Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Complexation with diol host compounds. 13. Crystal structures and thermal analyses of inclusion compounds of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol with cyclohexane, *O*-xylene, *m*-xylene and *p*-xylene

Luigi Nassimbeni[a]; Louise Johnson[a]; Fumio Toda[b]
[a] Department of Chemistry, University of Cape Town, Rondebosch, South Africa [b] Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Japan

To cite this Article Nassimbeni, Luigi , Johnson, Louise and Toda, Fumio(1993) 'Complexation with diol host compounds. 13. Crystal structures and thermal analyses of inclusion compounds of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol with cyclohexane, *O*-xylene, *m*-xylene and *p*-xylene', Supramolecular Chemistry, 2: 2, 233 — 241
To link to this Article: DOI: 10.1080/10610279308038321
URL: http://dx.doi.org/10.1080/10610279308038321

SUPRAMOLECULAR CHEMISTRY, Vol. 2, pp. 233–241
Reprints available directly from the publisher
Photocopying permitted by license only

Complexation with diol host compounds. 13. Crystal structures and thermal analyses of inclusion compounds of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol with cyclohexane, *o*-xylene, *m*-xylene and *p*-xylene

LUIGI NASSIMBENI*, LOUISE JOHNSON and FUMIO TODA†

Department of Chemistry, University of Cape Town, Private Bag, Rondebosch 7700, South Africa and †Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan

(Received July 1, 1992; in final form September 8, 1992)

It has been shown that host compound 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol is able to include polar guests and now we report on its ability to form clathrate compounds with apolar guests. The structures of this host with cyclohexane (1) and the ortho (2), meta (3) and para (4) xylenes have been determined and are discussed. Crystal data: (1) $2C_{30}H_{22}O_2C_6H_{12}$, $M_r = 913.20$ g mol^{-1}, monoclinic, $C2/c$, $a = 22.851(6)$, $b = 14.010(2)$, $c = 17.076(6)$ Å, $\beta = 108.71(3)°$, $V = 5178(2)$ Å^3, $Z = 4$, $D_c = 1.17$ g cm^{-3}, $N = 3326$, $R = 0.092$. (2) $2C_{30}H_{22}O_2 1\frac{1}{2}C_8H_{10}$, $M_r = 1976.5$ g mol^{-1}, triclinic, $P\bar{1}$, $a = 13.185(3)$, $b = 15.466(3)$, $c = 16.573(2)$ Å, $\alpha = 96.39(13)°$, $\beta = 106.96(15)°$, $\gamma = 114.94(18)°$, $V = 2822(2)$ Å^3, $Z = 2$, $D_c = 1.16$ g cm^{-3}, $N = 6152$, $R = 0.075$. (3) $2C_{30}H_{22}O_2 1\frac{1}{2}C_8H_{10}$, $M_r = 1976.5$ g mol^{-1}, triclinic, $P\bar{1}$, $a = 13.267(5)$, $b = 15.453(3)$, $c = 16.654(5)$ Å, $\alpha = 97.12(2)°$, $\beta = 107.09(3)°$, $\gamma = 114.68(3)°$, $V = 2843(2)$ Å^3, $Z = 2$, $D_c = 1.15$ g cm^{-3}, $N = 6505$, $R = 0.083$. (4) $2C_{30}H_{22}O_2 1\frac{1}{2}C_8H_{10}$, $M_r = 1976.5$ g mol^{-1}, triclinic, $P\bar{1}$, $a = 13.070(2)$, $b = 15.348(3)$, $c = 16.776(3)$ Å, $\alpha = 67.88(2)°$, $\beta = 74.27(1)°$, $\gamma = 65.29(1)°$, $V = 2817(1)$ Å^3, $Z = 2$, $D_c = 1.15$ g cm^{-3}, $N = 6711$, $R = 0.050$. Thermal analysis studies were also performed in order to examine their stability and the strength with which the guest species are held in the crystal lattice.

INTRODUCTION

Many of the compounds which act as host molecules in clathrates were discovered by chance,[1,2] and it is only in the last 20 years that research has been directed toward the synthesis of host compounds with specific properties. Recently Weber[3] has discussed the principles 'directed host design', and has classified inclusion compounds in terms of the type of host–guest interaction and the topology of the guest environment.

One of the most successful molecular host compounds is 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol, **H**, a compound based on the 'wheel-and-axle' host design which was originally synthesized by Toda in 1968.[4] This molecule is shown in Figure 1. This molecule is particularly versatile and usually capture guest molecules via hydrogen bonding between its hydroxy functions and electron accepting guests. Previously the inclusion compounds of **H** with polar guests have been studied and reported.[5–7] In this paper we report on the host–guest complexes obtained with apolar molecules: cyclohexane (**1**) and *o*-xylene (**2**), *m*-xylene (**3**) and *p*-xylene (**4**).

The absence of polar moieties in the guest molecule results in a clathrate system in which a network of hydrogen bonds between host molecules is observed.

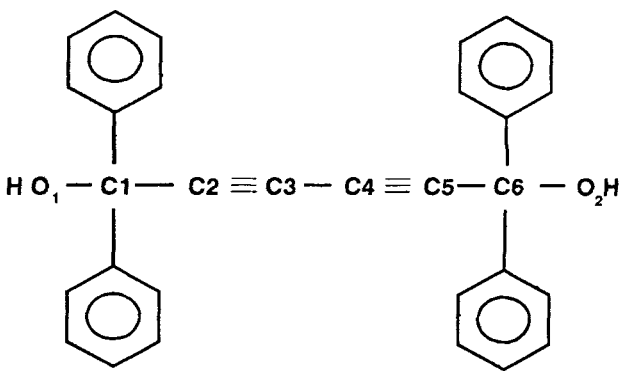

Figure 1 Host compound **H**.

* To whom correspondence should be addressed.

These are true clathrates since the guests are held in place only by the steric and electronic influence of the host molecules.

Structure determination and refinement

Suitable crystals of the inclusion compounds were obtained by slow evaporation of concentrated solutions of the host in the various guest liquids. The time required ranged from 3 days for the xylenes to 30 days for the cyclohexane. Preliminary cell dimensions and space group assignments were carried out photographically for the structural determinations. For all four compounds the intensity data were collected with crystals mounted in Lindemann capillary tubes in order to minimize crystal deterioration. Accurate cell parameters were then obtained by least-squares analyses of 24 reflections measured in the range $16° < \theta < 17°$ on a Nonius CAD4 diffractometer with graphite monochromated Mo K_α radiation (λ = 0.7107 Å). Crystal data and experimental details of the data collections are listed in Table 1.

