Complexation with Diol Host Compounds. Part 6. Structure and Dynamics of Enclathration by 1,1,6,6-Tetraphenyl-hexa-2,4-diyne-1,6-diol

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The host compound 1,1,6,6-tetraphenyl-hexa-2,4-diyne-1,6-diol forms inclusion compounds with acetone($Pbca$) and benzophenone($P2_1/c$). The structures of the nonporous α-phase of the host ($P1bar$), as well as those of the host–guest compounds, have been elucidated. The kinetics of the reaction of the host with both these guest molecules have been analyzed.   © 1991 Academic Press, Inc.

Introduction

Diol compounds have proved to be very versatile as hosts in the formation of inclusion compounds usually with concomitant hydrogen bond formation between host and guest molecules.

Recently Toda has reviewed these compounds and their uses with respect to the isolation and optical resolution of racemates (*1*), and their use in controlling guest reactions in clathrates (*2*).

The host compound, 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol, and its inclusion complexes with various n^*- and π^*-donors was announced by Toda in 1968 (*3*). The

crystal structure of the inclusion compound with acetone (*4*) and its use in the isolation of alcohols (*5*) have been reported. The solid state reactions between this host and a number of guest molecules including benzophenone, chalcone, and 2-pyridone have been studied (*6*).

In this work we report the structure of the unclathrated form of the host compound (α-phase), and the kinetics of the complexation reaction with acetone vapor. We also describe the kinetics of the solid state reaction with benzophenone, together with the crystal structure of the final product. The crystal structure of host · 2 acetone has been previously determined but only refined to a final R of 0.128. As accurate atomic parameters for subsequent molecular mechanics

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calculations were required, we repeated this crystal structure analysis.

Experimental

Crystal Structures

The host compound (I) proved to be very difficult to crystallize in the pure form. This is because its molecular shape corresponds to the "wheel and axle" or "dogbone" design and is such that it encapsulates a wide variety of solvent molecules. Suitable crystals were obtained eventually by dissolving the compound in a mixture (2 : 1 vol/vol) of diethyl ether and petroleum ether (b.p. 100–120°C) and allowing the solution to evaporate over a period of 2 weeks at room temperature.

Crystals of the host · 2 acetone compound, (II), are readily obtained by dissolving the host in excess acetone and allowing the solution to stand for a few hours. The host · benzophenone compound, (III), was obtained from a solution containing equimolar quantities of host and guest in cyclohexane and allowing this to evaporate slowly over a period of 3 days.

Preliminary cell dimensions and space group assignments were carried out photographically for the structural determinations. Accurate cell parameters were then obtained by least-squares analyses of twenty-five reflections measured in the range $16° < \Theta < 17°$ on a Nonius CAD4 diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.7107$ Å). Compound II is unstable in air, thus a small crystal was mounted in a Lindemann tube in order to minimize crystal deterioration. Crystal data and experimental details of the data collections are listed in Table I.

The structures of all three compounds were solved by direct methods and refined by full-matrix least-squares routines using the SHELX 86 and SHELX 76 program system (7). The nonhydrogen atoms were treated anisotropically in all cases and the aromatic hydrogens were constrained to 1.0 Å from their parent carbons, with a common temperature factor. The hydroxyl hydrogens possessed individual temperature factors and were located by difference electron density maps and refined with a simple bond length constraint to their parent oxygens. The final refinement parameters are shown in Table II. The fractional atomic coordinates and temperature factors of I, II, III are shown in Tables IIIa, IIIb, and IIIc, respectively.

Solid–Vapour Kinetics

The kinetics of the reaction between solid host and acetone vapor were studied by measuring the gain in mass of the host compound with time. The initial preparation of this host compound bears further comment: The process of clathration in solution is thought to occur by the host molecules surrounding a given guest and aggregating in such a way so as to yield a clathrate crystal (β-phase). The guest thus acts as a template and so yields a structure in which shape and symmetry are strongly dependent on the character of the guest molecule (8). The clathrate structure thus formed collapses to the original structure of the pure host compound (α-phase) when the guest molecules are removed.

The kinetics of the reaction

$$\text{host}_{(s)} + 2 \text{ acetone}_{(g)} \rightarrow \text{host} \cdot \text{acetone}_{(s)}$$
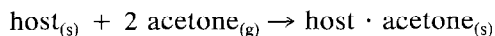
involve the formation of hydrogen bonds between the hydroxyls as donors and the acetone carboxyls as acceptors. The kinetics therefore depend on a diffusion process, and the crystal structure of the host which is exposed to the acetone vapor is of crucial importance.

