Complexation with Diol Host Compounds. Part 11.† Structures and Thermal Analyses of the Inclusion Compounds of 4,4'-Bis(diphenylhydroxymethyl)-biphenyl, $C_{38}H_{30}O_2$, with Acetone, Acetophenone, 1,4-Dioxane and *p*-Xylene

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Structures of the inclusion compounds of 4,4'-bis(diphenylhydroxymethyl)biphenyl with acetone (**1**), acetophenone (**2**), 1,4-dioxane (**3**) and *p*-xylene (**4**) have been determined. Crystal data: **1**; $C_{38}H_{30}O_2 \cdot 2C_3H_6O$, M_r = 634.81 g mol^{-1}, orthorhombic, $Pna2_1$, a = 29.169(6), b = 8.046(1), c = 15.235(2) Å, V = 3576(1) Å^3, Z = 4, D_m = 1.17(3) g cm^{-3}, D_c = 1.18 g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ = 0.39 cm^{-1}, F(000) = 1316. **2**; $C_{38}H_{30}O_2 \cdot 2C_8H_8O$, triclinic, $P\bar{1}$, M_r = 758.95 g mol^{-1}, a = 8.005(6), b = 11.464(3), c = 12.338(3) Å, α = 85.14(2), β = 76.89(4), γ = 73.71(4)°, V = 1058(1) Å^3, Z = 1, D_m = 1.17(2) g cm^{-3}, D_c = 1.19 g cm^{-3}, λ (Mo-Kα) = 0.710 69 Å, μ = 0.40 cm^{-1}, F(000) = 402. **3**; $C_{38}H_{30}O_2 \cdot 2C_4H_8O_2$, M_r = 654.80 g mol^{-1}, monoclinic, $P2_1/n$, a = 9.434(2), b = 14.152(5), c = 14.503(1), β = 105.36(1)°, V = 1866(1) Å^3, Z = 2, D_m = 1.20(2) g cm^{-3}, D_c = 1.22 g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ = 0.44 cm^{-1}, F(000) = 836. **4**; $C_{38}H_{30}O_2 \cdot 1.75C_8H_{10}$, M_r = 1408.89 g mol^{-1}, monoclinic, $P2_1/n$, a = 20.354(3), b = 21.142(4), c = 21.327(4) Å, β = 117.92(1)°, V = 8109(3) Å^3, Z = 8, D_m = 1.15(2) g cm^{-3}, D_c = 1.15 g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ = 0.71 cm^{-1}, F(000) = 3004. Depending on the host–guest interaction, they are H-bonded coordinatoclathrates in the case of **1–3** and a true clathrate type of inclusion compound in the case of **4** with H-bonded tetramer clusters of host molecules forming the inclusion matrix. The thermal decompositions of the compounds have been studied. Compound **1** contains acetone molecules in two different binding states, one being more strongly bound than the other giving two individual endotherms. Phase transitions before the melting point occur in compounds **1**, **3** and **4**. Compound **2** shows no melting point because of dissolution of the host compound in the released guest.

Most of the classical compounds which act as hosts in clathrate structures, were discovered by chance.[1,2] In the last twenty years, effort has been put into the synthesis of host molecules with specific properties and Weber has recently reviewed the principles of directed host design.[3,4] Host molecules of the 'wheel-and-axle' type were first synthesized by Toda,[5] when he described the synthesis of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol and its inclusion complexes with various n*- and π*-donors. We have investigated the kinetics of the solid–solid reaction between this host compound and benzophenone,[6] as well as the inclusion compounds it forms with various ketones,[7] and 1,4-dioxane.[8] We have described the structures of the related host 1,1,2,2-tetraphenylethane-1,2-diol[9] and its molecular inclusion complexes with lutidine guests.[10] We now present the results of the enclathration behaviour of the novel host compound 4,4'-bis(diphenylhydroxymethyl)biphenyl which is also based on the 'wheel-and-axle' design. The structures of the inclusion compounds formed with selected guests are described and their thermal stability is analysed.

Experimental

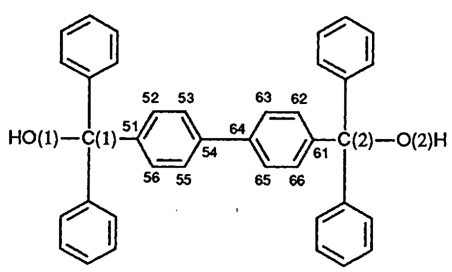
The host compound was synthesised as previously described.[11] The inclusion compounds **1–4** were obtained by dissolving the host compound in a minimum of the guest liquid. Single crystals suitable for X-ray diffraction were obtained by slow evaporation over a period which ranged from 1 to 10 days. Preliminary cell parameters and space group symmetry were determined photographically. X-Ray diffraction data were then measured on a Nonius CAD4 diffractometer using graphite-monochromated radiation and the ω–2θ technique. In all cases the crystals selected were sealed in Lindemann capillary tubes together with mother liquor to prevent desorption of the guest during data collection, and three reference reflections were monitored periodically to check crystal stability. The data reduction included correction for Lorentz and polarisation but not for absorption. Experimental details are given in Table 1.

