Correlation of the Loss of Solvent with the Crystal Structure of a 1 : 1 Solvate. Indanetrione 2-(*N*-*p*-t-Butylbenzoyl-*N*-phenylhydrazone) Acetone [1,2] Solvate

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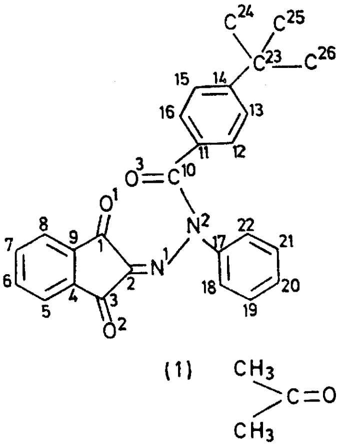
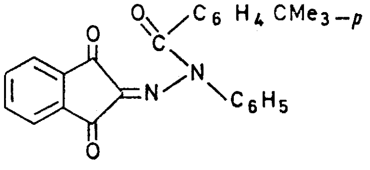
The process whereby the 1 : 1 acetone solvate (1) of indanetrione 2-(*N*-*p*-t-butylbenzoyl-*N*-phenylhydrazone) (2) loses solvent has been studied both by *X*-ray analysis of the structure and by optical microscopy. Crystals of (1) are monoclinic, $a = 10.574(4)$, $b = 28.706(14)$, $c = 10.060(4)$ Å, and $\beta = 121.0(1)°$; space group is $P2_1/c$, and $Z = 4$. The structure was solved by the symbolic-addition method and refined to R 0.090 on 3 535 non-zero reflections measured by diffractometer. The acetone molecules are ordered and occupy positions in an infinite channel which runs along the *c* crystallographic axis in a somewhat zig-zag fashion. The t-butyl groups, which form some of the walls of this channel, exhibit two-fold disorder in the crystal in a 55 : 45 ratio. After some time the yellow crystals of the solvate (1) were observed, under the microscope, to develop red streaks running along the *c* direction. As these streaks intensify and become more numerous, a series of black cracked regions appear which run normal to the direction of the red streaks. This behaviour is characteristic of crystals which have lost *ca.* 33% of the acetone. Single-crystal diffraction photographs taken when the crystals had lost significant amounts of acetone showed considerable disorder in the b^* direction (corresponding approximately to the larger cross-sectional direction of the channel), but considerable retention of structure in the a^*c^* plane. *X*-Ray powder pictures showed that, when all the acetone was lost from the crystal, the material remaining gave a powder pattern distinct from that obtained from (2) which had crystallised without incorporation of solvent. The observations on a macroscopic scale relating to loss of solvent are correlated with the crystal structure as determined by *X*-ray diffraction.

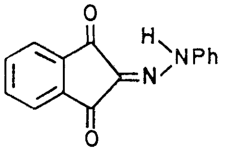
In addition to solid molecular complexes with two or more distinct types of molecules held together by specific interactions such as charge transfer [3] or hydrogen bonding [4] and those in which a host molecule forms a crystal structure with cages (clathrates) [5] or channels [6] containing variable numbers of guest molecules, there are many crystalline 'solvates' in which a large (and often rigid and awkwardly-shaped) host molecule crystallises with the incorporation of a fixed ratio of small (solvent) molecules arranged so as to fill spaces between the host molecules. Such crystals have been the step-children of crystalline complexes, and although the first-mentioned types of complexes have been the subject of reviews, the solvates have not even been collected together in compendia such as ref. 7. Inclusion compounds of all the foregoing types may lose the guest molecules under various conditions of heating or setting aside. The host may in certain cases be formed in a state with a stability quite different from that of the same substance crystallised without initial incorporation of solvent.[8-10] This behaviour is widely recognised, and is often of great practical importance in the pharmaceutical industry,[11,12] as is the more general phenomenon of polymorphism.[13,14] Furthermore, the



(1)



(2)



(3)

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[1] Taken from the Ph.D. Thesis of Sherrill A. Puckett, University of Illinois, 1975, available from University Microfilms, Ann Arbor, Michigan.

[2] Part of this work has been described at the 8th Jerusalem Symposium on 'Environmental Effects on Molecular Structure and Properties,' Jerusalem, April 1975.

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potential use of the loss of solvent from crystalline solvates to produce new forms of the host substances could be of obvious chemical interest and importance. The mechanism by which solvent is lost from a crystalline solvate may be related to the reverse of the process by which a gas reacts with a solid.[15,16]

This paper describes the determination of the crystal structure and the study of the loss of acetone from the 1 : 1 acetone solvate (1) of indanetrione 2-(*N*-*p*-t-butylbenzoyl-*N*-phenylhydrazone) (2).†

EXPERIMENTAL ‡

Indanetrione 2-(N-p-*t-Butylbenzoyl*-N-*phenylhydrazone*) (2).—To a solution of indanetrione 2-(*N*-phenylhydrazone) (3) [17] (2.0 g) in dry pyridine (50 ml) was added excess (× 4) of *p*-t-butylbenzoyl chloride. After 4.5 h, the dark red solution was decomposed with water, extracted into toluene, washed free of pyridine with acidified water, and dried (magnesium sulphate). Evaporation below room temperature gave a red oil. Recrystallisation of this oil from mixtures of ethyl ether–iso-octane gave solvent-free red crystals of (2): m.p. 159—161 °C; i.r. ($CHCl_3$) 1 700 and 1 734 cm^{-1}. Triclinic, $a = 10.076(7)$, $b = 11.854(6)$, $c = 10.463(5)$ Å, $\alpha = 99.61(4)$, $\beta = 115.29(4)$, $\gamma = 87.75(5)°$; U(Å^3) = 1 113; $D_m = 1.21$, $D_c = 1.22$ g cm^{-3}, $Z = 2$ (Found: C, 76.2; H, 5.3; N, 6.9. Calc. for $C_{26}H_{22}N_2O_3$: C, 76.0; H, 5.4; N, 6.8%).

Indanetrione 2-(N-p-*t-Butylbenzoyl*-N-*phenylhydrazone*) 1 : 1 *Acetone Solvate* (1).—Attempted purification of the t-butyl derivative (2) by recrystallisation from saturated acetone solutions gave orange crystals, m.p. 116—117 °C when heated at 10° min^{-1}. Upon further heating, the melt solidified and remelted at 160—165 °C. The presence of 1 : 1 stoicheiometric amounts of acetone in the crystals was confirmed by n.m.r. and microanalysis: δ ($CDCl_3$) 1.05 (6 H, s) (Found: C, 74.5; H, 5.9; N, 6.1. Calc. for $C_{29}H_{28}N_2O_4$: C, 74.3; H, 6.0; N, 6.0%).

The solvated crystals could be exposed to the atmosphere for several days without a noticeable change in their appearance. When washed with organic solvents such as pentane, however, the orange solvated crystals were rapidly transformed into a brilliant red, but opaque, modification. Grinding of the orange solvate crystals gave a powder which appeared to be more red in colour than the original uncrushed orange crystals.

