Complexation with Hydroxy Host Compounds. Part. 4.† Structures and Thermal Stabilities of Inclusion Compounds with Dioxane as the Guest

Susan A. Bourne,[a] **Louise Johnson,**[a] **Charles Marais,**[a] **Luigi R. Nassimbeni,***[,a] **Edwin Weber,**[b] **Konstantinos Skobridis**[b] **and Fumio Toda**[c]
[a] *Department of Chemistry, University of Cape Town, Rondebosch, 7700, South Africa*
[b] *Institut für Organische Chemie und Biochemie, der Universität Bonn, Gerhard-Domagk Strasse 1, D-5300 Bonn 1, Germany*
[c] *Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790, Japan*

Structures of the inclusion compounds of five hydroxy-containing hosts with dioxane have been solved. Crystal data: **1**, monoclinic, $C2/c$, $a = 8.648(1)$ Å, $b = 16.551(1)$ Å, $c = 17.038(4)$ Å, $\beta = 90°$, $V = 2398.64$ Å^3, $Z = 4$; **2**, triclinic, $P\bar{1}$, $a = 8.441(8)$ Å, $b = 10.544(2)$ Å, $c = 11.562(2)$ Å, $\alpha = 67.47(1)°$, $\beta = 83.96(5)°$, $\gamma = 89.08(5)°$, $V = 944.94$ Å^3, $Z = 2$; **3**, triclinic, $P\bar{1}$, $a = 9.378(7)$ Å, $b = 11.851(2)$ Å, $c = 14.891(2)$ Å, $\alpha = 87.85(1)°$, $\beta = 81.05(1)°$, $\gamma = 87.65(1)°$, $V = 1632.77$ Å^3, $Z = 1$; **4**, triclinic, $P\bar{1}$, $a = 9.298(4)$ Å, $b = 12.577(9)$ Å, $c = 12.859(6)$ Å, $\alpha = 115.63(5)°$, $\beta = 90.99(3)°$, $\gamma = 92.34(5)°$, $V = 1353.51$ Å^3, $Z = 2$; **5**, triclinic, $P\bar{1}$, $a = 8.8337(1)$ Å, $b = 8.646(3)$ Å, $c = 11.700(3)$ Å, $\alpha = 108.22(25)°$, $\beta = 94.22(2)°$, $\gamma = 99.82(2)°$, $V = 781.52$ Å^3, $Z = 1$. Host–guest hydrogen bonds are observed in all structures and a host–host hydrogen bond in structure **3**. O ··· O distances are between 2.703 and 2.865 Å. Thermal analysis revealed the strength of binding of the dioxane molecules. The energy of the guest molecules was evaluated using the method of atom–atom potentials. A correlation was observed between the minimum energy of the guest molecule and the enthalpy of the guest release reaction for **1**–**4**.

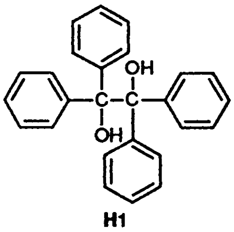
Organic host molecules which contain the hydroxy moiety have proved to be versatile in forming inclusion compounds. When there is hydrogen bonding between host and guest molecules, the compounds are classified as coordinato clathrates.[1] These host molecules have several useful properties, including the ability to isolate guest molecules selectively and to resolve optical isomers.[2] They have also been used in controlling the reactions of entrapped guest molecules.[3]

We have recently synthesized a series of lattice hosts derived from singly bridged triarylmethane frameworks, which form crystalline inclusion compounds with a variety of organic guest molecules.[4] We have also described the structures and thermal analysis of the suberol-derived host 10,11-dihydro-5-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol, in its non-porous α-phase, and the β-phases it forms with dioxane and acetone.[5]

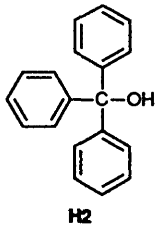
Diol host molecules have also proved useful, and we have studied the structures and thermal stabilities of a variety of inclusion compounds formed by the host *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene, with substituted pyridines[6] and selected ketones.[7,8]