Structure Solution and Refinement.—All four structures were solved by direct methods using SHELXS-86[12] and refined by full-matrix least squares using SHELX-76.[13] The structure of **1** showed the host molecule and the two guest molecules to be located in general positions, and it refined uneventfully. For **2** the host molecule was located on a centre of inversion at Wyckoff position f with the acetophenone molecules in general positions. A similar situation arose for **3** with the host molecule lying on a crystallographic centre at Wyckoff position c and the two guest dioxane molecules in general positions. Compound **4** has an unusual stoichiometry with a host:guest ratio of 1:1.75. With Z = 8 in the space group $P2_1/n$, this implies a cell content of 8 hosts and 14 *p*-xylene guest molecules. Thus in the crystallographic asymmetric unit we placed two host molecules labelled **A** and **B** in general positions, three *p*-xylene molecules (labelled **E**, **F** and **H**) in general positions, and half a *p*-xylene molecule labelled **I** on a centre of inversion at Wyckoff position a. Refinement proceeded in a parallel manner for all five structures. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were subjected to constrained refinement (dC–H = 1.00 Å). The hydroxy hydrogen atoms were located in difference electron density maps and allowed to refine independently. They were, however, constrained to fixed dis-

† Part 10. Preceding paper (ref. 11).

Table 1 Crystal data for compounds 1–4

	1	2	3	4
Data collection (21 °C)				
Crystal dimensions (mm)	0.31 × 0.38 × 0.41	0.31 × 0.38 × 0.47	0.38 × 0.38 × 0.44	0.38 × 0.38 × 0.44
Range scanned θ (°)	1–25	1–25	1–25	1–23
Range of indices h, k, l	+9, ±18, +34	±9, ±13, +14	±11, +16, +17	+23, ±22
Reflections for lattice parameters no., θ range (°)	24, 16–17	24, 16–17	24, 16–17	24, 16–17
Instability of standard reflections (%)	−6.9	4.0	35.3	−0.3
Scan mode	(ω–2θ)	(ω–2θ)	(ω–2θ)	(ω–2θ)
Scan width (°)	(0.80 + 0.35 tanθ)	(0.85 + 0.35 tanθ)	(0.85 + 0.35 tanθ)	(0.75 + 0.35 tanθ)
Vertical aperture length (mm)	4.0	4.0	4	4
Aperture width (mm)	(1.12 + 1.05 tanθ)	(1.12 + 1.05 tanθ)	(1.12 + 1.05 tanθ)	(1.12 + 1.05 tanθ)
Number of reflections collected (unique)	2681	2992	2712	8592
Number of reflections observed with $I_{rel} > 2\sigma I_{rel}$	1954	2105	1989	5226
Final refinement				
Number of parameters	352	256	240	894
R	0.075	0.132	0.060	0.072
wR	0.080	0.137	0.065	0.077
w	$[\sigma^2(F_o) + 0.005\,F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.001\,F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.001\,F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.001\,F_o^2]^{-1}$
S	1.60	13.98	1.72	2.80
Max. shift /esd	0.14	0.145	0.51	0.51
Max. height in difference electron density map (e Å^{-3})	0.31	0.53	0.22	0.46
Min. height in difference electron density map (e Å^{-3})	−0.25	−0.55	−0.31	−0.33



1 I•acetone (1:2)
2 I•$PhCOCH_3$ (1:2)
3 I•dioxane (1:2)
4 I•*p*-xylene (4:7)

Fig. 1 Structural formula of host compound

tances from their parent oxygens, according to a function of O–H *versus* O···O distance.[14] For **2**, however, the hydroxy hydrogen atoms could not be refined satisfactorily and were omitted from the final model.

Thermal Analysis.—Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on a Perkin-Elmer, PC7 Series system. Crystals were removed from their mother liquor, blotted dry and crushed before analysis. Sample analysis was on *ca.* 4 mg in each case. The temperature ranges were typically from ambient to 200 °C. DSC and TG runs were carried out at a heating rate of 10 °C min^{-1}. The purge gas was dry nitrogen flowing at 40 cm^3 min^{-1}.