We recorded the X-ray powder diffraction diagram of crushed crystals obtained from diethyl ether (α-form). We prepared the acetone clathrate as described above and again

TABLE I

CRYSTAL DATA AND EXPERIMENTAL DETAILS

Compound:	I	II	III
Molecular formula	$C_{30}H_{22}O_2$	$C_{30}H_{22}O_2 \cdot 2C_3H_6O$	$C_{30}H_{22}O_2 \cdot C_{13}H_{10}O$
Molecular weight (gmol^{-1})	414.49	530.64	596.71
Space group	$P1bar$	$Pbca$	$P2_1/c$
a (Å)	6.051(7)	16.078(3)	16.119(3)
b (Å)	12.606(13)	16.182(5)	9.181(3)
c (Å)	15.708(12)	11.517(4)	23.541(3)
α (°)	111.20(7)	90	90
β (°)	94.19(8)	90	108.62(1)
γ (°)	92.96(10)	90	90
Z	2	8	2
V (cm^3)	1110.2	2996.4	3301.4
D_c (gcm^{-3})	1.24	1.18	1.20
D_m (gcm^{-3})	1.23	1.16	1.19
λ(MoKα)(cm^{-1})	0.41	0.49	0.40
$F(000)$	436	1128	1256
Data collection (21°C)			
Crystal dimensions (mm)	$0.25 \times 0.38 \times 0.47$	$0.44 \times 0.50 \times 0.53$	$0.47 \times 0.25 \times 0.31$
Range scanned θ (°)	1–25	1–30	1–30
Range of indices h,k,l	$\pm7, \pm15, \pm18$	$+22, +22, +16$	$\pm19, +10, +28$
Reflections for lattice parameters: No., θ range (°)	24,16–17	24,16–17	24,16–17
Instability of standard reflections (%)	1.9	0.4	1.0
Scan mode	$(\omega\text{-}2\theta)$	$(\omega\text{-}2\theta)$	$(\omega\text{-}2\theta)$
Scan width in (°) vertical aperture length (mm)	$(0.90 + 0.35 \tan \theta)$ 6	$(0.85 + 0.35 \tan \theta)$ 6	$(0.90 + 0.35 \tan \theta)$ 6
Aperture width (mm)	$(1.12 + 1.05 \tan \theta)$	$(1.12 + 1.05 \tan \theta)$	$(1.12 + 1.05 \tan \theta)$
Number of reflections collected (unique)	3888	4355	5783
Number of reflections observed with $I_{rel} > 2rl_{rel}$	1987	2315	3345

TABLE II

FINAL REFINEMENT PARAMETERS

Compound	I	II	III
Number of parameters	358	192	425
R	0.068	0.065	0.045
wR	0.076	0.071	0.052
w	$(r^2F + 0.006F^2)^{-1}$	$(r^2F + 0.001F^2)^{-1}$	$(r^2F - 0.002F^2)^{-1}$
S	1.27	2.44	0.849
Maximum shift/e.s.d.	0.016	0.83	0.001
Maximum height in difference Fourier map (eA^{-3})	0.22	0.22	0.14
Minimum height in difference Fourier map (eA^{-3})	-0.21	-0.24	-0.23

TABLE IIIa

FRACTIONAL ATOMIC COORDINATES ($\text{Å} \times 10^4$) AND THERMAL PARAMETERS ($\text{Å}^2 \times 10^3$) WITH E.S.D.'S IN PARENTHESES FOR COMPOUND I