The objective of carrying out thermal analysis on these compounds was to reconcile thermodynamics with structure. Thus it should, in principle, be possible to relate the enthalpies of the guest release reaction and the crystal energies as measured by the host–guest interactions which occur in the crystal structure. Another parameter which measures the thermal stability is the temperature characterizing the onset of the endothermic guest release reaction, T_{on}, as measured by differential scanning calorimetry (DSC). However, for inclusion compounds which have different guests, the onset temperatures are also a function of the physical properties of the guests themselves. Thus, in order to bypass this difficulty we have elucidated the structures of five different hydroxy host compounds with the same guest, dioxane, and studied their thermal decompositions.

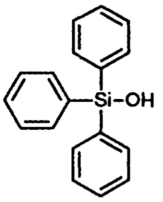
The five host compounds are: **H1**, 1,1,2,2-tetraphenylethane-1,2-diol; **H2**, triphenylmethanol; **H3**, triphenylsilanol; **H4**, tri-1-naphthylsilanol; **H5**, 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol.



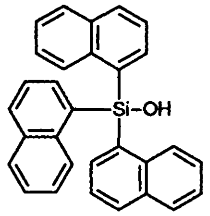
H1



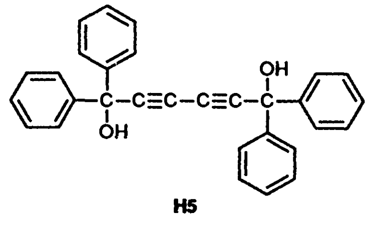
H2



H3



H4



H5

Experimental

Single crystals for diffraction measurements were grown by

---

† For Part 3 of this series see S. A. Bourne, L. R. Nassimbeni, E. Weber and K. Skobridis, *J. Org. Chem.*, in the press.

Table 1 Crystal data and experimental parameters

	1	**2**	**3**	**4**	**5**
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.648(1)	8.441(8)	9.378(7)	9.298(4)	8.8337(1)
b/Å	16.551(1)	10.544(2)	11.851(2)	12.577(9)	8.646(3)
c/Å	17.038(4)	11.562(2)	14.891(2)	12.859(6)	11.700(3)
α/°	90	67.47(1)	87.85(1)	115.63(5)	108.22(25)
β/°	100.40(2)	83.96(5)	81.05(1)	90.99(3)	94.22(2)
γ/°	90	89.08(5)	87.65(1)	92.34(5)	99.82(2)
V/Å^3	2398.64	944.94	1632.77	1353.51	781.52
Z	4	2	1	2	1
D_x g cm^{-3}	1.26	1.24	1.21	1.26	1.26
Crystal dimensions mm	0.38 × 0.41 × 0.44	0.41 × 0.41 × 0.50	0.34 × 0.38 × 0.38	0.41 × 0.41 × 0.50	0.31 × 0.38 × 0.41
2θ limit °	25	25	25	25	25
Max. h, k, l	±10, ±11, +20	±10, ±12, +13	±11, ±14, +17	±11, ±15, +15	±9, ±10, +13
N (measured)	4363	2824	5970	4973	2266
N (observed)	3008	2324	4468	3883	1685
R	0.077	0.052	0.041	0.038	0.077
R_w	0.087	0.047	0.053	0.048	0.088
w^a	0.001	0	0.005	0.002	0.001
Absorption correct					
Minimum transmission (%)			97.23	95.15	
Maximum transmission (%)			99.94	99.96	
Average transmission (%)			98.50	97.79	

[a] Weighting scheme: $(\sigma^2F + wF^2)^{-1}$.