Results and Discussion

The atomic coordinates for compounds **1–4** are given in Tables 2–5. Complete lists of bond lengths, angles, anisotropic thermal parameters and coordinates of calculated hydrogen atom positions have been deposited. For details of the deposition

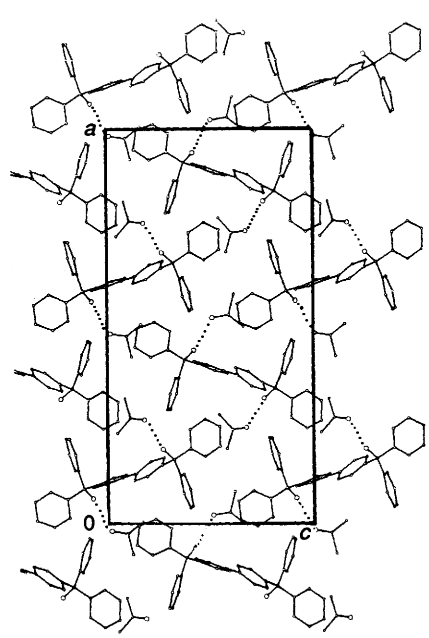


Fig. 2 Packing diagram for compound **1**

scheme see 'Instruction for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1. The structural formula of the host compound **I** with atomic nomenclature is shown in Fig. 1. The bond lengths and angles in the four host structures are in good agreement with those found in similar structures.[15,16] The carbon atoms bonded to the hydroxy moieties are tetrahedral and the angles are in the range 104.5 to 110.6°.

The packing of **1** is shown in Fig. 2 which displays a projection of the structure along [010]. This shows that the biphenyl rings of the host are slightly twisted, with a torsion angle C(53)–C(54)–C(64)–C(63) of 20°. Each hydroxy moiety of

Table 2 Fractional atomic coordinates ($\times 10^4$) with esds in parentheses for **1**

Atom	*x/a*	*y/b*	*z/c*
O(1)	1854(2)	7011(7)	2652(0)
C(1)	1599(3)	5890(9)	3171(6)
O(2)	615(2)	−4472(7)	−818(6)
C(2)	870(3)	−3213(10)	−1276(6)
C(12)	1229(2)	8570(6)	3649(6)
C(13)	856(2)	9509(6)	3940(6)
C(14)	433(2)	8747(6)	4080(6)
C(15)	381(2)	7047(6)	3930(6)
C(16)	754(2)	6108(6)	3639(6)
C(11)	1178(2)	6870(6)	3499(6)
C(22)	2362(2)	5528(8)	3965(5)
C(23)	2623(2)	5022(8)	4684(5)
C(24)	2410(2)	4321(8)	5414(5)
C(25)	1934(2)	4125(8)	5426(5)
C(26)	1673(2)	4631(8)	4708(5)
C(21)	1887(2)	5333(8)	3977(5)
C(32)	1717(2)	−3062(6)	−1679(6)
C(33)	2120(2)	−3809(6)	−1976(6)
C(34)	2129(2)	−5511(6)	−2149(6)
C(35)	1735(2)	−6467(6)	−2024(6)
C(36)	1332(2)	−5720(6)	−1727(6)
C(31)	1323(2)	−4018(6)	−1555(6)
C(42)	800(2)	−2628(9)	−2928(5)
C(43)	539(2)	−2148(9)	−3652(5)
C(44)	81(2)	−1694(9)	−3541(5)
C(45)	−116(2)	−1722(9)	−2706(5)
C(46)	146(2)	−2202(9)	−1982(5)
C(41)	604(2)	−2655(9)	−2093(5)
C(51)	967(3)	−1808(9)	−615(6)
C(52)	898(3)	−129(9)	−802(6)
C(53)	996(3)	1082(10)	−161(6)
C(54)	1161(3)	675(9)	652(6)
C(55)	1232(3)	−1022(9)	807(6)
C(56)	1148(3)	−2210(10)	179(7)
C(61)	1461(3)	4408(9)	2588(6)
C(62)	1638(3)	2843(9)	2658(7)
C(63)	1541(3)	1655(10)	2032(6)
C(64)	1266(2)	1944(8)	1317(6)
C(65)	1073(3)	3545(9)	1261(6)
C(66)	1171(3)	4716(9)	1874(7)
O(1GA)	2395(3)	521(9)	6743(6)
C(1GA)	2348(4)	−152(13)	6052(7)
C(2GA)	1873(6)	−818(22)	5777(13)
C(3GA)	2754(6)	−310(20)	5422(12)
O(1GB)	197(4)	3089(13)	5112(8)
C(1GB)	293(4)	3019(13)	5899(8)
C(2GB)	766(6)	2463(19)	6164(11)
C(3GB)	−22(7)	3353(24)	6609(14)