Atom	x/a	y/b	z/c	U_{iso}/U_{eq}
O(1)	7449(5)	515(3)	1903(2)	45(1)
H(1)	7607(99)	839(50)	1416(31)	95(22)
O(2)	−2513(5)	4509(3)	3121(3)	49(1)
H(2)	−2762(101)	4127(54)	3481(44)	91(23)
C(1)	5144(6)	188(3)	1912(3)	33(2)
C(2)	3944(7)	1221(4)	2146(3)	40(2)
C(3)	3060(7)	2093(3)	2362(3)	39(2)
C(4)	2032(7)	3079(4)	2610(3)	39(2)
C(5)	1102(7)	3937(4)	2848(3)	39(2)
C(6)	−270(6)	4917(3)	3110(3)	34(2)
C(11)	4967(7)	−332(3)	2651(3)	38(2)
C(12)	6730(9)	−916(5)	2830(4)	59(3)
H(12)	7917(98)	−996(52)	2477(42)	85(4)
C(13)	6542(14)	−1417(6)	3483(5)	87(4)
H(13)	8018(93)	−1763(47)	3673(39)	85(4)
C(14)	4752(16)	−1362(6)	3942(5)	88(4)
H(14)	4505(92)	−1644(49)	4421(43)	85(4)
C(15)	3016(13)	−769(6)	3780(5)	81(3)
H(15)	1724(98)	−626(51)	4149(41)	85(4)
C(16)	3139(9)	−275(4)	3129(4)	55(2)
H(16)	2209(98)	111(52)	2954(43)	85(4)
C(21)	4246(7)	−701(3)	973(3)	34(2)
C(22)	2099(7)	−722(4)	601(3)	42(2)
H(22)	1094(93)	−137(51)	933(40)	85(4)
C(23)	1330(8)	−1560(4)	−234(4)	50(2)
H(23)	−82(96)	−1464(49)	−484(42)	85(4)
C(24)	2676(9)	−2370(4)	−697(3)	54(2)
H(24)	2314(93)	−2843(52)	−1317(42)	85(4)
C(25)	4806(9)	−2349(4)	−326(4)	58(2)
H(25)	5647(94)	−2954(53)	−703(42)	85(4)
C(26)	5568(8)	−1527(4)	505(3)	50(2)
H(26)	7111(95)	−1489(47)	820(40)	85(4)
C(31)	−260(7)	5468(3)	2381(3)	39(2)
C(32)	−2160(10)	5422(5)	1826(4)	62(3)
H(32)	−3625(94)	5019(49)	1996(40)	85(4)
C(33)	−2019(15)	5908(7)	1161(5)	92(4)
H(33)	−3345(101)	5903(53)	920(44)	85(4)
C(34)	−119(18)	6431(6)	1045(5)	92(4)
H(34)	179(86)	6840(48)	531(41)	85(4)
C(35)	1735(14)	6497(6)	1610(5)	86(3)
H(35)	3077(95)	6837(51)	1469(40)	85(4)
C(36)	1689(10)	6013(5)	2268(4)	66(3)
H(36)	3110(94)	5855(50)	2512(41)	85(4)
C(41)	584(7)	5804(3)	4059(3)	135(2)
C(42)	−798(8)	6616(4)	4505(3)	46(2)
H(42)	−2114(96)	6589(51)	4250(42)	85(4)
C(43)	−100(11)	7454(4)	5348(4)	63(2)
II(43)	−1167(95)	8041(53)	5639(40)	85(4)
C(44)	2031(11)	7479(4)	5750(4)	60(2)
H(44)	2375(94)	8038(51)	6338(42)	85(4)
C(45)	3391(9)	6682(4)	5319(4)	53(2)
H(45)	4881(96)	6703(50)	5633(42)	85(4)
C(46)	2708(8)	5837(4)	4471(3)	46(2)
H(46)	3710(93)	5253(50)	4132(40)	85(4)

TABLE IIIb

FRACTIONAL ATOMIC COORDINATES ($\mathrm{\AA} \times 10^4$) AND THERMAL PARAMETERS ($\mathrm{\AA}^2 \times 10^3$) WITH E.S.D.'S IN PARENTHESES FOR COMPOUND II

Atom	x/a	y/b	z/c	U_{iso}/U_{eq}
O(1)	288(1)	875(1)	1745(1)	44(1)
H(1)	650(17)	1313(13)	1820(28)	88(10)
C(1)	−398(1)	1017(1)	2514(2)	35(1)
C(2)	−228(1)	577(1)	3620(2)	41(1)
C(3)	−84(1)	211(1)	4494(2)	43(1)
C(11)	−491(1)	1946(1)	2716(2)	37(1)
C(12)	−205(2)	2329(1)	3705(2)	62(1)
H(12)	31(2)	1990(1)	4352(2)	83(3)
C(13)	−243(2)	3186(2)	3810(3)	74(1)
H(13)	−21(2)	3461(2)	4524(3)	83(3)
C(14)	−581(2)	3655(2)	2943(3)	68(1)
H(14)	−629(2)	4267(2)	3030(3)	83(3)
C(15)	−849(2)	3277(2)	1962(3)	75(1)
H(15)	−1076(2)	3617(2)	1310(3)	83(3)
C(16)	−815(2)	2428(2)	1848(2)	60(1)
H(16)	−1028(2)	2161(2)	1124(2)	83(3)
C(21)	−1174(1)	636(1)	1966(2)	35(1)
C(22)	−1128(2)	198(1)	937(2)	48(1)
H(22)	−578(2)	118(1)	548(2)	83(3)
C(23)	−1840(2)	−130(2)	441(3)	64(1)
H(23)	−1800(2)	−449(2)	−300(3)	83(3)
C(24)	−2597(2)	−21(2)	958(3)	64(1)
H(24)	−3111(2)	−247(2)	587(3)	83(3)
C(25)	−2648(2)	403(2)	1993(3)	64(1)
H(25)	−3199(2)	474(2)	2382(3)	83(3)
C(26)	−1941(1)	728(2)	2493(2)	53(1)
H(26)	−1983(1)	1035(2)	3245(2)	83(3)
O(1G)	1482(2)	2031(1)	1313(3)	131(1)
C(1G)	1791(2)	2666(2)	1106(3)	73(1)
C(2G)	2452(4)	2709(3)	222(6)	166(3)
H(21G)	2875(4)	3149(3)	370(6)	160(0)
H(22G)	2018(4)	2922(3)	−323(6)	160(0)
H(23G)	2730(4)	2216(3)	−130(6)	160(0)
C(3G)	1602(5)	3435(3)	1659(7)	189(4)
H(31G)	2001(5)	3908(3)	1703(7)	160(0)
H(32G)	1738(5)	3024(3)	2280(7)	160(0)
H(33G)	1023(5)	3643(3)	1773(7)	160(0)

characterized the structure by X-ray powder diffraction (β-phase). This compound was then heated to 60°C for 12 hr under vacuum, and the X-ray diffraction diagram showed unambiguously that the structure has reverted to the α-phase.