Table 2 Fractional atomic coordinates (×10^4) with esds in parentheses for compound **1**

Atom	x/a	y/b	z/c
O(1)	1399(3)	2060(1)	1816(1)
C(1A)	933(4)	2061(2)	2583(2)
C(1B)	−319(11)	2141(5)	2048(7)
C(11)	1460(3)	2838(2)	3128(2)
C(12)	1523(4)	2887(2)	3946(2)
C(13)	2106(3)	3568(2)	4377(2)
C(14)	2667(4)	4210(2)	3983(2)
C(15)	2633(4)	4158(2)	3183(2)
C(16)	2019(4)	3481(2)	2761(2)
C(21)	1602(3)	1331(2)	3077(2)
C(22)	3191(4)	1237(2)	3067(2)
C(23)	4017(4)	590(2)	3421(2)
C(24)	3292(4)	21(2)	3804(2)
C(25)	1709(4)	98(2)	3824(2)
C(26)	875(4)	753(2)	3473(2)
O(1G)	2276(3)	3057(2)	591(2)
O(2G)	1562(18)	1832(10)	118(10)
C(1G)	1624(5)	3168(3)	−231(3)
C(2G)	3712(4)	2625(3)	627(2)

dissolving the host in a suitable solvent (diethyl ether for **H1**, **H2** and **H3**, chloroform for **H4**), adding excess dioxane and allowing the solutions to evaporate slowly at room temperature. For **H5**, the host dissolved in dioxane directly and yielded suitable crystals on slow evaporation. The stoichiometries of the resulting inclusion compounds were: compound **1**, **H1**·**G**; compound **2**, **H2**·**G**; compound **3**, **H3**·$\frac{1}{4}$**G**; compound **4**, **H4**·**G**; compound **5**, **H5**·2**G** (**G** = 1,4-dioxane).

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. Intensity data were collected on an Enraf–Nonius CAD4 diffractometer at 293 K using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) and the $\omega - 2\theta$ mode. During each data collection three reference reflections were monitored periodically to check crystal stability. The data reduction included Lorentz and polarization corrections for all five compounds and absorption corrections for compounds **3** and **4**.[9] For compound **5** there was considerable crystal decay and a linear decay correction was applied to the intensity data.[10]

Table 3 Fractional atomic coordinates (×10^4) with esds in parentheses for compound **2**

Atom	x/a	y/b	z/c
O(1)	1 666(2)	8 970(2)	8 936(2)
C(1)	999(3)	9 267(3)	7 773(3)
C(11)	1 819(3)	8 372(3)	7 113(3)
C(12)	1 656(4)	6 949(3)	7 715(3)
C(13)	2 445(4)	6 103(3)	7 196(3)
C(14)	3 409(4)	6 656(4)	6 064(4)
C(15)	3 553(4)	8 061(3)	5 454(3)
C(16)	2 768(3)	8 917(3)	5 977(3)
C(21)	−815(3)	8 977(3)	8 034(3)
C(22)	−1 636(3)	8 640(3)	7 219(3)
C(23)	−3 286(4)	8 459(3)	7 428(3)
C(24)	−4 104(4)	8 614(3)	8 456(4)
C(25)	−3 290(4)	8 940(4)	9 274(3)
C(26)	−1 645(4)	9 128(3)	9 066(3)
C(31)	1 345(3)	10 798(3)	6 996(3)
C(32)	462(4)	11 540(3)	6 032(3)
C(33)	853(4)	12 898(3)	5 281(3)
C(34)	2 125(4)	13 541(3)	5 493(3)
C(35)	3 014(4)	12 819(3)	6 468(3)
C(36)	2 637(3)	11 457(3)	7 210(3)
O(1G)	1 283(3)	6 330(2)	10 905(2)
C(1G)	1 149(5)	6 770(4)	11 926(3)
C(2G)	2 763(5)	7 109(4)	12 173(4)
O(2G)	3 741(3)	5 937(3)	12 458(3)
C(3G)	3 880(4)	5 493(4)	11 438(4)
C(4G)	2 274(4)	5 159(4)	11 190(4)

The unit cell parameters and space group assignments were first obtained photographically and later by least-squares analysis of 24 reflections measured on the diffractometer in the range 16 < θ < 17°. Crystal data and some experimental details are given in Table 1.