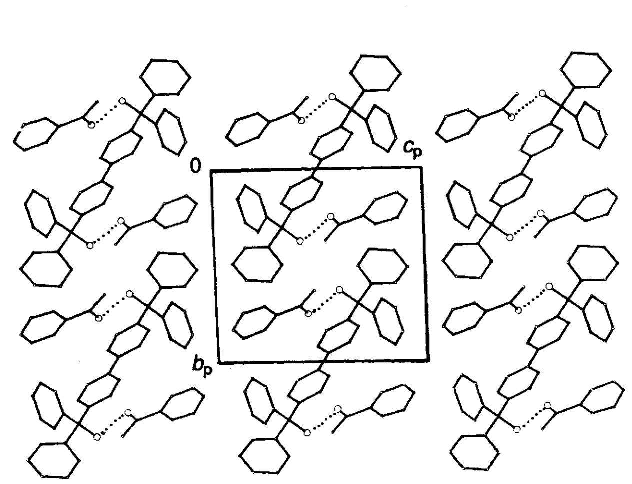


Fig. 3 Packing diagram for compound **2**

the host is hydrogen bonded to an acetone molecule with O(1)···O(1GA) = 2.873(3) Å and O(2)···O(1GB) = 3.002(3) Å. Thus there are two different guest molecules in the crystal, one acetone molecule being more strongly bound than the other. Compound **2** has a similar packing pattern as shown in Fig. 3, which is a projection viewed along [100]. Because the host lies on a centre of inversion, the biphenyl rings are coplanar, and each hydroxy moiety is again hydrogen bonded

Table 3 Fractional atomic coordinates ($\times 10^4$) with esds in parentheses for **2**

Atom	*x/a*	*y/b*	*z/c*
O(1)	1101(7)	6338(5)	5893(4)
C(1)	−296(9)	6980(6)	6773(6)
C(11)	−1099(9)	5993(7)	7429(6)
C(12)	−1672(12)	5999(8)	8538(8)
C(13)	−2495(15)	5126(10)	9117(9)
C(14)	−2760(15)	4279(10)	8545(10)
C(15)	−2199(14)	4236(9)	7414(11)
C(16)	−1349(11)	5114(7)	6838(8)
C(21)	518(10)	7559(7)	7503(7)
C(22)	−122(12)	8786(8)	7790(8)
C(23)	691(15)	9266(11)	8454(9)
C(24)	2145(17)	8551(14)	8856(10)
C(25)	2781(14)	7350(13)	8571(10)
C(26)	2019(12)	6870(9)	7924(8)
C(51)	−1673(9)	7899(6)	6258(7)
C(52)	−3493(11)	8201(8)	6747(7)
C(53)	−4739(10)	9007(8)	6286(7)
C(54)	−4349(9)	9578(6)	5246(6)
C(55)	−2503(11)	9295(9)	4790(9)
C(56)	−1259(11)	8480(9)	5238(8)
O(1G)	3230(8)	7583(6)	4429(6)
C(1G)	4857(12)	7194(7)	4072(8)
C(2G)	6028(13)	6362(8)	4701(9)
C(12G)	4391(7)	8401(6)	2323(6)
C(13G)	5026(7)	8787(6)	1244(6)
C(14G)	6829(7)	8369(6)	748(6)
C(15G)	7993(7)	7564(6)	1330(6)
C(16G)	7358(7)	7177(6)	2409(6)
C(11G)	5556(7)	7596(6)	2904(6)

Table 4 Fractional atomic coordinates ($\times 10^4$) with esds in parentheses for **3**