Loss of Acetone from Single Crystals of the Solvate (1).—Upon heating (1) at a constant rate of 10° min^{-1} on a microscope stage, the orange crystals began to melt at 116 °C with rapid evolution of acetone. By 117 °C the compound had completely melted and immediately began to resolidify as a red solid. The newly formed red solid melted upon further heating at 160—165 °C. A d.s.c. thermogram of (1) heated at 10° min^{-1} showed loss of solvent, detected as a broad endotherm beginning at 98 °C and centred at 123 °C; final melting of the red solid occurred at 160 °C. The orange, solvated crystals of (1) could be transformed into red material by washing with pentane, in which they were insoluble. Washing with water had no effect. When set aside in air for several months, single crystals of (1) became red and opaque. Several small crystals, which had remained at ambient temperatures for 2 months, appeared to be completely microcrystalline when examined under a microscope between crossed polarizing filters. The calculated ratio of hydrazone to acetone in this batch of crystals was then 3 : 2 based on n.m.r. results: δ ($CDCl_3$) 1.95 (4 H, s, acetone) and 1.09 (9 H, s, Bu^t).

A crystal of the acetone solvate (1) was placed on a microscope slide, inserted into the Mettler FP 2 hot stage, and the temperature adjusted to 45.0 °C when loss of solvent was recorded by photomicrography (Figure 1). After 21 h at 45 °C red streaks had developed throughout and along the length of the crystal. One end, which appeared to be more red than the rest of the crystal, had developed a large crack approximately perpendicular to the long morphological crystal axis. The regions of red colour accumulated in a direction parallel to the long axis of the crystal, thus giving the appearance of a poorly defined red frontal movement. As a particular area of the crystal turned red, new perpendicular cracks were formed. This pattern of fracturing travelled the length of the crystal immediately behind the red regions.

Loss of solvent from (1) was also followed by examining single-crystal *X*-ray photographs. When set aside for *ca.* 2 months, solvated crystals (1) had become completely opaque, although their n.m.r. spectrum indicated that only *ca.* 1/3 of the acetone originally in the crystal had escaped. However, at this stage the ' crystal ' did not give a characteristic powder photograph, but a diffraction pattern similar to that from a single crystal, although with some indication of disorder or twinning in the crystalline material. In particular, in the $hk2h$ net, as examined on a precession camera, there appeared to be a number of new diffraction maxima at somewhat irregular positions along the b^* axis, while the appearance of the $h0l$ net gave some indications that the c glide plane was no longer present and that the effective a axis length had doubled. The crystals appeared to have considerable retention of structure in the a^*c^* plane, but there were major changes in the b^* direction.

Examination on a powder camera of a ' crystal ' of the solvate (1) which had remained at room temperature for 11 months demonstrated that the material was microcrystalline. It is presumed that after 11 months there is no acetone remaining in the ' crystal.' The powder pattern resulting from a fully desolvated ' single crystal ' of (1) is significantly different from that of the pure powdered unsolvated t-butyl derivative (2) which had crystallised without incorporation of solvent (Figure 2). It was also different from the powder pattern of freshly-ground crystals of the acetone solvate (1). The freshly-ground solvate crystal gives powder photographs which have some of the features of the theoretical powder pattern calculated for the pure solvated crystals, and some of the features of the completely desolvated material (Figure 2). Therefore, it may be that the powder photograph of freshly-ground solvate crystals represents a composite photograph rather than a single crystalline form due to changes induced by the

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† *Note added in proof:* Since acceptance of this paper, the crystal structure of unsolvated (2) has been solved (R. A. Booker, I. C. Paul, and D. Y. Curtin, to be published). In addition there has been a further investigation of the extent of order and molecular motion of guests in cyclophosphazene clathrates (H. R. Allcock, R. W. Allen, E. C. Bissell, L. A. Smeltz, and M. Teeter, *J. Amer. Chem. Soc.*, 1976, **98**, 5120).

‡ For further details and spectra, see ref. 1.

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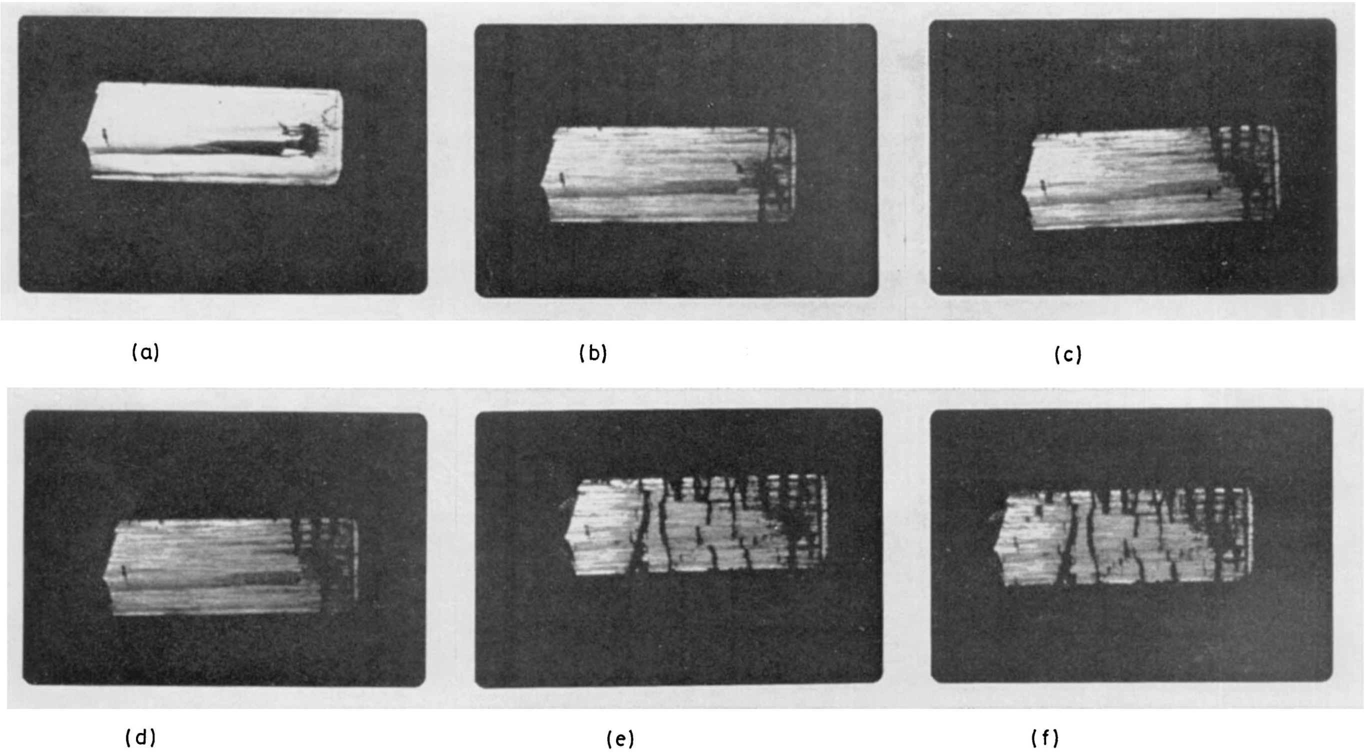

(a) (b) (c) (d) (e) (f)

FIGURE 1 Photographs of loss of acetone from a single crystal of (1) at 45 °C. As acetone escapes, red streaks develop throughout the length of the crystal. When a section becomes red, large cracks perpendicular to the long crystal axis are formed. (a) After 4, (b) 21, (c) 25, (d) 28, (e), 46, and (f) 69 h at 45 °C