The structures of all four compounds were determined by direct methods and refined by full-matrix least-squares routines using the SHELX86 and SHELX76 program system.[8,9] The non-hydrogen atoms were treated anisotropically except in the case of disordered molecules and the aromatic hydrogens were constrained to 1.0 Å from their parent carbons,

Table 1 Crystal data and experimental details

Compound	*1*	*2*	*3*	*4*
Molecular formula	$2C_{30}H_{22}O_2 \cdot C_6H_{12}$	$2C_{30}H_{22}O_2 \cdot 1\frac{1}{2}C_8H_{10}$	$2C_{30}H_{22}O_2 \cdot 1\frac{1}{2}C_8H_{10}$	$2C_{30}H_{22}O_2 \cdot 1\frac{1}{2}C_8H_{10}$
Molecular weight (g mol^{-1})	913.20	1976.50	1976.50	1976.50
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	22.851(6)	13.185(3)	13.267(5)	13.070(2)
b (Å)	14.010(2)	15.466(3)	15.453(3)	15.348(3)
c (Å)	17.076(6)	16.573(2)	16.654(5)	16.776(3)
α (°)	–	96.39(13)	97.12(2)	67.88(2)
β (°)	108.71(3)	106.96(15)	107.09(3)	74.27(1)
γ (°)	–	114.94(18)	114.68(3)	65.29(1)
Z	4	2	2	2
V (Å^3)	5178(2)	2822(2)	2843(2)	2817(1)
D_c (g cm^{-3})	1.17	1.16	1.15	1.17
D_m (g cm^{-3})	1.15(2)	1.15(1)	1.16(1)	1.16(1)
μ (Mo K_α) (cm^{-1})	0.38	0.33	0.33	0.33
F(000)	1936	1046	1046	1046
Data collection (21°C)				
Crystal dimensions (mm)	0.25 × 0.36 × 0.50	0.31 × 0.31 × 0.34	0.31 × 0.34 × 0.44	0.47 × 0.47 × 0.50
Range scanned θ (°)	1–25	1–23	1–23	1–23
Range of indices h, k, l	±27, +16, +20	±14, ±17, +18	±14, ±17, +18	±14, ±16, +18
Reflections for lattice parameters no., θ range (°)	24, 16–17	24, 15–17	24, 15–17	24, 16–17
Instability of standard reflections (%)	−1.3	−1.1	16.1 (Decay correction applied)	21.1
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
Scan width (°)	0.85 + 0.35 tan θ	0.85 + 0.35 tan θ	0.85 + 0.35 tan θ	0.85 + 0.35 tan θ
Vertical aperture length (mm)	4	4	4	4
Aperture width (mm)	1.12 + 1.05 tan θ	1.12 + 1.05 tan θ	1.12 + 1.05 tan θ	1.12 + 1.05 tan θ
Number of reflections collected (unique)	3326	6152	6505	6711
Number of reflections observed with $I_{rel} > 2\sigma I_{rel}$	1937	4060	4638	5249
Final refinement				
Number of parameters	312	600	596	711
R	0.092	0.075	0.083	0.050
R_w	0.107	0.082	0.104	0.056
w	$(\sigma^2 F_0 + 0.01 F_0^2)^{-1}$	$(\sigma^2 F_0 + 0.001 F_0^2)^{-1}$	$(\sigma^2 F_0 + 0.05 F_0^2)^{-1}$	$(\sigma^2 F_0 + 0.005 F_0^2)^{-1}$
s	2.27	3.82	1.09	0.90
Max. shift/e.s.d.	0.011	0.34	0.68	0.03
Max. height in difference electron density map (eÅ^{-3})	0.58	0.55	0.63	0.21
Min. height in difference electron density map (eÅ^{-3})	−0.32	−0.29	−0.35	−0.30

with a common temperature factor. The hydroxy 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 fractional atomic co-

Table 2(*a*) Fractional atomic co-ordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$) with e.s.d. values in parentheses for **1**

Atom	*x/a*	*y/b*	*z/c*	U_{equiv}/U_{iso} (*)
O(1)	4896(2)	1793(3)	6419(2)	53(2)
H(1)	4569(21)	1465(43)	6545(40)	81(16)*
O(2)	4201(2)	−1004(3)	2292(2)	55(2)
H(2)	4460(25)	−1247(49)	2814(21)	81(16)*
C(1)	4687(3)	2388(4)	5705(3)	47(2)
C(2)	4496(3)	1760(5)	4960(4)	56(3)
C(3)	4328(3)	1261(5)	4366(4)	55(3)
C(4)	4125(3)	696(5)	3674(4)	57(3)
C(5)	3935(3)	211(5)	3065(4)	57(3)
C(6)	3714(3)	−392(5)	2335(3)	51(2)
C(11)	5242(3)	2996(5)	5705(4)	56(3)
C(12)	5787(5)	2960(9)	6256(8)	156(7)
C(13)	6268(5)	3514(12)	6242(8)	193(8)
C(14)	6221(5)	4168(7)	5700(8)	105(5)
C(15)	5696(7)	4200(13)	5072(13)	259(13)
C(16)	5213(6)	3608(14)	5101(13)	277(12)
C(21)	4154(3)	3010(4)	5752(3)	47(2)
C(22)	4204(4)	3499(6)	6469(5)	84(4)
C(23)	3736(4)	4068(6)	6529(6)	95(4)
C(24)	3206(4)	4189(6)	5862(6)	85(4)
C(25)	3152(4)	3731(7)	5181(5)	87(4)
C(26)	3614(3)	3131(6)	5103(4)	76(3)
C(31)	3542(3)	234(5)	1552(4)	59(2)
C(32)	3963(5)	357(6)	1124(5)	101(5)
C(33)	3819(6)	944(8)	436(7)	131(6)
C(34)	3273(6)	1377(8)	171(6)	121(6)
C(35)	2857(5)	1287(7)	609(7)	110(5)
C(36)	2986(4)	697(6)	1287(5)	85(4)
C(41)	3166(3)	−1003(5)	2359(4)	54(3)
C(42)	2805(4)	−758(6)	2841(5)	83(4)
C(43)	2302(4)	−1319(8)	2823(6)	112(5)
C(44)	2164(4)	−2133(7)	2379(6)	92(4)
C(45)	2524(4)	−2371(6)	1879(5)	88(4)
C(46)	3014(3)	−1813(5)	1882(4)	67(3)
C(1G)	5000(0)	2136(15)	2500(0)	179(8)
C(2G)	5604(8)	2707(13)	2910(13)	133(8)
C(21G)	5547(10)	2707(13)	2383(15)	203(14)
C(3G)	5547(10)	3556(18)	2383(15)	197(13)
C(31G)	5604(8)	3556(18)	2910(13)	225(16)
C(4G)	5000(0)	4202(19)	2500(0)	250(13)

Table 2(*b*) Fractional atomic co-ordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$) with e.s.d. values in parentheses