The host compound thus prepared was placed in a bucket attached to a silica spring. The silica spring has been precalibrated with known masses and yielded an excellent extension–weight linear calibration. Liquid acetone was placed in the bottom of a water-thermostatted tube which was connected to a vacuum line. In this way the sample suspended in the bucket was exposed to acetone vapors.

TABLE IIIc

FRACTIONAL ATOMIC COORDINATES ($\mathring{A} \times 10^4$) AND THERMAL PARAMETERS ($\mathring{A}^2 \times 10^3$) WITH E.S.D.'S IN PARENTHESES FOR COMPOUND III

Atom	x/a	y/b	z/c	U_{iso}/U_{eq}
O(1A)	7967(1)	781(2)	5582(1)	46(1)
H(1A)	8413(16)	1543(26)	5651(14)	89(11)
C(1A)	7941(1)	−48(3)	5061(1)	38(1)
C(2A)	8851(1)	−125(3)	5034(1)	42(1)
C(3A)	9579(1)	−46(3)	5014(1)	40(1)
C(11A)	7604(1)	−1557(3)	5156(1)	38(1)
C(12A)	6828(2)	−2109(3)	4786(1)	66(1)
H(12A)	6474(2)	−1534(3)	4431(1)	84(2)
C(13A)	6533(2)	−3455(4)	4901(2)	91(2)
H(13)	5960(2)	−3831(4)	4633(2)	84(2)
C(14A)	7009(3)	−4278(4)	5376(2)	81(2)
H(14A)	6802(3)	−5266(4)	5448(2)	84(2)
C(15A)	7778(2)	−3725(4)	5751(2)	74(2)
H(15A)	8126(2)	−4304(4)	6107(2)	84(2)
C(16A)	8076(2)	−2371(3)	5643(1)	58(1)
H(16A)	8639(2)	−1983(3)	5921(1)	84(2)
C(21A)	7361(1)	680(3)	4488(1)	40(1)
C(22A)	7400(2)	245(3)	3934(1)	52(1)
H(22A)	7828(2)	−521(3)	3910(1)	84(2)
C(23A)	6853(2)	863(4)	3414(1)	67(1)
H(23A)	6886(2)	540(4)	3017(1)	84(2)
C(24A)	6267(2)	−1911(4)	3441(2)	78(1)
H(24A)	5876(2)	2365(4)	3065(2)	84(2)
C(25A)	6215(2)	2338(4)	3987(2)	85(2)
H(25A)	5781(2)	3097(4)	4005(2)	84(2)
C(26A)	6761(2)	1729(3)	4512(1)	61(1)
H(26A)	6721(2)	2051(3)	4909(1)	84(2)
O(1B)	6973(1)	2142(2)	6203(1)	50(1)
H(1B)	7276(22)	1491(35)	6003(16)	114(13)
C(1B)	6294(1)	1306(3)	6319(1)	41(1)
C(2B)	5726(2)	682(3)	5747(1)	47(1)
C(3B)	5265(2)	250(3)	5273(1)	50(1)
C(11B)	5734(1)	2349(3)	6546(1)	38(1)
C(12B)	5013(2)	1808(3)	6679(1)	48(1)
H(12B)	4872(2)	746(3)	6628(1)	84(2)
C(13B)	4491(2)	2727(4)	6880(1)	58(1)
H(13B)	3970(2)	2331(4)	6972(1)	84(2)
C(14B)	4687(2)	4196(4)	6955(1)	63(1)
H(14B)	4310(2)	4864(4)	7102(1)	84(2)
C(15B)	5402(2)	4730(3)	6827(1)	61(1)
H(15B)	5545(2)	5791(3)	6881(1)	84(2)
C(16B)	5928(2)	3811(3)	6621(1)	50(1)
H(16B)	6448(2)	4211(3)	6530(1)	84(2)
C(21B)	6709(1)	120(3)	6779(1)	42(1)
C(22B)	7070(2)	487(3)	7377(1)	54(1)
H(22B)	7029(2)	1515(3)	7506(1)	84(2)
C(23B)	7485(2)	−540(4)	7799(1)	65(1)
H(23B)	7731(2)	−254(4)	8231(1)	84(2)
C(24B)	7562(2)	−1946(4)	33(2)	70(1)