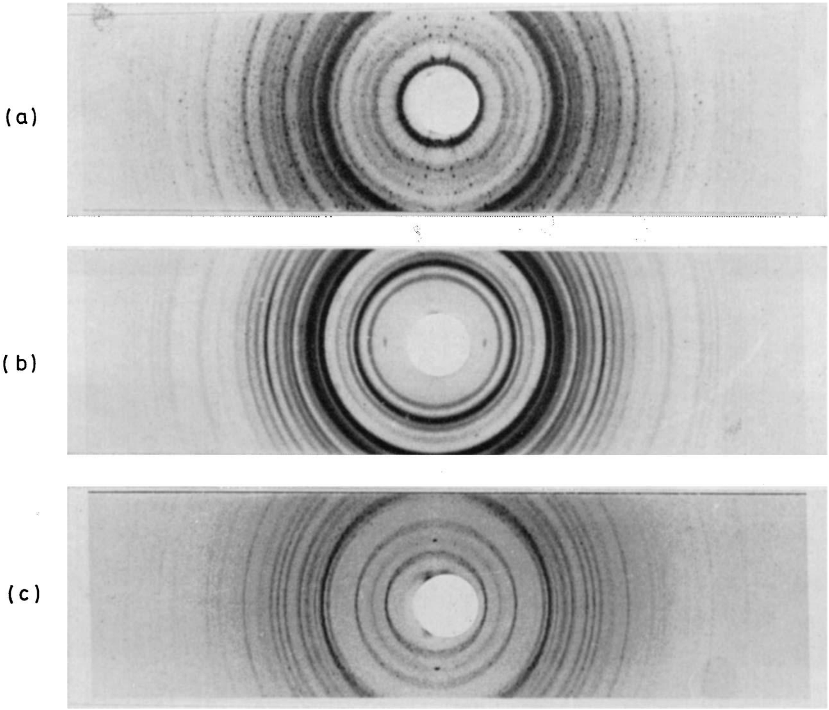

FIGURE 2 *X*-Ray powder pictures of: (a) freshly-ground single crystals of the solvate (1), (b) a 'single crystal' which had originally been (1) but which had been set aside 11 months and assumed to be completely desolvated, and (c) ground crystals of (2) which incorporated no solvent

grinding process. It does appear, however, that the completely desolvated crystals are of a new crystalline form, differing from that of the pure unsolvated crystals and from that of the solvated starting material. Some preliminary attempts to reconvert the desolvated red powder into the yellow acetone solvate by exposure to acetone vapour were unsuccessful.

X-*Ray Structure Determination of Indanetrione* 2-(N-p-*t-Butylbenzoyl*-N-*phenylhydrazone*) *Acetone* (1 : 1) *Solvate* (1).—Upon removal of the orange needles of the solvate (1) from the acetone mother liquor, it was found that the crystals were reasonably stable at room temperature for *ca.* 5 days, and could be kept indefinitely in stoppered vials in the refrigerator or freezer. Microanalysis showed that the ratio hydrazone : acetone was 1 : 1. *X*-Ray photographs and optical gonimetry showed that the long crystal axis was *c* and that the major faces were {100} and {010}.

Crystal Data.—$C_{26}H_{22}N_2O_3{\cdot}CH_3COCH_3$, $M = 468$. Monoclinic, $a = 10.574(4)$, $b = 28.706(14)$, $c = 10.060(4)$ Å, $\beta = 121.0(1)°$, $U = 2\,617$ Å^3, $D_m = 1.15$ g cm^{-3} (by flotation), $Z = 4$ (for 1 : 1 solvate), $D_c = 1.19$ g cm^{-3}, $F(000) = 992$. Cu-K_α radiation, $\lambda = 1.541\,78$ Å, μ(Cu-K_α) = 5.4 cm^{-1}. Systematic absences: $h0l$ when $l = 2n + 1$, $0k0$, when $k = 2n + 1$; space group $P2_1/c$.

Because of the tendency for (1) to lose solvent when exposed to the atmosphere the crystals were sealed in thin-walled glass capillaries. An effective seal was achieved by first placing the epoxy glue in the capillary and gently pushing the crystal through the glue, so that it became coated with glue. Red sealing wax was then used to close the capillary. The mounted crystal was then stored in the refrigerator to allow the glue to harden before data collection.

Intensity data were collected on a crystal with dimensions *ca.* 0.1 × 0.3 × 0.6 mm on a Picker FACS 1 diffractometer (Cu-K_α radiation). The long morphological axis of the crystal (*c* axis) was aligned along the ϕ axis of the diffractometer. Details of the procedures have been described previously.[16b] The intensities of 3 standard reflections, monitored every 50 reflections, fluctuated ±5% with the ambient room temperature, although attempts were made to maintain a constant room temperature of 22° throughout data collection. However, no systematic net loss of intensity for the three standards was observed. Of the 4 765 reflections measured in the 2θ range of 2—130°, 3 535 (74.2%) were considered observed at the 2σ significance level. No absorption corrections were applied. After data collection the crystal was still orange and there was no visual evidence for loss of acetone.

The structure was solved by a symbolic-addition procedure using the FAME MAGIC LINK SYMPL [18] series of programs. An *E* map calculated from the 350 *E* values which had been assigned phases revealed peaks for nearly all nonhydrogen atoms in the hydrazone molecule. Neither the methyl carbon atoms of the t-butyl group nor the atoms of the acetone could be found from this map. After three cycles of full-matrix least-squares refinement on this partial model, the positions of all non-hydrogen atoms except the three methyl carbon atoms of the t-butyl group were located from a Fourier map. Further refinement followed by a difference map demonstrated that the t-butyl group has orientational disorder in the crystal. Six positions of approximately equal electron density, corresponding to a staggered arrangement for the disordered carbon atoms of the t-butyl group, were included in further refinements. The molecule was then divided into two segments: first atoms C(1)—(9), C(17)—(22), O(1), O(2), N(1), N(2), and attached hydrogen atoms, and second C(10)—(16), C(23)—(29), O(3), O(4), and attached hydrogen atoms. Hydrogen atoms on the disordered t-butyl groups were not included. Initially, the parameters associated with the second segment of the molecule were refined. All positional and anisotropic thermal parameters of the non-hydrogen atoms, as well as positional and isotropic thermal parameters of the hydrogen atoms, were varied except for disordered carbon atoms, C(24)—(26), for which only occupancies were varied. After two cycles of refinement, all parameters varied had converged, giving *R* 0.115 and *R′* 0.128. The resulting occupancies for C(24), C(24′), C(25), C(25′), C(26), and C(26′) were 0.53(1), 0.51(1), 0.58(1), 0.41(1), 0.53(1), and 0.41(1). After normalising and averaging, the disordered groups of carbon atoms [(a) and (b)] were included with occupancies of 0.55 and 0.45 and the positional and anisotropic thermal parameters for non-hydrogen atoms and the positional and isotropic thermal parameters for the hydrogen atoms in the second segment were refined to give *R* 0.093 and *R′* 0.109. The hydrogen atoms of the t-butyl group were not included in these calculations. The first segment was then refined, varying positional and anisotropic thermal parameters for the non-hydrogen atoms and the positional and isotropic thermal parameters for the hydrogen atoms. At the end of this refinement, the positions of the hydrogen atoms attached to the disordered t-butyl group were calculated, assuming tetrahedral geometry around the carbon atoms and C–C–C–H torsion angles based on earlier work on a t-butyl group,[19] and were included in the structure-factor calculation but not refined. After two cycles of least-squares refinement on the second segment, *R* converged to a final value of 0.090; *R′* was 0.097.