Atom	*x/a*	*y/b*	*z/c*	U_{equiv}/U_{iso} (*)
O(1A)	1949(3)	6725(3)	2081(2)	44(2)
H(1A)	1453(51)	6873(51)	2350(41)	108(25)*
O(2A)	−1841(3)	4668(3)	−2958(2)	48(2)
H(2A)	−1895(45)	4263(31)	−2544(26)	58(16)*
C(1A)	2341(4)	7371(4)	1548(3)	39(3)
C(2A)	1401(5)	6940(4)	651(4)	45(3)
C(3A)	631(5)	6585(4)	−68(4)	45(3)
C(4A)	−234(5)	6224(4)	−907(4)	45(3)
C(5A)	−944(5)	5924(4)	−1643(4)	46(3)
C(6A)	−1767(5)	5571(4)	−2569(3)	43(3)
C(11A)	2526(3)	8390(3)	1958(2)	41(3)
C(12A)	1812(3)	8788(3)	1542(2)	61(4)
C(13A)	1985(3)	9701(3)	1960(2)	82(4)
C(14A)	2870(3)	10216(3)	2796(2)	80(5)
C(15A)	3583(3)	9818(3)	3213(2)	81(4)
C(16A)	3411(3)	8905(3)	2795(2)	73(4)
C(21A)	3513(3)	7437(3)	1524(2)	42(3)
C(22A)	4206(3)	7169(3)	2149(2)	60(4)
C(23A)	5319(3)	7297(3)	2149(2)	72(4)
C(24A)	5738(3)	7694(3)	1524(2)	74(4)
C(25A)	5044(3)	7962(3)	898(2)	74(4)
C(26A)	3932(3)	7834(3)	898(2)	59(3)
C(31A)	−3028(4)	5398(3)	−2666(2)	48(3)
C(32A)	−3270(4)	5709(3)	−1954(2)	68(4)
C(33A)	−4436(4)	5535(3)	−2067(2)	93(6)
C(34A)	−5360(4)	5050(3)	−2891(2)	94(5)
C(35A)	−5119(4)	4738(3)	−3602(2)	91(4)
C(36A)	−3953(4)	4912(3)	−3490(2)	71(4)
C(41A)	−1208(4)	6338(3)	−3035(3)	45(3)
C(42A)	−752(4)	6130(3)	−3649(3)	69(4)
C(43A)	−205(4)	6856(3)	−4038(3)	88(5)
C(44A)	−114(4)	7789(3)	−3814(3)	90(5)
C(45A)	−570(4)	7997(3)	−3200(3)	88(5)
C(46A)	−1117(4)	7271(3)	−2811(3)	68(4)
O(3B)	2044(3)	6679(3)	4286(2)	49(2)
H(3B)	2105(85)	6181(52)	3901(53)	172(39)*
O(4B)	−431(3)	3264(3)	7112(2)	43(2)
H(4B)	1014(52)	3077(57)	6515(19)	119(28)*
C(1B)	816(5)	7050(4)	5191(3)	41(3)
C(2B)	316(5)	6301(4)	5644(3)	46(3)
C(3B)	907(5)	5636(4)	5964(4)	44(3)
C(4B)	488(5)	4886(4)	6348(3)	44(3)
C(5B)	170(5)	4241(4)	6704(3)	44(3)
C(6B)	56(4)	3481(4)	7170(3)	37(3)
C(11B)	4084(4)	7230(3)	5274(2)	44(3)
C(12B)	4566(4)	7684(3)	4694(2)	65(4)
C(13B)	5713(4)	7856(3)	4746(2)	80(4)
C(14B)	6379(4)	7574(3)	5377(2)	75(4)
C(15B)	5899(4)	7120(3)	5957(2)	80(4)
C(16B)	4752(4)	6948(3)	5905(2)	61(4)
C(21B)	2859(4)	8025(3)	5544(2)	41(2)
C(22B)	2559(4)	8552(3)	4972(2)	78(4)
C(23B)	2660(4)	9467(3)	5301(2)	96(5)
C(24B)	3060(4)	9855(3)	6202(2)	71(4)
C(25B)	3360(4)	9329(3)	6775(2)	76(4)
C(26B)	3259(4)	8414(3)	6445(2)	66(4)
C(31B)	740(4)	2531(3)	6790(3)	44(3)
C(32B)	1336(4)	2479(3)	6230(3)	60(3)
C(33B)	1318(4)	1592(3)	5928(3)	79(4)
C(34B)	704(4)	757(3)	6185(3)	83(4)
C(35B)	108(4)	810(3)	6745(3)	100(6)
C(36B)	126(4)	1697(3)	7048(3)	79(5)
C(41B)	1577(3)	3944(3)	8138(3)	42(3)
C(42B)	1328(3)	4502(3)	8697(3)	60(3)
C(43B)	2114(3)	4956(3)	9570(3)	77(5)
C(44B)	3148(3)	4852(3)	9884(3)	87(4)
C(45B)	3396(3)	4294(3)	9325(3)	99(5)
C(46B)	2611(3)	3841(3)	8452(3)	74(4)
C(1X)	2766(13)	8828(12)	8796(8)	174(13)
C(1O)	2131(9)	6881(8)	8226(7)	140(7)
C(1G)	3739(12)	8623(7)	8748(5)	121(7)
C(2G)	3409(9)	7571(7)	8463(5)	98(6)
C(3G)	4231(14)	7278(12)	8398(7)	152(13)
C(4G)	5448(14)	7972(16)	8600(9)	167(12)
C(5G)	5808(12)	8994(16)	8905(9)	172(11)
C(6G)	4925(18)	9287(13)	8960(7)	158(11)
C(1Z)	−951(23)	−761(20)	266(19)	310(12)
C(2Z)	−540(16)	341(14)	599(11)	190(6)
C(3Z)	−250(15)	−768(12)	−247(10)	176(5)
C(4Z)	−1018(22)	−1570(19)	−111(16)	139(8)
C(5Z)	−1355(23)	−377(21)	863(17)	160(9)

Table 2(*c*) Fractional atomic co-ordinates ($\times 10^4$) and thermal parameters (Å^2 $\times 10^3$) e.s.d. values in parentheses for **3**