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TABLE IIIc—*Continued*

Atom	x/a	y/b	z/c	U_{iso}/U_{eq}
H(24B)	7866(2)	−2688(4)	7940(2)	84(2)
C(25B)	7217(2)	−2335(4)	7038(2)	78(2)
H(25B)	7278(2)	−3359(4)	6912(2)	84(2)
C(26B)	6788(2)	−1314(3)	6615(1)	66(1)
H(26B)	6531(2)	−1610(3)	6186(1)	84(2)
O(1G)	10900(1)	−2102(2)	8917(1)	81(1)
C(1G)	10389(2)	−1188(3)	8623(1)	50(1)
C(11G)	10405(2)	−825(3)	8011(1)	46(1)
C(12G)	11149(2)	−1139(3)	7853(1)	61(1)
H(12G)	11672(2)	−1581(3)	8156(1)	94(4)
C(13G)	11167(2)	−846(4)	7287(2)	77(2)
H(13G)	11708(2)	−1057(4)	7180(2)	94(4)
C(14G)	10443(3)	−260(4)	6863(2)	80(2)
H(14G)	10458(3)	−46(4)	6450(2)	94(4)
C(15G)	9702(2)	27(4)	7009(1)	72(1)
H(15G)	9175(2)	436(4)	6699(1)	94(4)
C(16G)	9676(2)	−245(3)	7578(1)	57(1)
H(16G)	9133(2)	−25(3)	7681(1)	94(4)
C(21G)	9772(2)	−467(3)	8883(1)	47(1)
C(22G)	9575(2)	1001(3)	8802(1)	54(1)
H(22G)	9819(2)	1597(3)	8537(1)	94(4)
C(23G)	9043(2)	1644(3)	9086(1)	66(1)
H(23G)	8917(2)	2711(3)	9035(1)	94(4)
C(24G)	8684(2)	831(5)	9437(1)	78(2)
H(24G)	8287(2)	1298(5)	9634(1)	94(4)
C(25G)	8871(2)	−629(5)	9517(1)	78(2)
H(25G)	8609(2)	−1223(5)	9772(1)	94(4)
C(26G)	9419(2)	−1274(3)	9247(1)	63(1)
H(26G)	9564(2)	−2332(3)	9315(1)	94(4)

The apparatus is shown diagrammatically in Fig. 1. The increments by which the silica spring extended with time were measured using a cathetometer. The vapor pressure was controlled by maintaining the water flowing through the double-walled tube at a certain temperature, the latter being recorded by a thermocouple which was inserted in a glass finger in the bottom of the reaction chamber.

Solid–Solid Reaction

The solid state reaction between the host and benzophenone was performed by mixing predried powdered samples of host and guest in a molar ratio of 1 : 1 and then by
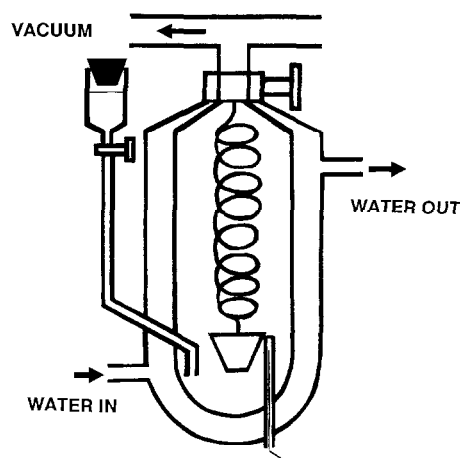

FIG. 1. Gas–solid reaction apparatus.

SHAKING TIME = 0

2 MINUTES

6 MINUTES

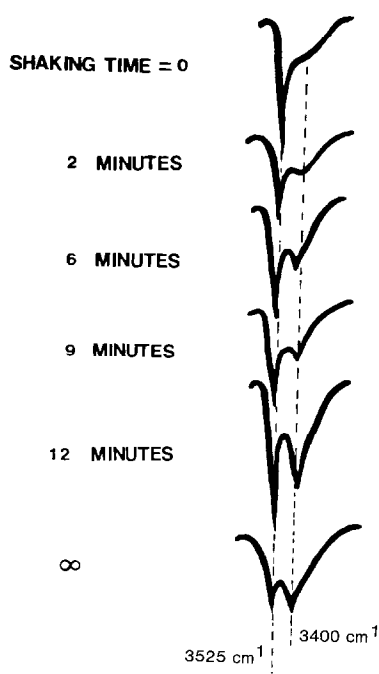9 MINUTES

12 MINUTES

∞

3400 cm⁻¹

3525 cm⁻¹

FIG. 2. IR spectra showing hydrogen bond formation in the solid–solid reaction.

shaking them in a test tube at a constant frequency. The powder samples were sieved beforehand to ensure equality of particle size.

We attempted to follow the reaction by a variety of analytical techniques; however, X-ray powder diffraction, Raman spectroscopy, and solid state NMR proved insufficiently reproducible due to difficulty in reproducing quantitative results. The reaction was followed by removing small samples of the host · benzophenone mixture every 2 min. Suitable results were obtained finally using infrared spectroscopy and spectra were recorded in NUJOL mull or KBr disks over the range 3000 cm^{-1} to 3600 cm^{-1}. At the beginning of the reaction, a strong absorption band at 3525 cm^{-1} due to free OH stretching was observed (Fig. 2) (10). As the reaction proceeds, this band decreases in size and a band at 3400 cm^{-1} appears. This is due to hydrogen bonding occurring with the free OH and this peak increases in size as the reaction proceeds. Even at the beginning of the reaction, we measured a shoulder at 3400 cm^{-1} due to the absorption of the free OH of water. Difficulties with reproducibility of the sampling technique and maintaining the system vigorously dry prevented us from obtaining quantitative results. The reaction is effectively completed after 16 min of shaking at room temperature.