Atom	*x/a*	*y/b*	*z/c*
O(1)	785(2)	8 540(1)	6 005(2)
H(1)	509(42)	8 867(23)	6 514(20)
C(1)	−397(3)	7 936(2)	5 516(2)
C(11)	−30(3)	7 659(2)	4 584(2)
C(12)	−1 118(4)	7 519(3)	3 736(3)
C(13)	−743(6)	7 235(3)	2 910(3)
C(14)	708(7)	7 103(3)	2 937(4)
C(15)	1 787(5)	7 237(3)	3 770(4)
C(16)	1 421(4)	7 506(2)	4 595(3)
C(21)	−424(3)	7 052(2)	6 128(2)
C(22)	−632(3)	6 154(2)	5 752(2)
C(23)	−581(4)	5 374(2)	6 337(3)
C(24)	−324(4)	5 482(3)	7 303(3)
C(25)	−135(4)	6 373(3)	7 694(3)
C(26)	−183(4)	7 155(2)	7 120(2)
C(61)	−1 834(3)	8 502(2)	5 334(2)
C(62)	−3 091(3)	8 189(2)	5 538(2)
C(63)	−4 329(3)	8 770(2)	5 406(2)
C(64)	−4 346(3)	9 693(2)	5 065(2)
C(65)	−3 087(3)	9 979(2)	4 819(3)
C(66)	−1 868(3)	9 402(2)	4 944(3)
O(1G)	318(3)	9 559(2)	7 548(2)
O(2G)	486(3)	11 011(2)	8 881(2)
C(1G)	−878(5)	10 158(4)	7 536(4)
C(2G)	−819(6)	10 569(4)	8 441(5)
C(3G)	1 672(5)	10 434(4)	8 873(4)
C(4G)	1 648(5)	10 043(4)	7 962(5)

