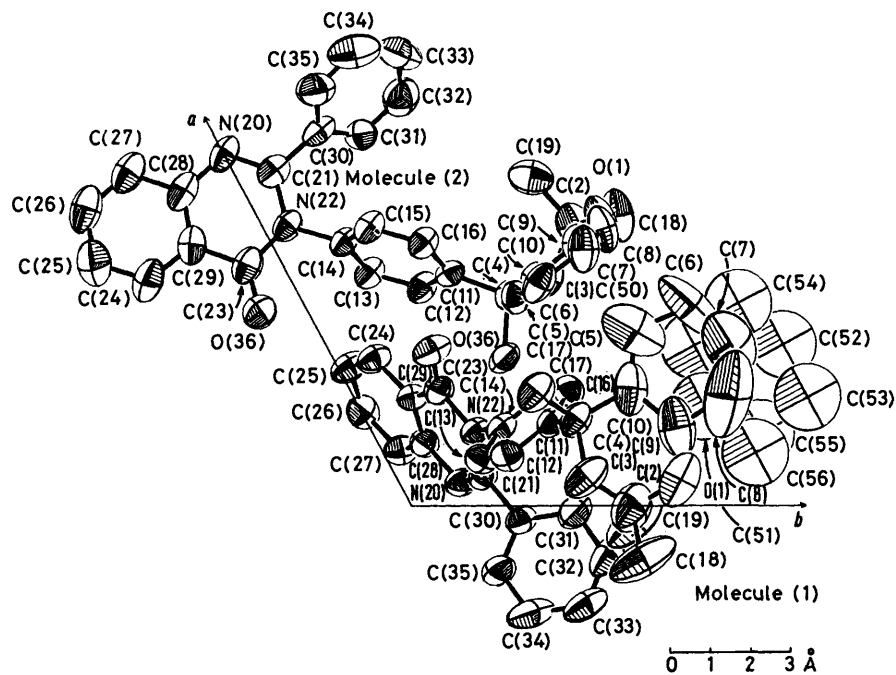

FIGURE 1 The two independent host molecules of (III) and the one guest molecule in the asymmetric unit as projected on the *ab* plane

C(9), C(10), C(4), and O(1) by 0.22 and −0.40 Å respectively; the corresponding displacements for the other molecule are 0.32 and −0.36 Å. A half-chair conformation has also been found for Dianin's compound

sufficient free volume to allow for the possible inclusion of very small guest molecules.

The packing arrangement adopted by the molecules of compound (III) appears to be solvent dependent.
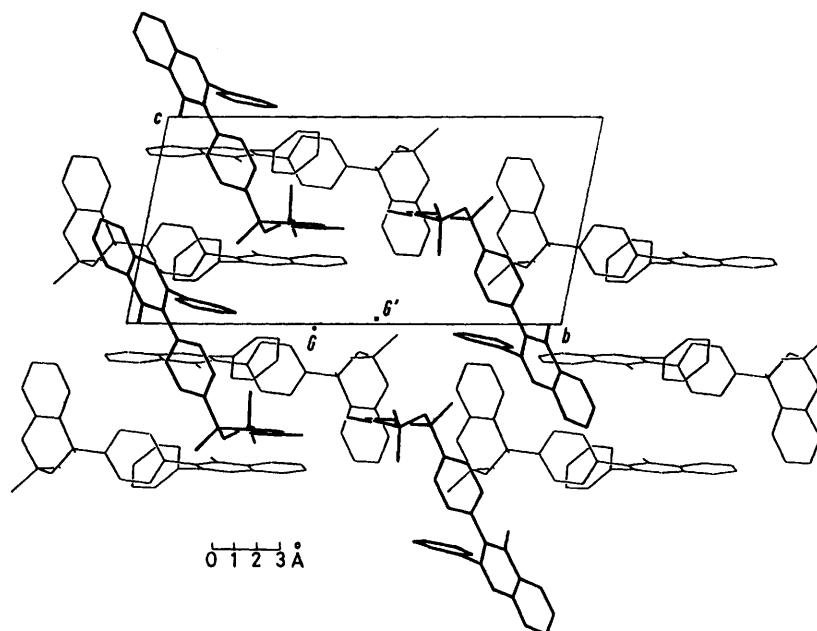

FIGURE 2 A packing diagram for compound (III), showing a view perpendicular to the bc plane. The points G and G' represent the approximate centres of the two guest molecules in the cavity. The cage is completed by several host molecules (which are closer to the viewer), which have been omitted for clarity

(Ia), with displacements of 0.33 and −0.36 Å calculated from the available [17] data for the ethanol clathrate.

The shape of the large centrosymmetric cavity may be readily appreciated by a consideration of the contours shown in Figure 3.   These contours were obtained after
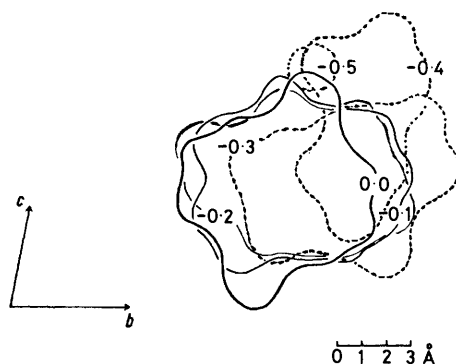

FIGURE 3   The space available in the cage in cross-section at various fractional levels parallel to the bc plane. The contours shown represent only half the centrosymmetric cage

allowing for the van der Waals volumes of the cage wall atoms, and represent the greatest degree of freedom for a hydrogen atom at each level. For each of the large cages there are also two very much smaller cavities (not shown in Figure 3).   These additional enantiomeric voids have an extremely irregular shape and have only

Recrystallisation from methanol and ethanol gives two distinct unsolvated forms (see Table 11).   The adducts

TABLE 11

Some data for other crystal modifications of (III)

Solvent	Space group	Z	Host : guest ratio	$U/\text{Å}^3$	M.p./°C
Cyclohexane	$P\bar{1}$ (or $P1$)	4	2 : 1	2 920.4	120—136
$BrCF_2CF_2Br$	$P\bar{1}$ (or $P1$)	4	2 : 1	2 870.4	121—128
t-Butyl alcohol	$P2_1/c$	4	1 : 1	3 063.7	90—100
Methanol	} $P2_1/c$	4	a	2 512.1	176.5—178.5
Nitromethane [b]					
Ethanol	$P\bar{1}$ (or $P1$)	4	a	2 465.5	176.5—178.5

[a] Unsolvated form.   [b] Also forms a 1 : 1 adduct.

formed from cyclohexane and $BrCF_2\cdot CF_2Br$ are isomorphous with the methylcyclohexane clathrate already described, though in contrast the inclusion compound formed from t-butyl alcohol is monoclinic with a host : guest ratio of 1 : 1.

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