Results and Discussion

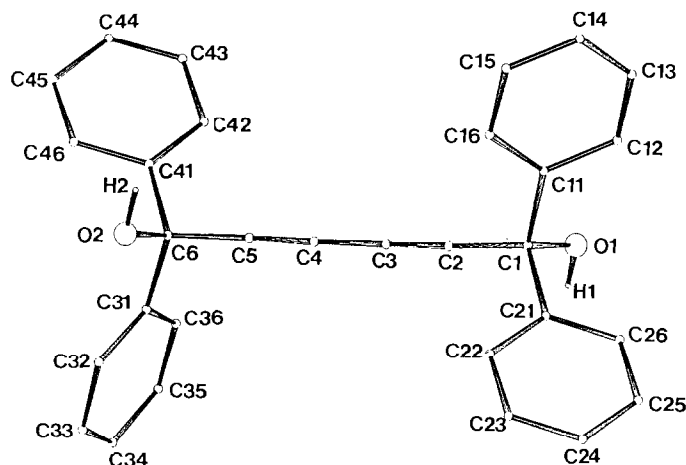The crystal structure of the α-form shows the conformation of the two hydroxyl

C44
C43
C45
C46
H2
C41
C42
O2
C6 C5 C4 C3 C2 C1
O1
H1
C31
C36
C32
C35
C33
C34

C14
C15
C13
C16
C12
C11
C21
O1
H1
C22
C26
C23
C25
C24

FIG. 3. Perspective view of the host molecule.

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TABLE IV

BOND LENGTHS (Å)

	I	II	III		(d)
			A	B	
C1–C2	1.466(6)	1.485(3)	1.490(3)	1.481(3)	1.472(12)
C2–C3	1.195(6)	1.191(3)	1.192(3)	1.194(3)	1.181(14)
C3–C4	1.360(6)	1.378(3)	1.382(3)	1.376(3)	1.377(12)
C4–C5	1.195(7)	—	—	—	
C5–C6	1.474(6)	—	—	—	
C1–C11	1.533(7)	1.529(2)	1.530(4)	1.526(3)	1.513(14)
C1–C21	1.533(5)	1.528(3)	1.528(3)	1.530(3)	
C6–C31	1.539(7)	—	—	—	
C6–C41	1.537(5)	—	—	—	
C11–C12	1.376(9)	1.376(4)	1.376(5)	1.380(5)	
C1–O1	1.436(5)	1.433(2)	1.433(3)	1.431(3)	1.440(12)
C6–O2	1.430(5)	—	—	—	
O1–H1	0.997(63)	0.972(24)	0.979(25)	0.982(39)	
O2–H2	0.881(80)	—	—	—	

groups to be *trans*, as is shown in Fig. 3. The bond lengths and angles are within the range of values found for compounds of this type. The values of selected bond lengths are shown in Table IV, and they all lie within two standard deviations of the average bond lengths. The packing of the structure (with van der Waal radii) is shown in Fig. 4a and Fig. 4b. Surprisingly, no hydrogen bonding takes place, and the structure has a high packing factor of 17.4 Å/nonhydrogen atom ($D_c = 1.24$ gcm^{-3}).
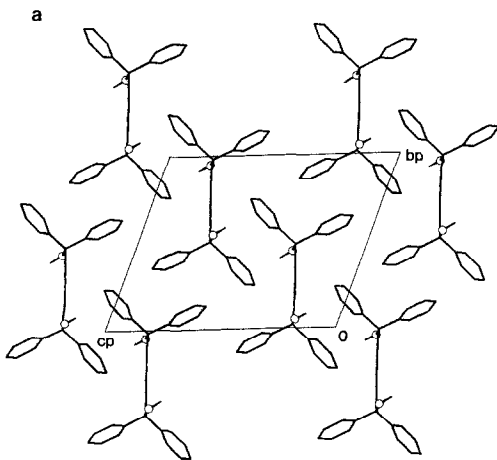
FIG. 4a. Packing diagram of host I viewed along [100].
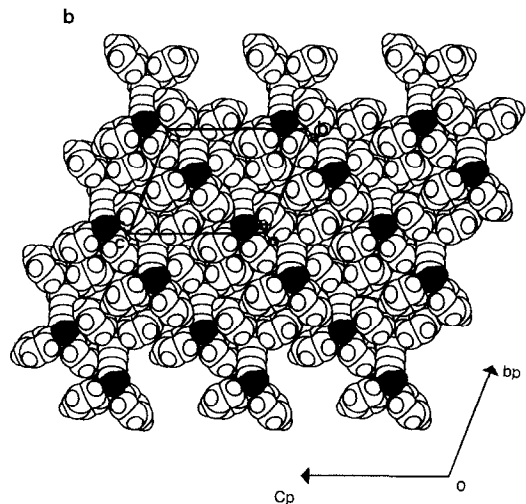
FIG. 4b. Packing diagram illustrating van der Waal radii of the α-form of the host viewed along [100], with hydroxyls shaded.
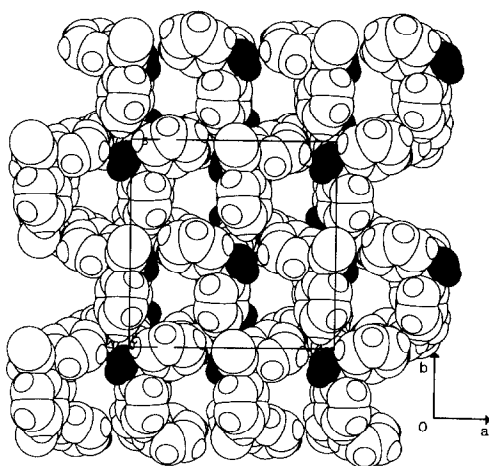
FIG. 5. Packing diagram of II with van der Waal radii, with hydroxyl moieties shaded and guest omitted.