In a difference map, calculated near the conclusion of the refinement, there were clearly visible areas of positive electron density around two of the atoms of the acetone molecule. While no attempt was made to assign co-ordinates to these hydrogen atoms, the identity of the carbon and oxygen atoms of the acetone molecule was obvious.

Final atomic co-ordinates are listed in Table 1; as the refinement procedure required that the structure be divided into two portions, it is possible that the estimated standard deviations obtained from the least-squares process are somewhat underestimated. Final thermal parameters and the values of *h,k,l*, $|F_o|$, and F_c are listed in Supplementary Publications No. SUP 21788 (36 pp., 1 microfiche).* Scattering curves for carbon, nitrogen, and oxygen were from ref. 20, and for hydrogen from ref. 21.

RESULTS AND DISCUSSION

The *X*-ray analysis establishes the benzoylphenylhydrazone structure for (2) and shows that the incorporated acetone molecules are in fixed positions

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* For details, see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

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within the crystal lattice of the solvate (1) (Figure 3). Figure 4 shows a stereoscopic view of the molecule of (2) as found in the solvate (1). The stereochemistry about the C(10)–N(2) amide bond is such that the two phenyl rings, C(11)—(16) and C(17)—(22), are mutually in a *syn*-orientation. For a detailed discussion of conformational features in this class of molecules, see ref. 17. A number of other relevant molecules have been described.[22-24] Bond lengths and angles are given in Table 2.

TABLE 1

Final co-ordinates for the atoms in the crystal of (1), with estimated standard deviations in parentheses

	x	*y*	*z*
N(1)	0.025 5(4)	0.416 68(12)	0.282 2(4)
N(2)	−0.041 5(4)	0.459 14(12)	0.226 4(4)
O(1)	0.261 5(4)	0.482 17(11)	0.283 2(4)
O(2)	0.182 0(4)	0.333 87(11)	0.434 2(4)
O(3)	0.122 2(3)	0.498 13(9)	0.447 0(3)
O(4)	0.712 9(6)	0.251 03(19)	0.172 4(7)
C(1)	0.280 9(5)	0.444 83(16)	0.347 0(5)
C(2)	0.167 1(5)	0.413 40(15)	0.345 8(5)
C(3)	0.239 9(5)	0.368 43(16)	0.419 2(5)
C(4)	0.399 1(5)	0.374 55(16)	0.473 1(5)
C(5)	0.514 7(6)	0.343 60(21)	0.551 5(7)
C(6)	0.652 8(7)	0.358 65(26)	0.587 6(8)
C(7)	0.675 9(7)	0.402 92(24)	0.547 0(8)
C(8)	0.560 9(6)	0.433 69(20)	0.466 5(7)
C(9)	0.421 5(5)	0.418 83(16)	0.431 0(5)
C(10)	0.015 6(4)	0.499 74(13)	0.316 9(5)
C(11)	−0.058 7(4)	0.544 38(13)	0.245 6(5)
C(12)	−0.112 4(5)	0.555 08(15)	0.088 7(5)
C(13)	−0.162 1(5)	0.599 33(16)	0.035 6(6)
C(14)	−0.166 6(4)	0.634 20(14)	0.128 0(5)
C(15)	−0.113 1(5)	0.622 84(15)	0.283 7(5)
C(16)	−0.060 6(4)	0.579 17(15)	0.340 2(5)
C(17)	−0.199 6(4)	0.452 58(15)	0.125 1(5)
C(18)	−0.292 3(5)	0.455 53(18)	0.186 8(6)
C(19)	−0.440 8(6)	0.446 25(22)	0.090 1(7)
C(20)	−0.496 8(6)	0.434 88(21)	−0.064 1(7)
C(21)	−0.403 3(6)	0.432 98(23)	−0.122 2(7)
C(22)	−0.255 3(6)	0.441 88(19)	−0.029 7(6)
C(23)	−0.220 4(6)	0.683 62(17)	0.069 1(6)
C(24) [a]	−0.302(3)	0.687 5(7)	−0.103(2)
C(24′)	−0.367(4)	0.682 0(11)	−0.067(4)
C(25)	−0.342(2)	0.696 1(5)	0.112(2)
C(25′)	−0.224(3)	0.715 6(6)	0.177(2)
C(26)	−0.094(2)	0.716 7(4)	0.153(2)
C(26′)	−0.115(2)	0.704 5(6)	0.013(3)
C(27)	0.788 5(12)	0.310 4(3)	0.062 9(11)
C(28)	0.760 4(7)	0.290 4(2)	0.180 9(10)
C(29)	0.792 9(9)	0.320 4(3)	0.316 7(11)
H(5) [b]	0.499(6)	0.310 2(20)	0.584(7)
H(6)	0.728(6)	0.339 2(19)	0.633(7)
H(7)	0.784(7)	0.420 2(20)	0.591(7)
H(8)	0.573(5)	0.471 6(17)	0.449(5)
H(12)	−0.112(5)	0.527 6(16)	0.020(5)
H(13)	−0.212(5)	0.603 0(16)	−0.085(6)
H(15)	−0.106(4)	0.646 0(13)	0.365(5)
H(16)	−0.016(5)	0.572 1(15)	0.449(5)
H(18)	−0.242(5)	0.461 5(15)	0.313(5)
H(19)	−0.508(8)	0.444 3(25)	0.150(9)
H(20)	−0.603(5)	0.429 8(16)	−0.132(6)
H(21)	−0.454(7)	0.427 4(22)	−0.230(8)
H(22)	−0.166(7)	0.438 6(21)	−0.059(8)
H(24a) [c]	−0.336	0.718 2	−0.134
H(24b)	−0.246	0.675 1	−0.148
H(24c)	−0.391	0.665 0	−0.150
H(24′a)	−0.417	0.707 9	−0.128
H(24′b)	−0.371	0.657 8	−0.164
H(24′c)	−0.448	0.659 8	−0.067
H(25a)	−0.383	0.724 9	0.083
H(25b)	−0.424	0.670 4	0.073
H(25e)	−0.302	0.690 6	0.230
H(25′a)	−0.272	0.744 0	0.120
H(25′b)	−0.306	0.701 3	0.202
H(25′c)	−0.144	0.717 7	0.271
H(26c)	−0.127	0.747 6	0.119
H(26b)	−0.052	0.714 2	0.269
H(26c)	−0.009	0.707 9	0.145
H(26′a)	−0.141	0.734 8	−0.024
H(26′b)	−0.007	0.702 9	0.102
H(26′c)	−0.110	0.683 4	−0.064

[a] Unprimed carbon atoms, C(24)—(26) had an occupancy 0.55, primed set occupancy 0.45. [b] Hydrogen atoms are numbered according to the atom to which they are attached. [c] Hydrogen atoms attached to the disordered carbon atoms of the Bu^t groups were not refined.