Atom	*x/a*	*y/b*	*z/c*	U_{equiv}/U_{iso} (*)
O(1A)	1826(3)	5332(2)	7950(2)	51(2)
H(1A)	1703(44)	5572(35)	7435(20)	75(16)*
O(2A)	−1925(3)	3272(2)	2904(2)	48(2)
H(2A)	−1316(33)	3180(37)	2745(32)	72(16)*
C(1A)	1750(4)	4425(3)	7551(3)	44(2)
C(2A)	935(4)	4075(3)	6630(3)	49(2)
C(3A)	209(4)	3767(3)	5891(3)	49(2)
C(4A)	−634(4)	3411(3)	5053(3)	46(2)
C(5A)	−1390(4)	3059(3)	4316(3)	50(2)
C(6A)	−2309(4)	2621(3)	3425(3)	41(2)
C(12A)	3933(3)	5069(3)	8471(2)	73(3)
C(13A)	5094(3)	5252(3)	8581(2)	88(4)
C(14A)	5334(3)	4962(3)	7862(2)	99(4)
C(15A)	4413(3)	4489(3)	7034(2)	99(5)
C(16A)	3251(3)	4306(3)	6924(2)	68(3)
C(11A)	3010(3)	4596(3)	7641(2)	51(2)
C(22A)	1236(3)	2763(2)	7855(2)	71(3)
C(23A)	708(3)	2041(2)	8243(2)	94(4)
C(24A)	151(3)	2214(2)	8789(2)	102(4)
C(25A)	122(3)	3109(2)	8947(2)	95(4)
C(26A)	650(3)	3832(2)	8560(2)	75(3)
C(21A)	1207(3)	3659(2)	8013(2)	47(2)
C(32A)	−3413(3)	1072(3)	2162(2)	73(3)
C(33A)	−3574(3)	163(3)	1728(2)	88(4)
C(34A)	−2829(3)	−215(3)	2124(2)	104(5)
C(35A)	−1923(3)	316(3)	2954(2)	103(5)
C(36A)	−1762(3)	1225(3)	3388(2)	76(3)
C(31A)	−2507(3)	1602(3)	2992(2)	46(2)
C(42A)	−4160(3)	2852(3)	2834(2)	59(3)
C(43A)	−5268(3)	2721(3)	2829(2)	74(3)
C(44A)	−5705(3)	2292(3)	3426(2)	76(3)
C(45A)	−5033(3)	1995(3)	4030(2)	91(4)
C(46A)	−3924(3)	2126(3)	4037(2)	77(3)
C(41A)	−3488(3)	2555(3)	3439(2)	47(2)
O(1B)	402(3)	6727(2)	7894(2)	45(2)
H(1B)	925(43)	6923(41)	8519(12)	86(18)*
O(2B)	−2004(3)	3330(2)	10710(2)	50(2)
H(2B)	−2067(61)	3843(35)	11071(38)	106(25)*
C(1B)	−774(4)	6504(3)	7846(3)	40(2)
C(2B)	−1173(4)	5751(3)	8304(3)	43(2)
C(3B)	−1483(4)	5104(3)	8655(3)	50(3)
C(4B)	−1900(4)	4366(3)	9040(3)	47(2)
C(5B)	−2303(4)	3704(3)	9359(3)	50(2)
C(6B)	−2782(4)	2961(3)	9803(3)	45(2)
C(12B)	−4502(3)	2334(3)	10321(2)	66(3)
C(13B)	−5630(3)	2176(3)	10289(2)	82(3)
C(14B)	−6301(3)	2465(3)	9675(2)	80(3)
C(15B)	−5844(3)	2910(3)	9092(2)	84(4)
C(16B)	−4717(3)	3068(3)	9124(2)	66(3)
C(11B)	−4046(3)	2780(3)	9738(2)	45(2)
C(22B)	−3249(4)	1604(2)	8524(2)	67(3)
C(23B)	−3369(4)	681(2)	8176(2)	78(4)
C(24B)	−3091(4)	138(2)	8731(2)	73(3)
C(25B)	−2692(4)	518(2)	9636(2)	93(5)
C(26B)	−2572(4)	1441(2)	9984(2)	75(3)
C(21B)	−2850(4)	1984(2)	9429(2)	43(2)
C(32B)	−1377(3)	7499(2)	8780(2)	67(3)
C(33B)	−1377(3)	8382(2)	9082(2)	86(4)
C(34B)	−766(3)	9221(2)	8839(2)	92(4)
C(35B)	−156(3)	9177(2)	8295(2)	114(5)
C(36B)	−156(3)	8293(2)	7993(2)	91(4)
C(31B)	−767(3)	7454(2)	8235(2)	47(2)
C(42B)	−2604(3)	6161(3)	6540(2)	73(3)
C(43B)	−3380(3)	5697(3)	5664(2)	94(4)
C(44B)	−3151(3)	5103(3)	5420(2)	86(4)
C(45B)	−2144(3)	4974(3)	5453(2)	81(3)
C(46B)	−1367(3)	5439(3)	6329(2)	65(3)
C(41B)	−1597(3)	6032(3)	6873(2)	46(2)

Table 2(*c*) *continued*

Atom	*x/a*	*y/b*	*z/c*	U_{equiv}/U_{iso} (*)
C(1G)	−4943(10)	−1465(10)	3804(6)	145(8)
C(2G)	−5445(17)	−2360(9)	3571(7)	225(12)
C(3G)	−6396(18)	−3012(9)	3346(8)	184(12)
C(4G)	−7338(15)	−2891(10)	3396(7)	155(10)
C(5G)	−6961(10)	−1846(10)	3671(5)	127(8)
C(6G)	−5824(8)	−1148(7)	3870(5)	107(5)
C(8G)	−7898(11)	−1580(9)	3694(8)	159(4)
C(9G)	−3726(15)	−675(13)	4017(11)	217(6)
C(1Z)	−669(12)	9174(11)	5061(9)	164(4)
C(2Z)	−629(13)	9926(13)	5529(10)	185(5)
C(3Z)	−75(16)	9176(13)	4474(11)	200(5)
C(1M)	−1548(26)	9128(22)	5870(19)	195(10)
C(2N)	−1166(21)	8206(19)	4777(17)	161(8)

Table 2(*d*) Fractional atomic co-ordinates ($\times 10^4$) and thermal parameters (Å^2 $\times 10^3$) e.s.d. values in parentheses for **4**