Table 5 Fractional atomic coordinates (× 10⁴) with esds in parentheses for **4**

Atom	x/a	y/b	z/c
O(1A)	531(2)	6 397(2)	2 037(2)
H(1A)	807(4)	6 095(3)	2 398(3)
O(2A)	4 215(2)	9 328(2)	6 792(2)
H(2A)	4 620(3)	9 072(3)	6 842(4)
C(1A)	1 016(3)	6 826(2)	1 932(3)
C(2A)	3 775(3)	9 730(2)	6 185(3)
C(12A)	641(2)	7 892(2)	1 289(2)
C(13A)	174(2)	8 260(2)	707(2)
C(14A)	−445(2)	7 986(2)	143(2)
C(15A)	−595(2)	7 345(2)	161(2)
C(16A)	−128(2)	6 977(2)	743(2)
C(11A)	491(2)	7 250(2)	1 307(2)
C(22A)	1 926(2)	5 937(2)	2 178(2)
C(23A)	2 432(2)	5 594(2)	2 042(2)
C(24A)	2 565(2)	5 768(2)	1 480(2)
C(25A)	2 191(2)	6 283(2)	1 053(2)
C(26A)	1 685(2)	6 625(2)	1 189(2)
C(21A)	1 553(2)	6 452(2)	1 751(2)
C(32A)	3 571(2)	10 376(2)	7 063(2)
C(33A)	3 125(2)	10 733(2)	7 267(2)
C(34A)	2 369(2)	10 804(2)	6 804(2)
C(35A)	2 057(2)	10 518(2)	6 138(2)
C(36A)	2 500(2)	10 161(2)	5 933(2)
C(31A)	3 258(2)	10 089(2)	6 396(2)
C(42A)	4 929(2)	9 935(1)	6 065(2)
C(43A)	5 378(2)	10 324(1)	5 898(2)
C(44A)	5 186(2)	10 956(1)	5 721(2)
C(45A)	4 544(2)	11 200(1)	5 711(2)
C(46A)	4 093(2)	10 811(1)	5 877(2)
C(41A)	4 287(2)	10 178(1)	6 054(2)
C(51A)	1 451(3)	7 228(2)	2 599(3)
C(52A)	1 169(3)	7 339(2)	3 072(3)
C(53A)	1 538(3)	7 731(2)	3 650(3)
C(54A)	2 193(3)	8 032(2)	3 782(3)
C(55A)	2 483(3)	7 904(3)	3 322(3)
C(56A)	2 122(3)	7 508(2)	2 744(3)
C(61A)	3 343(3)	9 296(2)	5 536(3)
C(62A)	3 270(3)	9 436(2)	4 881(3)
C(63A)	2 890(3)	9 027(3)	4 312(3)
C(64A)	2 570(3)	8 475(2)	4 386(3)
C(65A)	2 628(3)	8 348(3)	5 051(3)
C(66A)	3 008(3)	8 751(2)	5 619(3)
O(1B)	−366(2)	6 517(2)	2 965(2)
H(1B)	−662(4)	6 251(3)	2 563(3)
O(2B)	−4 160(2)	9 334(2)	−1 763(2)
H(2B)	−4 545(3)	9 107(3)	−1 717(4)
C(1B)	−825(3)	6 959(2)	3 105(3)
C(2B)	−3 765(3)	9 780(2)	−1 192(3)
C(12B)	−1 515(2)	6 735(2)	3 827(2)
C(13B)	−2 040(2)	6 391(2)	3 935(2)
C(14B)	−2 428(2)	5 898(2)	3 477(2)
C(15B)	−2 292(2)	5 747(2)	2 911(2)
C(16B)	−1 768(2)	6 090(2)	2 803(2)
C(11B)	−1 379(2)	6 583(2)	3 261(2)
C(22B)	−291(2)	7 999(2)	3 759(2)
C(23B)	215(2)	8 329(2)	4 357(2)
C(24B)	741(2)	8 000(2)	4 946(2)
C(25B)	760(2)	7 341(2)	4 936(2)
C(26B)	254(2)	7 009(2)	4 338(2)
C(21B)	−271(2)	7 339(2)	3 749(2)
C(32B)	−4 177(2)	10 818(2)	−879(2)
C(33B)	−4 667(2)	11 167(2)	−729(2)
C(34B)	−5 303(2)	10 882(2)	−768(2)
C(35B)	−5 449(2)	10 247(2)	−957(2)
C(36B)	−4 958(2)	9 896(2)	−1 107(2)
C(31B)	−4 323(2)	10 182(2)	−1 068(2)
C(42B)	−2 554(2)	10 280(2)	−1 037(2)
C(43B)	−2 167(2)	10 649(2)	−1 296(2)
C(44B)	−2 543(2)	10 925(2)	−1 967(2)
C(45B)	−3 306(2)	10 831(2)	−2 378(2)
C(46B)	−3 693(2)	10 461(2)	−2 119(2)
C(41B)	−3 318(2)	10 186(2)	−1 449(2)
C(51B)	−1 252(3)	7 384(2)	2 454(3)
C(52B)	−969(3)	7 501(3)	1 981(3)
C(53B)	−1 339(3)	7 898(2)	1 408(3)
C(54B)	−1 989(3)	8 211(2)	1 292(3)
C(55B)	−2 255(3)	8 090(3)	1 775(3)
C(56B)	−1 897(3)	7 688(3)	2 336(3)
C(61B)	−3 271(3)	9 399(2)	−524(3)
C(62B)	−3 185(3)	9 550(3)	144(3)
C(63B)	−2 755(3)	9 175(3)	727(3)
C(64B)	−2 392(3)	8 638(2)	679(3)
C(65B)	−2 457(3)	8 501(2)	16(3)
C(66B)	−2 881(3)	8 872(2)	−569(3)
C(1EG)	4 683(5)	4 436(4)	2 074(5)
C(2EG)	4 197(4)	4 703(4)	1 445(5)
C(3EG)	4 440(5)	5 058(4)	1 062(5)
C(4EG)	5 167(5)	5 170(3)	1 257(5)
C(5EG)	5 665(4)	4 894(3)	1 883(5)
C(6EG)	5 427(5)	4 535(4)	2 291(4)
C(1ME)	4 412(5)	4 048(4)	2 511(5)
C(2Me)	5 447(6)	5 590(4)	840(6)
C(1FG)	6 773(5)	2 806(3)	−163(5)
C(2FG)	7 402(5)	2 909(3)	490(4)
C(3FG)	8 054(4)	2 618(4)	662(4)
C(4FG)	8 126(4)	2 197(3)	201(5)
C(5FG)	7 500(5)	2 103(4)	−456(5)
C(6FG)	6 836(5)	2 399(4)	−621(4)
C(1MF)	6 043(5)	3 124(4)	−362(6)
C(2MF)	8 853(5)	1 870(5)	395(6)
C(1HG)	5 636(4)	7 282(4)	2 301(4)
C(2HG)	5 335(4)	7 812(4)	2 412(4)
C(3HG)	4 770(5)	7 755(5)	2 590(4)
C(4HG)	4 512(5)	7 194(5)	2 653(5)
C(5HG)	4 810(5)	6 618(5)	2 548(4)
C(6HG)	5 399(4)	6 689(4)	2 374(4)
C(1MH)	6 314(6)	7 334(5)	2 118(6)
C(2MH)	3 869(7)	7 110(6)	2 864(7)
C(1IG)	5 437(5)	4 960(4)	4 619(5)
C(2IG)	5 245(6)	4 700(4)	5 662(5)
C(6IG)	4 379(5)	5 316(4)	4 746(5)
C(1MI)	4 158(7)	5 055(6)	5 824(7)

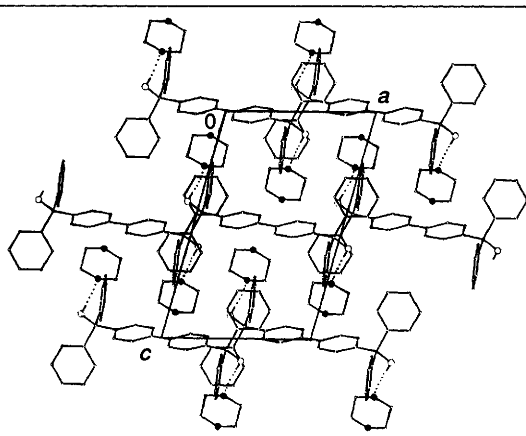


Fig. 4 Packing diagram for compound **3**

to the carbonyl oxygen atom of acetophenone, with the O···O distance at 2.872(1) Å.