TABLE 2

Bond lengths (Å) and angles (°) in the crystal of (1)

(*a*) Distances

C(1)–C(2)	1.499(7)	C(14)–C(15)	1.403(7)
C(2)–C(3)	1.489(7)	C(15)–C(16)	1.370(6)
C(1)–O(1)	1.211(6)	C(11)–C(16)	1.387(6)
C(3)–O(2)	1.215(6)	C(17)–N(2)	1.454(6)
C(2)–N(1)	1.294(7)	C(17)–C(18)	1.407(7)
N(1)–N(2)	1.376(5)	C(18)–C(19)	1.381(8)
C(3)–C(4)	1.489(7)	C(19)–C(20)	1.385(10)
C(4)–C(5)	1.383(8)	C(20)–C(21)	1.384(10)
C(5)–C(6)	1.380(9)	C(21)–C(22)	1.372(9)
C(6)–C(7)	1.394(10)	C(17)–C(22)	1.386(8)
C(7)–C(8)	1.378(9)	C(23)–C(14)	1.530(7)
C(1)–C(9)	1.478(7)	C(23)–C(24)	1.49(3)
C(4)–C(9)	1.398(7)	C(23)–C(24′)	1.45(4)
C(8)–C(9)	1.393(8)	C(23)–C(25)	1.60(2)
C(10)–C(11)	1.481(6)	C(23)–C(25′)	1.44(2)
C(10)–O(3)	1.211(6)	C(23)–C(26)	1.50(2)
N(2)–C(10)	1.409(6)	C(23)–C(26′)	1.60(2)
C(11)–C(12)	1.409(7)	C(27)–C(28)	1.480(15)
C(12)–C(13)	1.373(7)	C(28)–C(29)	1.497(14)
C(13)–C(14)	1.383(7)	C(28)–O(4)*	1.223(9)

(*b*) Angles

C(2)–C(1)–O(1)	127.7(5)	C(11)–C(12)–C(13)	119.3(4)
C(2)–C(1)–C(9)	105.5(4)	C(12)–C(13)–C(14)	123.1(5)
O(1)–C(1)–C(9)	126.6(5)	C(23)–C(14)–C(13)	123 1(4)
C(1)–C(2)–C(3)	108.1(4)	C(23)–C(14)–C(15)	120.3(4)
C(1)–C(2)–N(1)	132.8(4)	C(13)–C(14)–C(15)	116.6(4)
C(3)–C(2)–N(1)	118.6(4)	C(14)–C(15)–C(16)	121.4(4)
C(2)–C(3)–O(2)	127.2(5)	C(14)–C(23)–C(24)	113.5(10)
C(2)–C(3)–C(4)	106.1(4)	C(14)–C(23)–C(24′)	109.0(15)
O(2)–C(3)–C(4)	126.8(5)	C(14)–C(23)–C(25)	107.1(7)
C(2)–N(1)–N(2)	119.2(4)	C(14)–C(23)–C(25′)	116.7(11)
C(3)–C(4)–C(5)	129.3(5)	C(14)–C(23)–C(26)	108.9(8)
C(3)–C(4)–C(9)	109.4(4)	C(14)–C(23)–C(26′)	107.2(10)
C(5)–C(4)–C(9)	121.3(5)	C(11)–C(16)–C(15)	121.3(4)
C(4)–C(5)–C(6)	117.0(6)	C(17)–N(2)–N(1)	109.6(4)
C(5)–C(6)–C(7)	122.0(7)	C(17)–N(2)–C(10)	121.0(4)
C(6)–C(7)–C(8)	121.4(7)	C(18)–C(17)–C(22)	121.3(5)
C(7)–C(8)–C(9)	116.8(6)	C(18)–C(17)–N(2)	119.6(4)
C(1)–C(9)–C(4)	110.8(4)	C(22)–C(17)–N(2)	119.1(4)
C(1)–C(9)–C(8)	127.7(5)	C(17)–C(18)–C(19)	118.4(5)
C(4)–C(9)–C(8)	121.5(5)	C(18)–C(19)–C(20)	120.6(6)
N(1)–N(2)–C(10)	120.6(4)	C(19)–C(20)–C(21)	119.7(6)
N(2)–C(10)–O(3)	121.2(4)	C(20)–C(21)–C(22)	121.3(6)
N(2)–C(10)–C(11)	117.3(4)	C(17)–C(22)–C(21)	118.7(5)
O(3)–C(10)–C(11)	121.5(4)	C(27)–C(28)–C(29)	117.6(8)
C(10)–C(11)–C(12)	122.6(4)	C(27)–C(28)–O(4)	123.1(8)
C(10)–C(11)–C(16)	118.8(4)	C(29)–C(28)–O(4)	119.3(8)
C(12)–C(11)–C(16)	118.2(4)		

* C–H Lengths range from 0.88(8) to 1.14(7) Å.

The methyl carbon atoms, C(24)—(26), of the t-butyl group exhibit disorder in the solid state in *ca.* 55 : 45 ratio. The absence of any other atoms near the t-butyl

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[22] J. A. McMillan, S. A. Puckett, D. Y. Curtin, and I. C. Paul, to be published.

[23] S. A. Puckett, I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, 1976, **98**, 787, 2371.

[24] F. Bechtel, G. Bravic, J. Gaultier, and C. Hauw, *Acta Cryst.*, 1974, **B30**, 1499.

group may account for this disorder, which is shown in Figure 4, where solid bonds are drawn between the central carbon atom, C(23), and the set of sites of higher occupancy.

The loss of acetone from the crystals of (1) has been followed by microscopy and *X*-ray diffraction techniques. It seems probable that the red colour detected by photomicroscopy (Figure 1), and which develops as streaks elongated along the *c* axis of the crystal, corresponds to regions of the material which have, at least partially, lost acetone. The dark fissures which run almost perpendicular to these red streaks are probably due to some recrystallisation of desolvated material. The directionality of escape of solvent, by being parallel to the most highly developed face of the crystal, is similar to that observed in the desolvation of the other organic solvates, phloroglucinol dihydrate[9] and the hemietherate of phenylazotribenzoylmethane.[10] However, in the latter case the final microcrystalline product of the desolvation gave powder pictures which were identical with those obtained from a sample of phenylazotribenzoylmethane which had been crystallised without incorporation of solvent and then powdered,[10] whereas in the present example there appears to be an intermediate stage where there is a crystal structure which preserves the original axial directions but causes some changes in the repeat distances and also some disordering along the *b* direction. With further desolvation, a microcrystalline product is obtained which, however, has a powder pattern different from that of crystals of (2) obtained by crystallisation from ether–iso-octane without incorporation of solvent. An interesting pattern of behaviour has also been reported for the cephalexin : acetonitrile 1 : 2 solvate,[11] where by use of powder *X*-ray pictures, the authors characterised a 'desolvated crystal' form which preserved many features of the solvated crystals after loss of virtually all solvent, and which did not then revert to the solvent-free form. There has also been reported an *X*-ray investigation of a series of crystalline forms of cephaloridine.[12] On the basis of powder pictures, one of these forms, a hydrate, exhibits an apparently reversible and progressive change in cell parameters as water is lost or readsorbed. The anhydrous material, while it has lost some crystallinity, retains the basic lattice structure of the hydrate.