Atom	*x/a*	*y/b*	*z/c*	U_{equiv}/U_{iso} (*)
O(1A)	4746(1)	8251(1)	2093(1)	45(1)
H(1A)	5401(24)	8193(21)	2228(18)	77(9)*
O(2A)	6494(1)	10310(1)	−2901(1)	48(1)
H(2A)	6151(24)	10695(22)	−2557(18)	74(9)*
C(1A)	5008(2)	7589(2)	1592(1)	37(1)
C(2A)	5517(2)	8026(2)	706(2)	43(1)
C(3A)	5940(2)	8375(2)	−8(2)	46(1)
C(4A)	6429(2)	8750(2)	−842(2)	46(1)
C(5A)	6850(2)	9046(2)	−1566(2)	44(1)
C(6A)	7331(2)	9415(2)	−2482(1)	41(1)
C(11A)	3901(2)	7489(2)	1565(1)	38(1)
C(12A)	3872(2)	7074(2)	971(2)	57(2)
C(13A)	2897(3)	6924(2)	972(2)	72(2)
C(14A)	1956(2)	7184(2)	1559(2)	70(2)
C(15A)	1975(2)	7604(2)	2136(2)	64(2)
C(16A)	2942(2)	7762(2)	2144(2)	51(1)
C(21A)	5834(2)	6565(2)	2036(1)	40(1)
C(22A)	5514(2)	6077(2)	2885(2)	63(1)
C(23A)	6232(3)	5165(2)	3325(2)	79(2)
C(24A)	7275(3)	4742(2)	2918(2)	82(2)
C(25A)	7608(3)	5215(2)	2072(2)	80(2)
C(26A)	6889(2)	6124(2)	1632(2)	60(1)
C(31A)	7562(2)	8626(2)	−2920(1)	47(1)
C(32A)	6870(3)	8761(2)	−3477(2)	71(2)
C(33A)	7083(4)	8035(3)	−3853(3)	96(2)
C(34A)	7978(4)	7158(3)	−3673(3)	98(3)
C(35A)	8676(3)	7011(2)	−3104(3)	90(2)
C(36A)	8468(2)	7744(2)	−2733(2)	66(2)
C(41A)	8394(2)	9643(2)	−2567(2)	44(1)
C(42A)	8864(2)	9473(2)	−1859(2)	61(2)
C(43A)	9826(3)	9702(3)	−1964(2)	80(2)
C(44A)	10328(3)	10082(2)	−2768(3)	79(2)
C(45A)	9869(3)	10267(2)	−3485(2)	77(2)
C(46A)	8898(2)	10049(2)	−3383(2)	64(1)
O(1B)	4608(1)	8371(1)	−5723(1)	45(1)
H(1B)	4069(25)	8821(22)	−6002(19)	73(10)*
O(2B)	3752(1)	11724(1)	−2908(1)	41(1)
H(2B)	4126(21)	11774(18)	−3426(16)	51(7)*
C(1B)	4196(2)	7990(2)	−4827(1)	38(1)
C(2B)	3967(2)	8741(2)	−4393(1)	42(1)
C(3B)	3728(2)	9393(2)	−4074(1)	43(1)
C(4B)	3407(2)	10130(2)	−3686(1)	42(1)
C(5B)	3098(2)	10766(2)	−3342(1)	40(1)
C(6B)	2771(2)	11506(2)	−2873(1)	36(1)
C(11B)	3098(2)	7810(2)	−4766(1)	39(1)
C(12B)	2136(2)	8133(2)	−4214(2)	56(1)
C(13B)	1160(2)	7966(2)	−4192(2)	69(2)
C(14B)	1135(3)	7483(2)	−4719(2)	67(2)
C(15B)	2103(3)	7147(2)	−5264(2)	68(2)

Table 2(*d*) *continued*

Atom	*x/a*	*y/b*	*z/c*	U_{equiv}/U_{iso} (*)
C(16B)	3078(2)	7306(2)	−5287(2)	56(1)
C(21B)	5112(2)	7006(2)	−4438(1)	40(1)
C(22B)	5113(2)	6612(2)	−3558(2)	57(1)
C(23B)	5923(3)	5704(2)	−3210(2)	72(2)
C(24B)	6745(3)	5188(2)	−3732(2)	69(2)
C(25B)	6750(3)	5579(2)	−4608(2)	79(2)
C(26B)	5937(2)	6486(2)	−4967(2)	64(1)
C(31B)	2430(2)	10994(2)	−1911(1)	36(1)
C(32B)	3250(2)	10308(2)	−1400(2)	61(2)
C(33B)	2962(3)	9797(2)	−548(2)	75(2)
C(34B)	1847(3)	9974(2)	−193(2)	69(2)
C(35B)	1032(3)	10661(2)	−695(2)	73(2)
C(36B)	1309(2)	11173(2)	−1548(2)	56(1)
C(41B)	1842(2)	12471(2)	−3250(1)	38(1)
C(42B)	1162(2)	12555(2)	−3797(2)	57(1)
C(43B)	298(3)	13451(2)	−4082(2)	75(2)
C(44B)	103(3)	14253(2)	−3847(2)	74(2)
C(45B)	787(3)	14191(2)	−3316(2)	80(2)
C(46B)	1650(2)	13309(2)	−3022(2)	64(2)
C(1G)	4891(4)	3370(3)	1271(2)	94(3)
C(2G)	5650(5)	2400(3)	1570(2)	105(3)
C(3G)	6740(5)	2236(3)	1653(3)	109(3)
C(4G)	7123(4)	3013(3)	1458(2)	94(2)
C(5G)	6381(4)	3964(3)	1153(2)	90(2)
C(6G)	5290(4)	4150(3)	1060(2)	85(2)
C(1MG)	3692(4)	3591(4)	1169(3)	137(4)
C(2MG)	8307(4)	2819(4)	1584(3)	137(3)
C(11G)	211(6)	4149(5)	−217(4)	115(4)
C(12G)	794(4)	4126(5)	342(3)	119(3)
C(13G)	598(5)	4933(7)	566(3)	121(4)
C(3MG)	442(6)	3222(5)	−474(4)	190(5)

ordinates and temperature factors of **1**, **2**, **3** and **4** are shown in Tables 2(*a*)–2(*d*), respectively. The structure of **1** was determined and refined *C*2/*c*. The space group *Cc* was discounted as the correct choice of space group upon considering values of the correlation matrix coefficients and *R* values. Disordered guest species are often observed in inclusion compounds in which there is no specific host–guest bonding and especially those in which the guest species is fairly volatile. In the case of **1**, a model of disorder was invoked for isotropic refinement of six guest atoms which had site occupancy factor of 0.50. The cyclohexane guest had a chair conformation. Packing diagrams viewed along [010] are shown in Figures 2(*a*) and 2(*b*) with the guest shown as disordered.

The xylene inclusion compounds **2**, **3** and **4** were successfully determined and refined in the triclinic space group $P\bar{1}$. Their crystal packing is illustrated viewed along [010] in Figures 3(*a*)–3(*c*). The structures of **2** and **3** are isomorphous, and in all three cases one of the xylene guest molecules was located at a centre of symmetry. This meant that in the cases of **2** and **3** it was necessary to model the asymmetric *ortho*- and *meta*-xylene molecules as disordered with the methyl carbons having a site occupancy factor of 0.50.

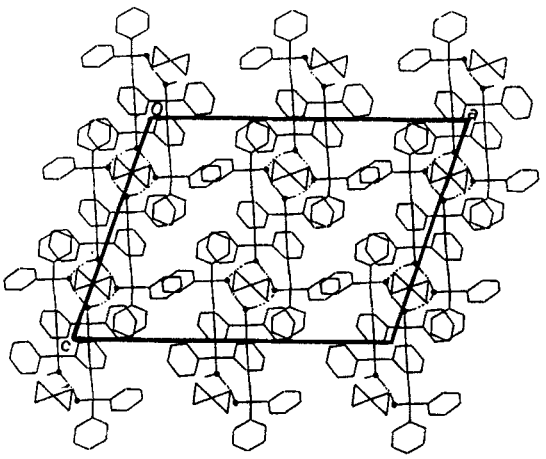

Figure 2(*a*) Packing diagram of **1** viewed along [010] with the guests shown as disordered.