The host conformation in **3** is similar to that found in **2**, because the host molecule again lies on a centre of symmetry. The hydrogen bonding pattern is characterised by host-hydroxy to dioxane-oxygen atom hydrogen bonds with O···O distances of 2.780(4) Å. This is shown in Fig. 4, which is a projection viewed along [010]. Only one dioxane oxygen atom is hydrogen bonded, so there are no ribbons of hydrogen bonded chains running through the structure. We have mapped the topology of this structure by using the program OPEC,[17] and found the dioxane to lie in discrete pockets as shown in Fig. 5. This classifies this inclusion compound as a cage-type.[18]

The structure of **4** is complicated and is shown in projection in Fig. 6 viewed along [010] with the guest molecules omitted for clarity. With xylene as guest molecules, there is no host–guest hydrogen bonding, but the host molecules are hydrogen bonded into tetramers with O···O distances varying from 2.799(6) Å to 2.913(6) Å. The conformation of the hydroxy moieties in this host compound varies, and is dependent on the hydrogen bonding pattern. The torsion angle O(1)–C(1)–C(2)–O(2) in the four inclusion compounds has the value 179°, 180°, 180° and for **4**; 60°(A) and 56°(B). This variability is an expression of the torsional flexibility of this and similar host compounds[19] which twist their 'backbone' to accommodate different guest molecules. Induced-fit processes such as modelled here are very important for enzyme recognition.

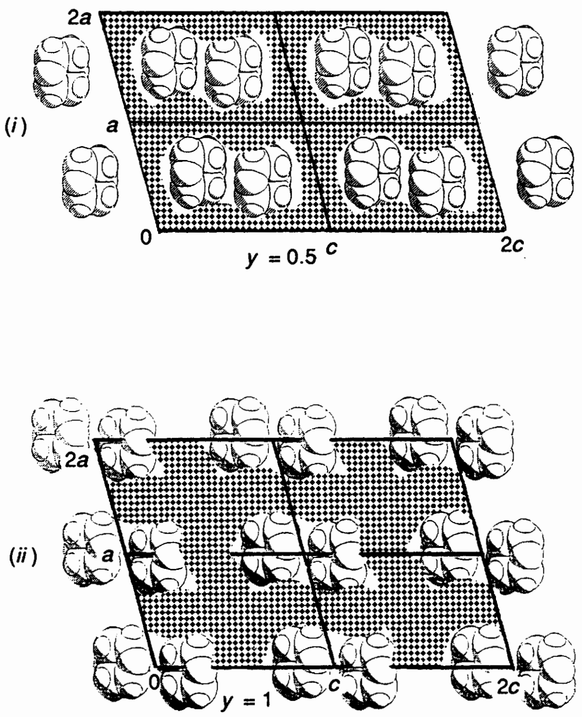


Fig. 5 OPEC mapping of compound **3**

Table 6 Percentage weight loss obtained from thermal gravimetric results

Compound	Calculated	Experimental
1	18.3	18.0
2	31.7	32.8
3	25.4	24.9
4	26.4	26.2

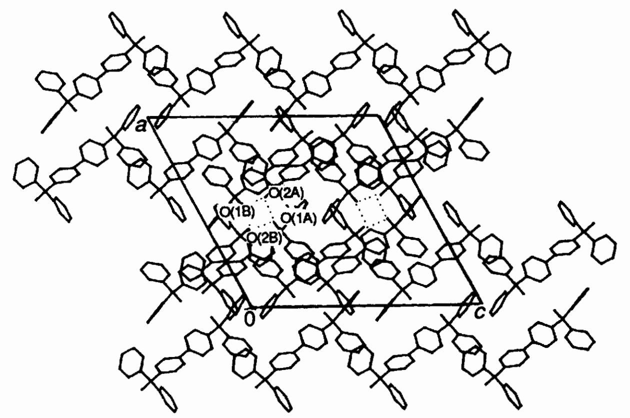


Fig. 6 Packing diagram for compound **4** (guest molecules omitted for clarity)