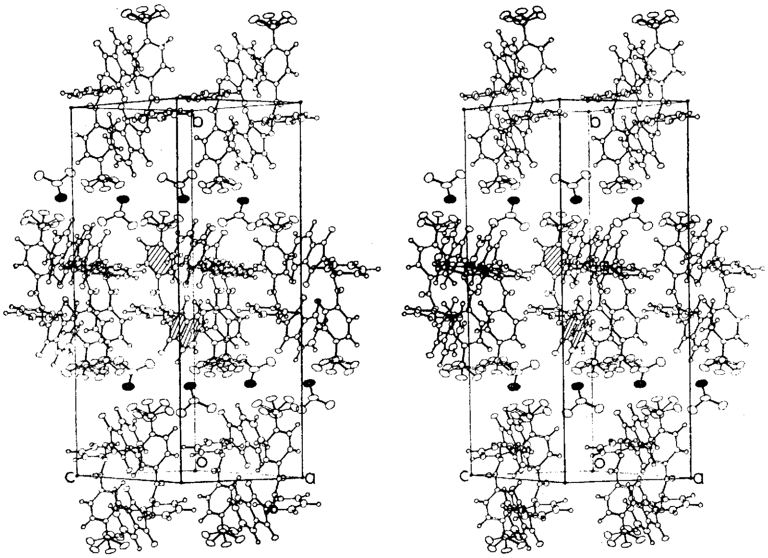

FIGURE 3 Stereoscopic view of the crystal structure of the solvate (1). The bonds of the acetone molecule and the oxygen atom of the acetone molecule are shaded. Two planes of the reference molecule are lightly shaded. Some of the hydrazone molecules at the top and bottom of the drawing are omitted for clarity

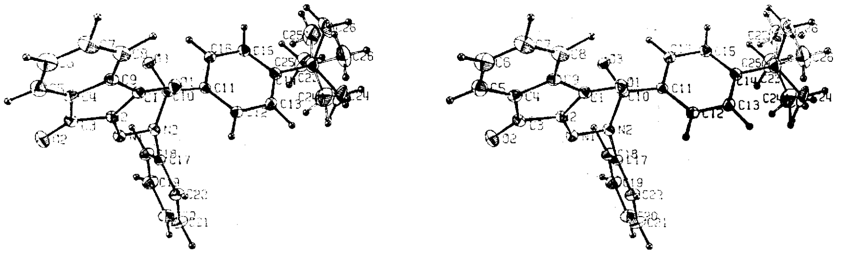

FIGURE 4 Stereoscopic view of the molecule (2) as it is found in the acetone solvate (1). The two orientations of the Bu^t group are shown by solid and open bonds respectively

Some of the observations made on the crystals of the acetone solvate (1) can be correlated with the observed crystal structure (Figures 3 and 5). The crystal is mainly composed of the large indanetrione 2-(*N*-*p*-t-butylbenzoyl-*N*-phenylhydrazone) molecules. However, the acetone molecules are contained in infinite channels running along the *c* crystallographic axis. Unlike some examples of such infinite channels,[25] the acetone molecules are in fixed positions within the channel and the geometry of the acetone molecules was reasonably well defined by the analysis. From a final difference map, the general regions occupied by the methyl hydrogen atoms of the acetone molecules could be seen. While the hydrogen atoms probably exhibit orientational disorder, the oxygen atom of the acetone molecule could be clearly distinguished from the methyl carbon atoms. The length of the acetone C(28)–O(4) bond is 1.223(9) Å, with C(27)–C(28) 1.480(15) and C(29)–C(28) 1.497(14) Å.

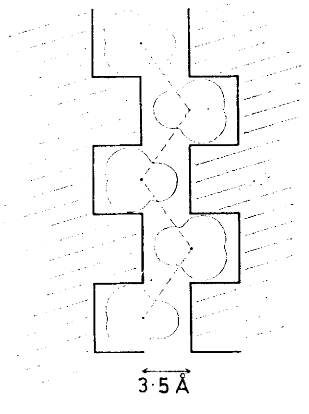

FIGURE 5 Schematic view of the channel showing the zig-zag axis and the compartments containing acetone molecules

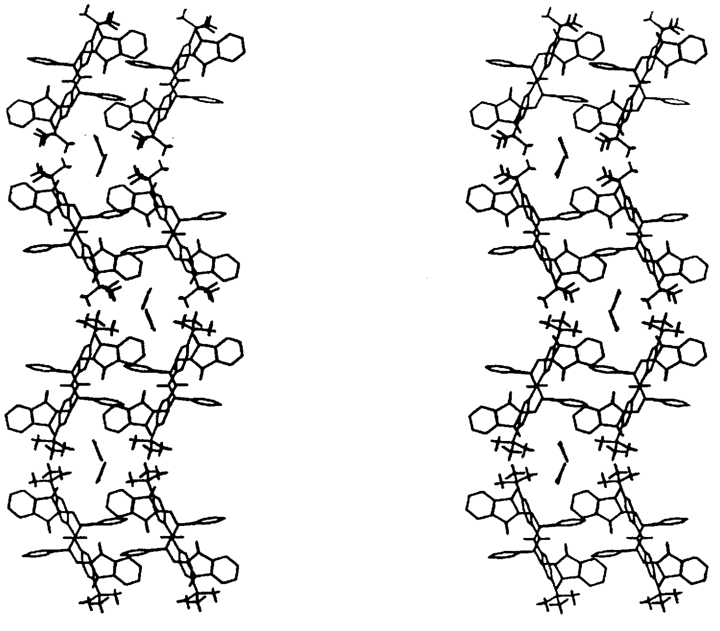

FIGURE 6 Stereoscopic view of the crystal structure of the solvate (1) looking along the *c* axis (*i.e.* along the axis of the channel). The only hydrogen atoms shown are those of the Bu^t groups. Surrounding the top channel in this picture, the Bu^t groups have the *C*-methyl groups in positions indicated by unprimed atoms in Table 1, surrounding the middle channel the upper *C*-methyl groups are represented by unprimed atoms, the lower groups by primed atoms, and in the lowest channel, all *C*-methyl groups are represented by primed atoms

A three-dimensional model of the crystal structure in which both the guest acetone molecules and the surrounding portions of the host are represented by van der Waals contact radii was constructed on glass sheets. Inspection of the model reveals that the axis of the channel is not a straight line but in fact zig-zags by as much as 3.5 Å in the *b* direction (see Figure 5) and that the acetone molecules are contained in the ' compartments ' of the channel. This inclusion of the acetone molecules in separate compartments may be largely responsible for the high degree of molecular order and the relative stability of the crystal. This ' zig-zag ' effect can also be recognized in Figure 3.

Figure 6, a view down the channels, shows that adjacent acetone molecules within the channel are related by the *c* glide operation. The acetone molecules lie approximately parallel to the (100) plane, with the C=O bond directed nearly along the *b* axis. This alignment means that the longest molecular axis [joining the C(Me) · · · C(Me) vector] is along the direction of the channel and the next longest (along the C=O bond axis) is nearly along the larger cross-sectional dimension (in the *b* direction) of the channel. The orientation of the acetone molecules in the channel prevents close over-

[25] C. A. Maier and I. C. Paul, *Chem. Comm.*, 1971, 181.

lapping contacts of the C=O · · · C=O type and the shortest contact between acetone molecules within the channel is 3.99 Å between the oxygen atom and a methyl carbon in the adjacent molecule. There are no very short contacts between acetone molecules and the surrounding molecules of (2), making up the channel, which would suggest very specific guest-channel interactions. A single acetone molecule is contained by three t-butyl groups, two of which are disposed on one side and the third on the other side of the plane of the carbonyl group, by the edge of an indane group, and by the 'open' side of the C:N·NPh group with the face of the C(17)—(22) phenyl ring forming one of the walls of the channel; all five of these groups come from different molecules of (2). As the terminal carbon atoms of the t-butyl group take up two different orientations in the crystal, the type of non-polar interactions present in the channels will depend on the orientation of the t-butyl group. Figure 6 shows the three possible types of $Bu^t : Bu^t$ interactions for the three different channels: those between a pair of sets of unprimed methyl carbon atoms, those between one set of unprimed and one set of primed methyl carbons, and those between a pair of sets of primed methyl carbon atoms. The shortest acetone–channel contacts are 3.26(1) and 3.24(1) Å between O(4) · · · C(5) and O(4) · · · C(6) in the molecule at $x, 1/2 - y, -1/2 + z$. Shortest intermolecular contacts are included in the Supplementary Publication. A direct correlation between the colour change resulting from the loss of acetone with the loss of intermolecular interactions between the acetone and the molecules of (2) appears unlikely, since we have recently observed colours ranging from yellow to deep red for a number of analogues of (2) which crystallise without solvent.[17]