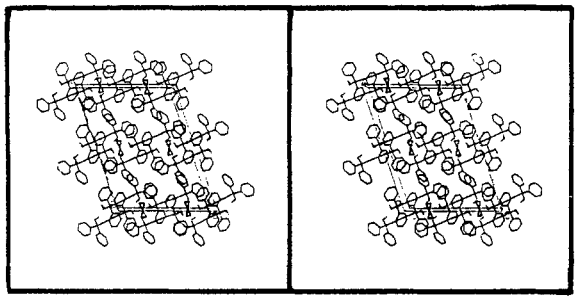

Figure 2(*b*) Stereo view of Figure 2(*a*).

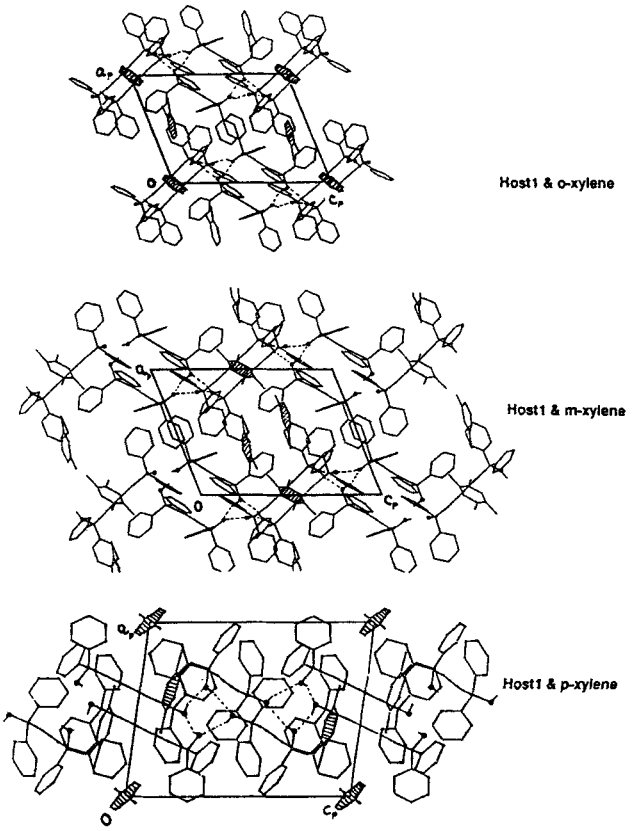

Figure 3 Packing diagrams of **2**, **3** and **4** viewed along [010].

Thermal analysis

Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG) were performed using a Perkin Elmer PC7 series system. Before analysis, crystals were removed from their respective mother liquors, blotted dry and evenly crushed. A constant stream of nitrogen (flow rate 40 ml min^{-1}) was passed over the samples. The temperature range for the DSC was usually 30–220°C and the heating rate was 10°C min^{-1}.

TG was used to confirm host–guest stoichiometry and also to obtain an estimate of the activation energy for the decomposition of the clathrate using the method described by Flynn and Wall.[10]

RESULTS AND DISCUSSION

In complex **1**, with a host–guest ratio of 2:1, the self-association between the molecules of **H** creates a cavity in which the cyclohexane molecule is trapped. The hydrogen bonding network formed by host–host hydrogen bonding results in tetramers between which the guest species is sandwiched. OPEC[11] maps were calculated to determine the shape of the guest cavity. Figure 4(*a*) shows a cross section of the cavity looking along [010] at $y = 0.42$ and Figure 4(*b*) is a view along [001]. The oxygen-to-oxygen distances are: O(1)–O(2) = 2.736(7) Å $(x, -y, z + \frac{1}{2})$, O(2)–(O1) = 2.723(5) Å $(-x + 1, y, -z + 1)$.

The packing factor (PF) expressed as volume per non-hydrogen atom was calculated to be 18.49 $Å^3$. This is higher than the value of 17.35 calculated for the (unclathrated) α-form of **H**.[5] This implies that the structure of **1** is more loosely packed that the α-form which is confirmed by the presence of guest cavities.

For structures **2**, **3** and **4**, four hydroxy moieties of four **H** molecules are involved in hydrogen bonding and the hydrogen bonding distances are shown in Table 3(*a*). The resultant packing orientates the long axes so that a channel is formed around the xylene guests. The channels which run parallel to [100] are shown in Figure 5 which illustrates the representative packing found in **2**, **3** and **4**. Concave sites created by the molecular axis of **H** molecules are occupied by guests which are trapped as molecules of crystallization in the lattice. In order to compare the packing modes of **2**, **3** and **4** the packing factors and occupied volumes were calculated. The non-porous alpha-phase of the host compound crystallized[5] in the space group $P\bar{1}$ with $Z = 2$ and a cell volume (V) of 1110.18 $Å^3$. The volume occupied by one host molecule may be taken as constant at 555.09 $Å^3$ in a host–guest structure. The cell volumes of the xylene inclusion compounds corresponded to stoichiometry 4H:3G, and when the host volume was subtracted, the volume available per guest was evaluated. These are shown in Table 3(*b*).

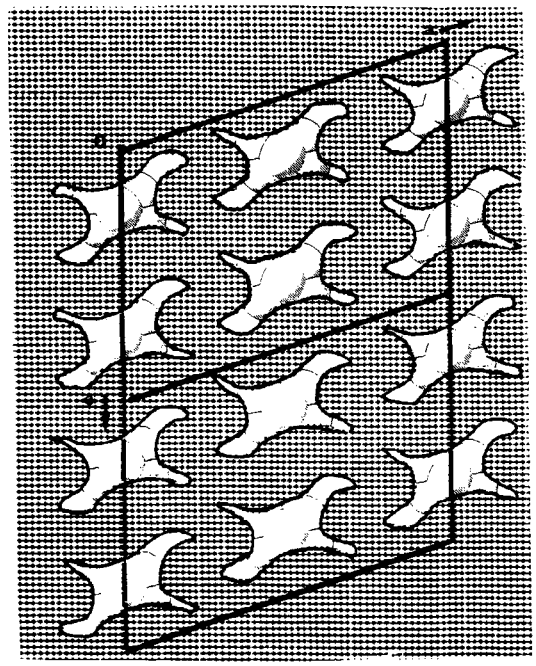

Figure 4(*a*) An OPEC[11] map of the guest cavity of **1** viewed along [010] at $y = 0.42$.

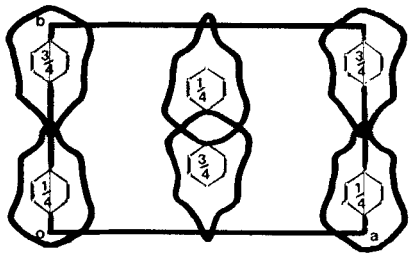

Figure 4(*b*) A view of the guest cavity of **1** viewed along [001] showing the guest cavities at $z = 0.25$ and at $z = 0.75$.