The packing of Compound II, with the atoms displaying van der Waals radii (Fig. 5), in which the acetone molecules have been omitted, and the resulting channels running in the [001] direction can be clearly seen. A more accurate result for this structure than was previously published (4) was obtained with a lower residual factor of 0.065 as compared to 0.128, and lower standard deviations in the molecular parameters. The $O \cdots O$ hydrogen bond distance between the host hydroxyl and the guest carbonyl oxygen is 2.726(3) Å, characterizing this as a medium strength hydrogen bond. The $O-H \cdots O$ bond angle was 152.7° (2.4).

The results of the kinetics of acetone absorption are shown in Fig. 6, which shows the extent of guest absorption α for the reaction

$$host_{(s)} + 2\ acetone_{(g)} \rightarrow host\ (acetone)_{2(s)}$$
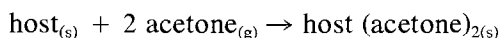
at six different temperatures varying from 23 to 48°C. These data were fitted to the equation for one-dimensional diffusion $\alpha^2 = t$, corresponding to the movement of the acetone through the channels running parallel to the c-axis. The rate constants were obtained by a least squares procedure, and
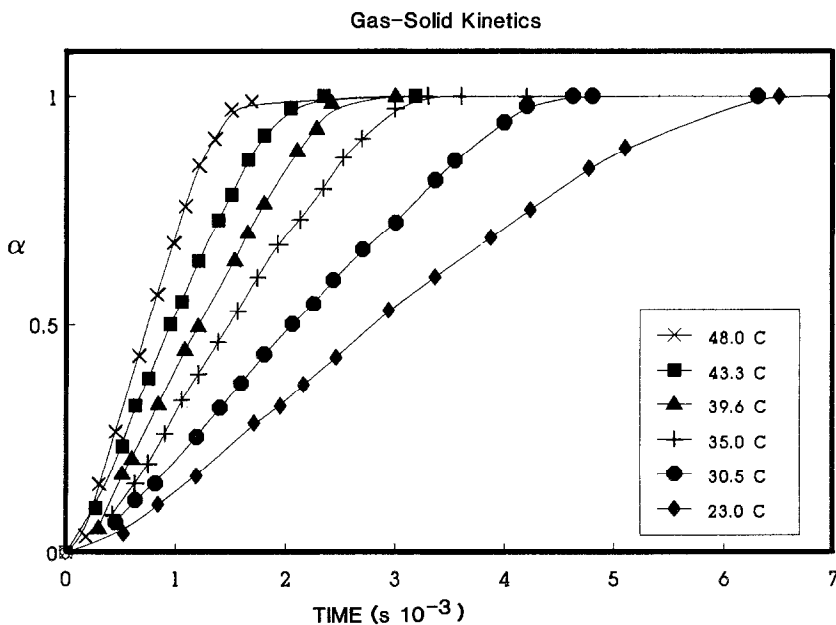

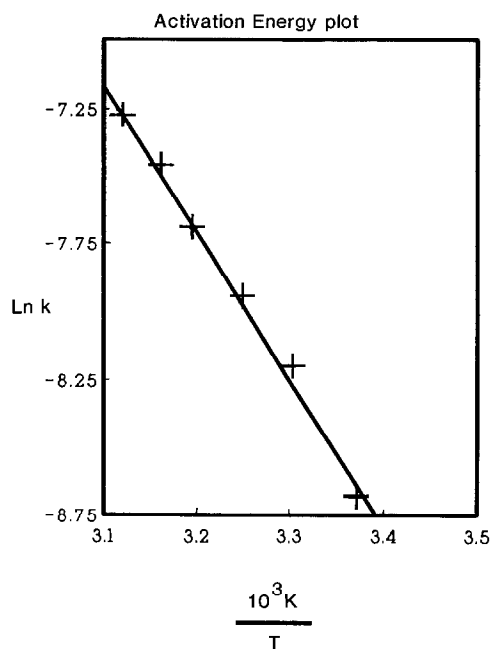FIG. 6. Extent of acetone–host reaction at various temperatures.