It would appear that the acetone molecules escape from the crystal by diffusion along the channels, *i.e.* along the crystallographic *c* axis. Such a mechanism would be consistent with the appearance of the red streaks running along the macroscopic crystal in the *c* direction. Once a certain amount of acetone has left the crystal, then it is probable that there would be some collapse of the crystal structure in the *a* and *b* directions, and possibly some minor change in the glide-related molecules of (2) (along *c*). As the cross-sectional dimension of the channel is greater in the *b*, than in the *a* direction, it is reasonable that the greatest effect of loss of acetone molecules would be exhibited by changes in the *b* direction, *i.e.* by the greater change in the b^* direction of the *X*-ray diffraction pattern. This mechanism would be consistent with the observation that in the initial stages of loss of acetone, the crystals showed considerable retention of structure in the a^*c^* plane, but greater changes in the b^* direction. However, at some point this 'desolvated lattice' collapses and recrystallisation takes place forming a microcrystalline array. Definite identification of such recrystallisation with the appearance of black fissures across the crystal has not been established.

Sakurai and Okunuki [26] found that on heating single crystals of the 1 : 1 complex of thymine and *p*-benzoquinone at 70 °C, the quinone molecules escaped and left a white thymine crystal which had a twin-like structure based on the anhydrous thymine crystal structure.[27] This result is of particular interest as the 1 : 1 complex had a structure with alternate layers consisting of only thymine and *p*-benzoquinone molecules, and as the thymine layer had a similar molecular arrangement to that found in the thymine crystal itself. The behaviour of the 1 : 1 complex of thymine and *p*-benzoquinone is somewhat reminiscent of that of an intercalate.[28] The loss of solvent from single crystals of $Ni(NCS)_2$ (4-methylpyridine) clathrates has been studied recently.[29] Pictures have been presented of crystals of the benzene clathrate which show the development of cracks on the surface.

Table 3 summarises some of the more versatile organic complexing substances for comparison with the hydrazone (2). Such non-organic complexes as the inert gas hydrates [30] and the zeolites [31] have been omitted. The host compounds have also been limited to those which form a number of different complexes with various guest molecules, although these complexes often have closely similar crystal structures. The crystal structure is almost invariably different from that of the stable form of the host when it crystallizes without solvent and the acceptance of a particular guest is determined to a major degree by its molecular size and shape. The specific complexes listed are those whose crystal structures have been determined. Stabilities vary widely. For example, some deoxycholic acid complexes [32] have been reported to be so stable that their constituents could be separated only by chemical destruction of the host substance or by exchange of one guest for another. Others, *e.g.* the acetone solvate of BSX,[33] lose the guest substance readily in air at room temperature or below. It has been implied [34] that, as might be expected, stability depends markedly on the degree of perfection of the crystals. It appears that our acetone solvate (1) is roughly intermediate in stability in comparison with the range of complexes in the Table.

Comparison of the approximate size of the cavities available to the guest molecules in complex (1) with the other channel complexes listed shows it to be typical of those complexes with the more modest dimensions.

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[26] T. Sakurai and M. Okunuki, *Acta Cryst.*, 1971, **B27**, 1445.

[27] K. Ozeki, N. Sakabe, and J. Tanaka, *Acta Cryst.*, 1969, **B25**, 1038.

[28] See *e.g.* J. M. Thomas, *Trans. Roy. Soc.*, 1974, **A277**, 251; D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and J. O. Williams, *J.C.S. Dalton*, 1974, 2207

[29] W. Kemula, J. Lipkowski, and D. Sybilska, *Roczniki Chem.*, 1974, **48**, 3.

[30] G. A. Jeffrey, *Accounts Chem. Res.*, 1969, **2**, 344.

[31] See *e.g.* A. A. Amora and K. Seff, *J. Chem. Phys.*, 1973, **77**, 906; K. Self, *Accounts Chem. Res.*, 1976, **9**, 121.

[32] L. F. Fieser and M. Fieser, 'Steroids,' Reinhold, New York, 1959, pp. 56—61.

[33] G. F. Claringbull and R. W. H. Small, *Acta Cryst.*, 1971, **B27**, 863.

[34] H. R. Allcock and M. T. Stein, *J. Amer. Chem. Soc.*, 1974, **96**, 49.

TABLE 3

Survey of some of the principal types of inclusion compounds

Host	Extent of order	Guest	Approx. composition	Space group	Cavity type	Approx. cavity size/Å
Hydroquinone (quinol)	Some disorder	Sulphur dioxide [a]	$3C_6H_6O_2\cdot0.88SO_2$	$R\bar{3}$	Spherical cage	4
Dianin's compound (chroman)	Some disorder	Ethanol [b]	$6C_{18}H_{20}O_2\cdot2C_2H_5OH$	$R\bar{3}$	Hour-glass cage	5 × 11
	Some disorder	Chloroform [b]	$6C_{18}H_{20}O_2\cdot CHCl_3$	$R\bar{3}$	Hour-glass cage	5 × 11
	Some disorder	Heptanol [c]	$6C_{18}H_{20}O_2\cdot C_7H_{15}OH$	$R\bar{3}$	Hour-glass cage	5 × 11
α-Cyclodextrin	Some disorder	Propanol [d]	$C_{36}H_{60}O_{30}\cdot C_3H_8O\cdot4.8H_2O$	$P2_12_12_1$	Cylindrical cage	5 × 8
	Ordered	Water [e]	$C_{36}H_{60}O_{30}\cdot6H_2O$	$P2_12_12_1$	Cylindrical cage	5 × 8
	Ordered	Iodine [f]	$C_{36}H_{60}O_{30}\cdot I_2\cdot4H_2O$	$P2_12_12_1$	Cage	5 × 8
	Some disorder	Potassium acetate, water [g]	$C_{36}H_{60}O_{30}\cdot1.54(K^+CH_3CO_2^-)\cdot9.7H_2O$	$P2_12_12_1$	Channel	5
	Ordered	*p*-Iodoaniline [h]	$C_{36}H_{60}O_{30}\cdot C_6H_6NI\cdot3H_2O$	$P2_12_12_1$	Cage	5 × 8
Trithymotide		None [i]	$C_{33}H_{36}O_6$	$Pbn2_1$		
Urea	Some disorder	1,4-Dichlorobutane [j]	$6CH_4NO\cdot C_4H_8Cl_2$	$P6_122$	Channel	5.3
Deoxycholic acid	Some disorder	*p*-Di-iodobenzene [k]	$4DCA\cdot2C_6H_4I_2$	$P2_12_12_1$	Channel	4 × 7.5
	Ordered	Phenanthrene [k]	$4DCA\cdot4/3C_{14}H_{10}$	$P2_12_12_1$	Channel	4 × 7.5
	Ordered	Acetic acid [l]	$4DCA\cdot4CH_3CO_2H$	$P2_12_12_1$	Channel	
	Disorder	Di-t-butyl diperoxycarbonate [m]	$4DCA\cdot1C_9H_9O_5$	$P2_12_12$	Channel	
Tris-(*o*-phenylenedioxy)-phosphonitrile trimer	Highly disordered	Benzene [n]	$2C_{18}H_{12}N_3O_6P_3\cdot C_6H_6$	$P6_3$	Channel	4.5
	(or rotating)	Bromobenzene [n]	$2C_{18}H_{12}N_3O_6P_3\cdot C_6H_5Br$	$P6_3$	Channel	4.5
Tris-(2,3-naphthylenedioxy)cyclotriphosphazene	Highly disordered (possibly rotating)	Benzene [o]	$C_{30}H_{18}N_3O_6P_3\cdot3C_6H_6$	$P6_3/m$	Channel	9—10
Tris-(1,8-naphthylenedioxy)cyclotriphosphazene	Ordered	*p*-Xylene [p]	$2C_{30}H_{18}N_3O_6P_3\cdot C_8H_{10}$	$P\bar{1}$	Channel	5—7
BSX	Ordered	dmf [q]	$C_8H_{14}N_6O_{10}\cdot C_3H_7NO$	$P2_1/n$	Channel	5 × 6
	Ordered	Dioxan [r]	$C_8H_{14}N_6O_{10}\cdot C_4H_8O_2$	$P2_1/n$	Channel	5 × 8
Perhydrotriphenylene	Some disorder	Chloroform [s,t]	$C_{18}H_{30}\cdot0.5CHCl_3$	$P6_3/m$	Channel	6
	Highly disordered	Cyclohexane [s,t]	$C_{18}H_{30}\cdot0.39C_6H_{12}$	$R\bar{3}$	Channel	6
	Highly disordered	n-Heptane [s,t]	$C_{18}H_{30}\cdot0.23C_7H_{16}$	$P6_3/m$	Channel	6
Triphenylmethane	Ordered	Benzene [u]	$C_{19}H_{16}\cdot C_6H_6$	$R\bar{3}$	Channel	6
	Some disorder	Thiophen [u]	$C_{19}H_{16}\cdot C_4H_4S$	$R\bar{3}$	Channel	6
	Some disorder	Pyrrole [u]	$C_{19}H_{16}\cdot C_4H_5N$	$R\bar{3}$	Channel	6
	Some disorder	Aniline [u]	$C_{19}H_{16}\cdot C_6H_7N$	$R\bar{3}$	Channel	6
Indanetrione 2-(*N*-*p*-t-butylbenzoyl-*N*-phenylhydrazone) (2)	Ordered [v]	Acetone [v]	$C_{26}H_{22}N_2O_3\cdot C_3H_6O$	$P2_1/c$	Channel	4 × 5.5