According to packing factors **4**, with the lowest value, is the most efficiently packed since it exhibits the most complementary van der Waals packing of host and guest components. Compounds **2** and **3** are less tightly packed with their disordered guests occupying comparatively larger volumes.

The torsion angles O(1)–C(1)–C(2)–O(2) for the four compounds were calculated to be: (**1**) 58°; (**2**) 65° (A) 63° (B); (**3**) 62° (A) 62° (B); (**4**) 66° (A) 62° (B). There is a *gauche* conformation of the hydroxy moieties which appears to be a consequence of the host–host bonding interaction, the dominant bonding feature in these compounds where the included guest is apolar. This is because in order to form stable inclusion compounds with apolar guests, the host molecules only interact significantly with each other by forming tetramers of hydrogen bonds.

Table 3(*a*)

	Host–o-xylene	*Host–m-xylene*	*Host–p-xylene*
$O1_{host\ A} \rightarrow O2_{host\ A}$ (Å)	2.710(6)($-x$. $-y+1$, $-z$)	2.708(5)($-x$, $-y+1$, $-z+1$)	2.734(2)($-x$, $-y$, $-z$)
$O1_{host\ A} \rightarrow O2_{host\ B}$ (Å)	2.716(6)($-x$, $-y+1$, $-z+1$)	2.725(6)($-x$, $-y$, $-z$)	2.698(3)($-x+1$, $-y+2$, $-z$)
$O1_{host\ B} \rightarrow O2_{host\ B}$ (Å)	2.688(5)($-x$, $-y+1$, $-z+1$)	2.689(5)($-x$, $-y+1$, $-z+2$)	2.687(2)($-x+1$, $-y+2$, $-z-1$)
$O1_{host\ B} \rightarrow O2_{host\ A}$ (Å)	2.723(6)($-x$, $-y+1$, $-z$)	2.728(5)($-x$, $-y+1$, $-z+2$)	2.720(2)($-x+1$, $-y+2$, $-z-1$)

Table 3(*b*)

Compound	*Cell volume, V (Å^3)*	*Volume/guest (Å^3)*	*Packing factor (Å^3/non-H atom)*
Host	1110.18	–	17.35
Host–*o*-Xylene	2822.25	200.63	18.57
Host–*m*-Xylene	2843.57	207.74	18.71
Host–*p*-Xylene	2816.75	198.80	18.53

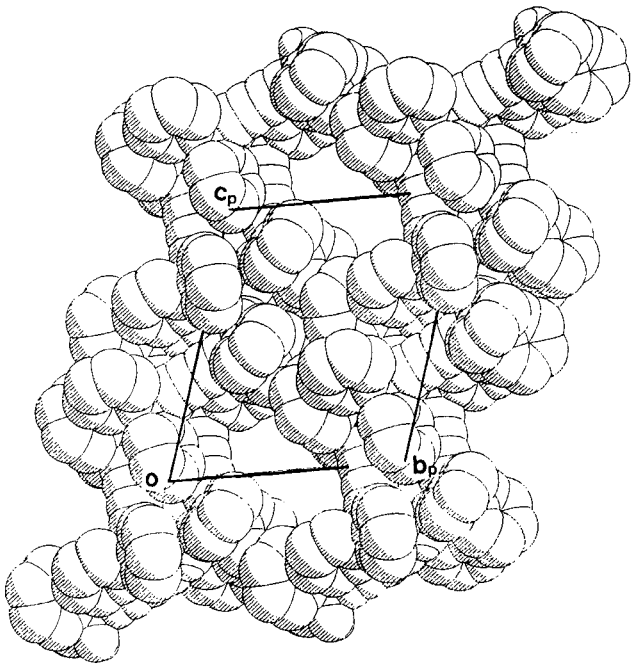

Figure 5 A spacefill plot of the host molecules of **4** illustrating the guest channel which is typical of **2**, **3** and **4**.

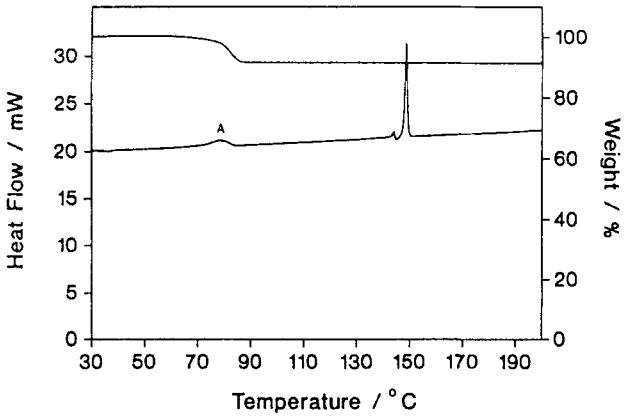

Figure 6 Thermal analysis traces of **1**.

Thermal analyses

The DSC trace of **1** is shown in Figure 6 and shows a small diffuse endotherm corresponding to the guest release. The guest release reaction has an onset temperature of 73°C, lower than the normal boiling point of 80.7°C, testifying to the fact that the guest is weakly held. The second endotherm corresponds to the melting of **H**. The TG trace shows there to be good correlation between the experimental and calculated guest weight loss thus confirming the host–guest ratio of 2:1.

The thermal analysis traces of **2**, **3** and **4** are shown in Figures 7(*i*)–(*iii*), respectively. The xylene clathrates show a one step decomposition which corresponds to the stoichiometric loss of the guest in each case. This confirms the crystallographic host–guest stoichiometry of 4:3. Each DSC trace contains three endotherms A, B and C. Endotherm A corresponds to desorption of the xylene guest with recrystallization of the α-phase host, **H**. Endotherm B is due to premelting of the host, followed by the main melting endotherm C.

Table 4 contains the thermal analysis data pertaining to **2**, **3** and **4**. The difference between the onset temperature and boiling point may be used as an indication of how firmly the guest is held in the inclusion lattice. This difference indicates greatest stability in the case of **4** in which there is no guest disorder and more efficient packing of the *p*-xylene molecule. We derived activation energies by appropriate plots of the logarithm of the heating rate versus reciprocal temperature for various stages of decomposition of the inclusion compounds. The activation energies vary from 62 to 78 kJ mol^{-1}. These values are similar to those obtained for the guest release of Hofmann-type hosts containing aromatic guests.[12]