Activation Energy plot

FIG. 7. Arrhenius plot of the acetone$_{(g)}$–Host$_{(s)}$ reaction.

TABLE V

CORRELATION COEFFICIENTS OF KINETIC ANALYSIS

Temperature(°C)	ln$k$	Correlation
23.0	−8.686	0.984
30.5	−8.194	0.983
35.0	−7.946	0.990
39.6	−7.689	0.986
43.3	−7.469	0.991
48.0	−7.277	0.983

correlation coefficients varying between 0.98 and 1.00 were obtained (Table V).

The Arrhenius plot of ln k versus $1/T$, shown in Fig. 7, yielded a satisfactory straight line, giving an activation energy of 45.33 kJ mol^{-1}.

The packing of compound III is shown in Fig. 8, which shows the structure viewed along [010]. The hydrogen bonding scheme explains the stoichiometry of this inclusion compound as 1 host : 1 guest. Thus the hy-
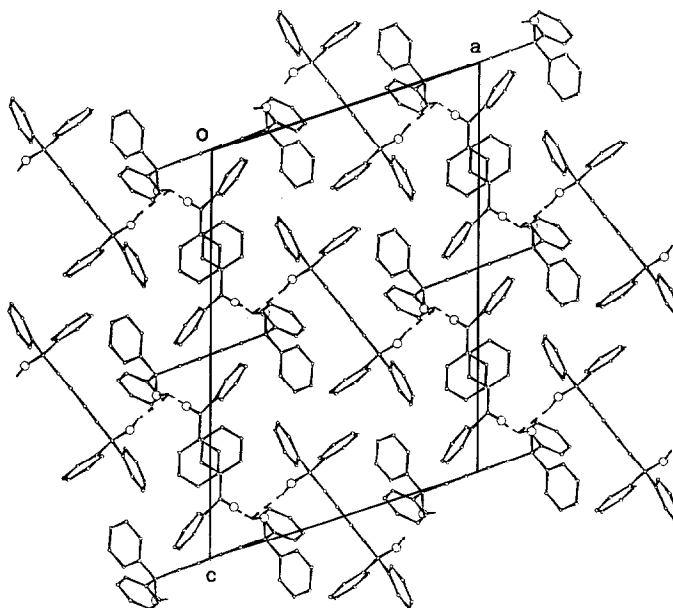

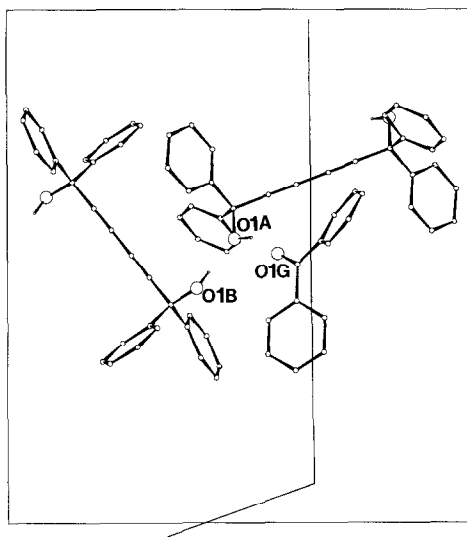FIG. 8. Packing diagram of III showing hydrogen bonding, viewed along [010].

FIG. 9. Details of hydrogen bonding scheme in III.

droxyl oxygen atom O(1A), of the host molecule centered in Wyckoff position c, acts as a hydrogen bond donor to the carbonyl oxygen of the benzophenone [d O⋯O = 2.670(2) Å; O–H⋯O bond angle = 153.8°(2.6)]. It is also a receptor for the hydroxyl oxygen atom O(1B) of the host molecule centered on Wyckoff position d [d O⋯O = 2.786(3) Å; [O–H⋯O bond angle = 163.3°(2.9)]. This is shown in Fig. 9. This results in columns of H-bonded host molecules running parallel to a, with the guest benzophenones hydrogen bonded to alternate host molecules.

The mechanism of the host : acetone and host : benzophenone reactions are complex. We suggest that in both cases the guest mol-

ecules attack on the [100] face of the α-phase triclinic crystals, as this is the only plane which exposes the hydroxyl moieties. The reaction thus requires a concomitant phase change and the host–guest compound thus formed separates from the reactive surface of the α-phase permitting the guest molecules to react with the next layer of host molecules. We have noted a considerable swelling of the powdered α-phase when exposed to acetone vapor. Such a mechanism has been proposed for the analogous reaction of p-chlorobenzoic acid with ammonia gas (9).

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