[a] D. E. Palin and H. M. Powell, *J. Chem. Soc.*, 1947, 208. See also ref. 5. This structure was not refined to a high degree of accuracy so the extent of disorder of the guest molecule is somewhat uncertain.

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

[c] J. L. Flippen and J. Karle, *J. Phys. Chem.*, 1971, **75**, 3566.

[d] W. Saenger, R. K. McMullan, J. Fayos and D. Mootz, *Acta Cryst.*, 1974, **B30**, 2019; only the propan-1-ol molecule included within the cage.

[e] P. C. Manor and W. Saenger, *J. Amer. Chem. Soc.*, 1974, **96**, 3630; only two water molecules included within the cage.

[f] R. K. McMullan, W. Saenger, F. Fayos, and D. Mootz, *Carbohydrate Res.*, 1973, **31**, 211.

[g] A. Hybl, R. E. Rundle, and D. E. Williams, *J. Amer. Chem. Soc.*, 1965, **87**, 2779; one acetate anion and two water molecules per $C_{36}H_{60}H_{30}$ moiety inside the channel, remaining ions and water molecules occupy lattice sites outside channel, or link channels together.

[h] Water molecules not within cage, dimensions of which, although not given, appear similar to those of the other structures.

[i] S. Brunie and G. Tsoucaris, *Cryst. Struct. Comm.*, 1974, **3**, 481; see also D. J. Williams and D. Lawton, *Tetrahedron Letters*, 1975, 111. See ref. 5 for complexes. A preliminary report on the pyridine complex of tri-*o*-thymotide (TOT) indicated that there are two TOT molecules per pyridine molecule and that the pyridine molecule was ordered; the dimensions of the cavity are not available (S. Brunie, A. Navaza, and G. Tsoucaris, *Acta Cryst.*, 1975, **A31**, S 127). Preliminary reports have also been given for the 2 : 1 complex of TOT and ethyl alcohol and for the 1 : 1 complex of TOT and cetyl alcohol (D. J. Williams and D. Lawton, *Tetrahedron Letters*, 1975, 111); these two complexes were of the cavity and channel types, respectively.

[j] J. Otto, *Acta Cryst.*, 1972, **B28**, 543; see also ref. 6.

[k] S. C. DeSanctis, E. Giglio, V. Pavel, and C. Qualiata, *Acta Cryst.*, 1972, **B28**, 3656.

[l] B. M. Craven and G. T. DeTitta, *J.C.S. Chem. Comm.*, 1972, 530; co-ordinates not given so dimensions of channel could not be estimated, but are probably similar to those for other choleic acids since cell dimensions very similar.

[m] N. Friedman, M. Lahav, L. Leiserowitz, R. Popovit-Biro, C.-P. Tang, and Z. V. I. Zaretzkii, *J.C.S. Chem. Comm.*, 1975, 864. Dimensions of channel not given. Chemical reaction carried out between guest peroxide and host steroid.

[n] L. A. Siegel and J. H. van den Hende, *J. Chem. Soc. (A)*, 1967, 817. A recent reinvestigation of this structure gave a better refinement in the space group $P6_3/m$; however the other conclusions were unchanged (H. R. Allcock, R. W. Allen, E. C. Bissell, L. A. Smeltz, and M. Teeter, *J. Amer. Chem. Soc.*, 1976, **98**, 5120).

[o] See ref. 34.

[p] H. P. Allcock, M. T. Stein, and E. C. Bissell, *J. Amer. Chem. Soc.*, 1974, **16**, 4796.

[q] R. E. Cobbledick and R. W. H. Small, *Acta Cryst.*, 1973, **B29**, 1659.

[r] R. E. Cobbledick and R. W. H. Small, *ibid.*, 1973, **B29**, 2585.

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Such a comparison can only be approximate, as channels are generally not of uniform diameter throughout their length. There is also considerable variation in the degree of order of the guest in the channel or cage formed by the host. Some guests, *e.g.* the benzene or bromobenzene molecule in the tris-(*o*-phenylenedioxy)-phosphonitrile trimer[35] exhibit almost complete orientational disorder and may in fact be rotating in the crystal, whereas others [*e.g.* the acetone molecules of (1)] are quite highly ordered.

The specific formation of an acetone solvate (1) by the host substance (2) deserves comment. As described in the experimental section the use of pentane–diethyl ether as recrystallisation solvent led to solvent-free crystals of (2) with, presumably, a quite different crystal structure since the space group was $P\bar{1}$. Crystal forms obtained with and without solvent have been described as pseudopolymorphs[11] or pseudomorphs.[33] We have not yet made a serious attempt to investigate the possibility of incorporation of small molecules other than acetone into a solvate of the hydrazone (2).

In this context, the tris-(*o*-phenylenedioxy)phosphonitrile trimer[35] is of particular interest because it can be prepared in a solvent-free form by sublimation, the solvent-free crystals being highly reactive to even the vapour of the guest substance; sublimed samples brought into contact with the vapour swelled and the crystals disintegrated as the complex was formed.

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