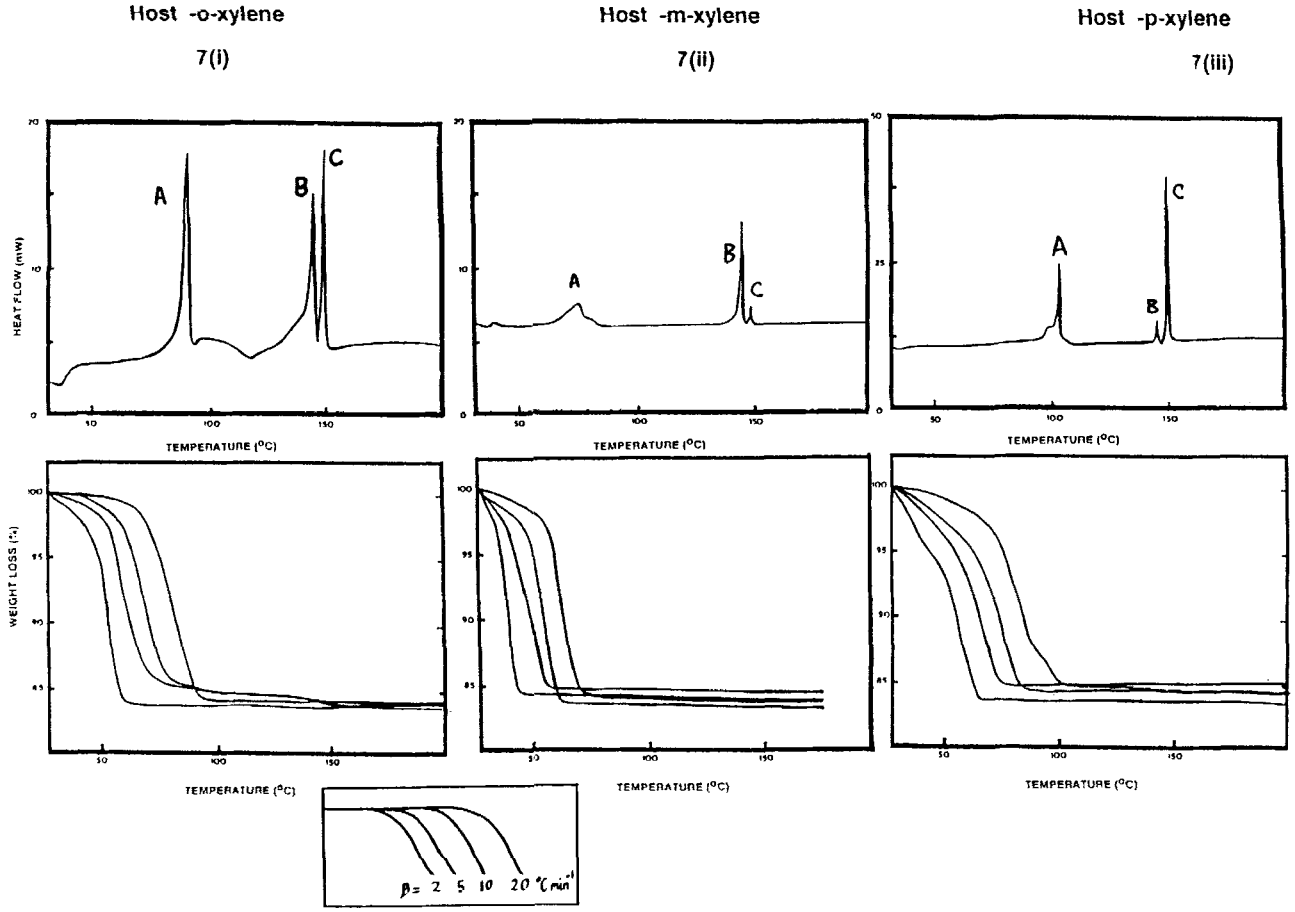

Figure 7 Thermal analysis traces of (i) **2**, (ii) **3** and (iii) **4**.

Table 4

	2	*3*	*4*
Host:guest ratio	4:3	4:3	4:3
TGA % loss (experimental)	16.3	16.1	15.6
TGA % loss (calculated)	16.1	16.1	16.1
T_b (°C)	144.0	139.3	137.5
T_{on} (°C)	87.1	66.8	102.0
$T_{on} - T_b$ (°C)	−56.9	−72.5	−35.5
E_a (kJ mol^{-1})	71 – 78	68 – 69	62 – 74

TGA = thermodynamic analysis.
TGA = thermogravimetric analysis.
T_b = normal blg pt.
T_{on} = onset temperature.

Host compounds similar to **H** appears to be able to adopt the hydroxy moiety conformation most conducive to stable inclusion compound formation. The hydroxy moieties act as sensors, and in the presence of a polar guest able to receive hydrogen bonds, the host **H** adopts a *trans* conformation of the hydroxy functions with host–guest interactions being the dominant stabilizing influence in the structure.[13]

When there is no hydrogen bond-receiving functionality present, **H** alters its conformation so as to best form a stable crystal compound. It does so by twisting its backbone from the *trans* conformation found in **H**-polar inclusion compounds and the alpha-form to result in a *gauche* conformation of the hydroxy groups which permits interaction with another molecule of **H** in the crystal structure. The apolar guests act as steric spacers and are involved in pi-pi interactions with the phenyl rings on **H**.

REFERENCES

1 Hagan, M.; *Clathrate Inclusion Compounds*, Reinhold, New York, **1962**.
2 Mandelcorn, L.; *Non-stoicheoimetric Compounds*, Academic Press, New York, **1964**.
3 Weber, E.; *Inclusion Compounds*, vol 4, Atwood, J.L., Davies, J.E.D. and MacNicol, D.D. (Eds.), Oxford University Press, **1991**, Chapter 5.

4 Toda, F.; Akagi, K.; *Tetrahedron Lett.* **1968**, *33*, 3695.
5 Bond, D.R.; Johnson, L.; Nassimbeni, L.R.; Toda, F.; *J. Solid State Chem.* **1991**, *92*, 68.
6 Johnson, L.; Nassimbeni, L.R.; Toda, F.; *Acta Cryst.* **1992**, *B48*, 827.
7 Bourne, S.A.; Johnson, L.; Marais, C.; Nassimbeni, L.R.; Weber, E.; Skobridis, K.; Toda, F.; *J. Chem. Soc., Perkin Trans.* 2, **1991**, 1707.
8 Sheldrick, G.M.; SHELXS-86, Crystallographic Computing 3, Sheldrick, G.M., Kruger, C. and Goddard, R. (Eds.), Oxford University Press, **1985**, p. 175.
9 Sheldrick, G.M.; SHELX-76: A Program for Crystal Structure Determination, University of Cambridge, **1976**.
10 Flynn, J.H.; Wall, L.A.; *Polym. Lett.* **1966**, *4*, 32.
11 Gavezotti, A.; *OPEC – Organic Packing Energy Calculations manual*, Milan University, Italy, unpublished.
12 Kitazawa, T.; Mizushima, Y.; Shiraha, J.; Taguchi, R.; Katoh, A.; Hasagawa, T.; Nishikiori, S-I.; Iwamoto, T.; *J. Incl. Phenom. Mol. Recogn. Chem.* **1991**, *10*, 29.
13 Johnson, L.; Nassimbeni, L.R.; Weber, E.; Skobridis, K.; *J. Chem. Soc., Perkin Trans 2*, **1992**, 2131.