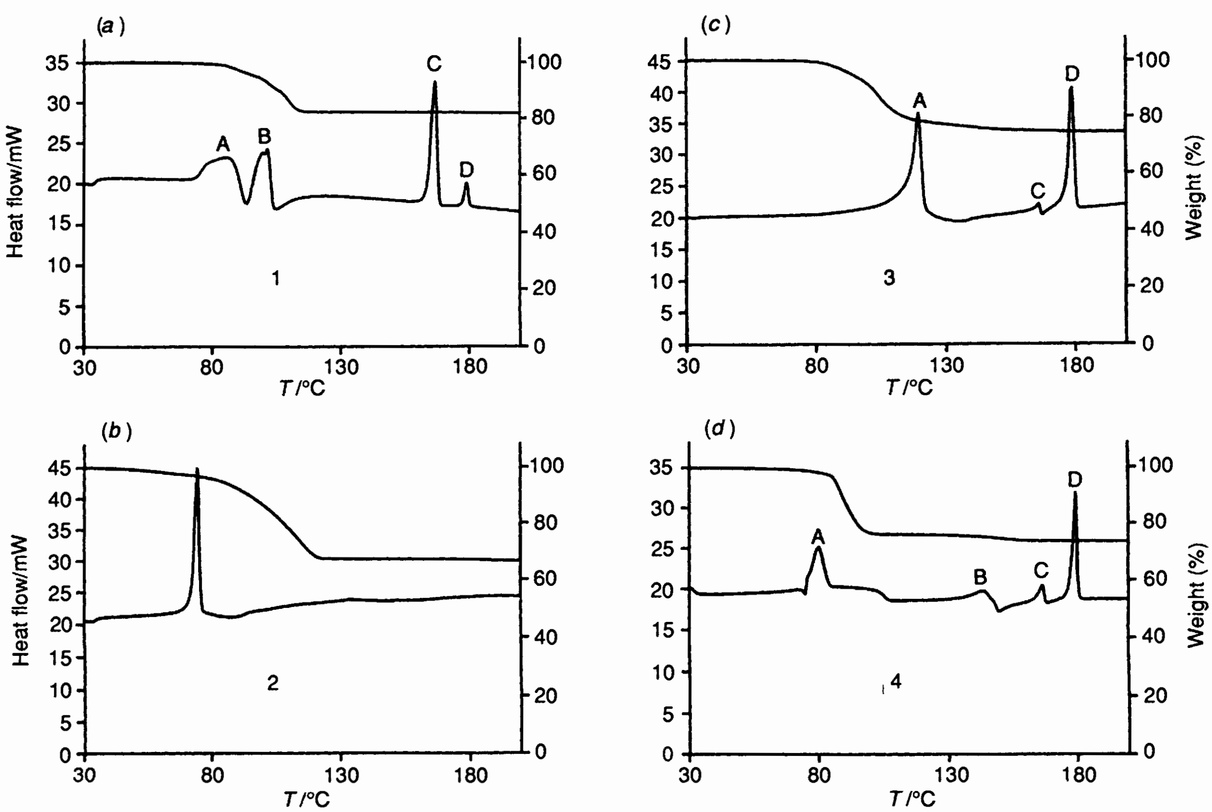


Fig. 7 DSC and TG traces for compounds **1–4**

Thermal Analysis.—Fig. 7 shows the DSC and TG traces for **1**–**4** and the results of the thermal analysis are summarised in Table 6. There is good agreement between the calculated and observed weight losses of the TG for all four compounds, thus confirming their host:guest ratios.

The DSC traces of **1**, **3** and **4** have similar features. For **1** we observe two endotherms A (T_{on} = 74 °C) and B (T_{on} = 94 °C) which correspond to the desorption of acetone. This is followed by endotherms C (T_{on} = 164 °C) and D (T_{on} = 178 °C). The latter two endotherms occur consistently in all three compounds and correspond to a structural phase change occurring between 175 °C and 182 °C (endotherm C), and the melting point of the host compound (endotherm D). We have observed a similar phenomenon with the decomposition of the inclusion compound formed between 1,1,2,2-tetraphenylethane and 3,5-lutidine.[10] In **3**, the single endotherm A corresponds to the desorption of dioxane, while in **4** the xylene desorption is shown by a first sharp endotherm A (T_{on} = 75 °C) followed by a second broad endotherm B which peaks at 143 °C, and corresponds to a further weight loss of 3.8%.

The DSC traces of **2** show only a single endotherm (T_{on} = 69.3 °C) which corresponds to the release of the guest with concomitant dissolution of the host compound. We have reported a similar result with the decomposition of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol·2 dioxane.[8]

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