Structure Solution and Refinement.—All five structures were solved by direct methods using SHELXS-86[11] and refined by full matrix least-squares using SHELX-76.[12] Refinement proceeded in a parallel manner for all five structures. Non-

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

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Si(1)	693(1)	337(0)	7 194(0)
O(1)	1 860(2)	688(1)	6 842(1)
C(111)	662(2)	1 444(2)	6 269(1)
C(112)	1 717(3)	2 258(2)	6 143(2)
C(113)	1 802(3)	3 031(2)	5 419(2)
C(114)	826(4)	3 036(3)	4 830(2)
C(115)	−248(3)	2 260(3)	4 951(2)
C(116)	−319(3)	1 463(2)	5 661(2)
C(121)	−1 111(2)	−307(2)	7 495(1)
C(122)	−2 336(2)	355(2)	7 810(2)
C(123)	−3 674(3)	−106(2)	8 043(2)
C(124)	−3 823(3)	−1 250(3)	7 966(2)
C(125)	−2 643(3)	−1 922(2)	7 659(2)
C(126)	−1 296(3)	−1 455(2)	7 420(2)
C(131)	1 250(2)	968(2)	8 208(1)
C(132)	2 207(3)	379(3)	8 700(2)
C(133)	2 574(4)	804(3)	9 478(3)
C(134)	1 955(3)	1 839(3)	9 798(2)
C(135)	1 090(3)	2 444(3)	9 302(2)
C(136)	736(3)	2 019(2)	8 512(2)
Si(2)	2 775(1)	−3 939(0)	7 609(0)
O(2)	2 897(2)	−2 929(1)	6 833(1)
C(211)	917(2)	−4 502(2)	7 810(1)
C(212)	389(3)	−4 918(2)	7 065(2)
C(213)	−951(3)	−5 384(2)	7 155(2)
C(214)	−1 804(3)	−5 443(2)	7 990(2)
C(215)	−1 326(3)	−5 047(3)	8 738(2)
C(216)	30(3)	−4 575(2)	8 651(2)
C(221)	4 057(2)	−5 083(2)	7 120(1)
C(222)	4 039(3)	−6 159(2)	7 535(2)
C(223)	4 971(3)	−7 022(2)	7 174(2)
C(224)	5 932(3)	−6 827(3)	6 384(2)
C(225)	5 960(3)	−5 784(3)	5 967(2)
C(226)	5 043(3)	−4 915(2)	6 327(2)
C(231)	3 270(2)	−3 458(2)	8 693(1)
C(232)	4 508(3)	−3 856(2)	9 023(2)
C(233)	4 891(3)	−3 450(2)	9 808(2)
C(234)	4 035(3)	−2 622(2)	10 276(2)
C(235)	2 803(3)	−2 214(2)	9 973(2)
C(236)	2 420(3)	−2 626(2)	9 192(2)
O(1G)	3 697(2)	−547(2)	5 255(1)
C(1G)	3 838(3)	296(3)	4 556(2)
C(2G)	5 062(3)	−1 119(2)	5 309(2)

hydrogen atoms were refined anisotropically and aromatic and dioxane hydrogens were constrained to 1.00 Å from their parent atoms. The hydroxy hydrogens were located in Fourier maps and allowed to refine independently. They were, however, constrained to fixed distances from their parent oxygens, according to a function of O–H *vs.* O ··· O distance.[13]

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 on filter paper and crushed before analysis. Sample weight in each case was *ca.* 5 mg. The temperature ranges were from ambient to approximately 50 °C beyond the melting point of the host compounds at a heating rate of 10 °C min^{-1}. The purge gas was dry nitrogen at a flow rate of 40 $\text{cm}^3\ \text{min}^{-1}$.

Results and Discussion

The atomic coordinates of compounds **1**–**5** are given in Tables 2–6. Atom labelling is according to Fig. 1 which shows perspective views of the molecular structures. Complete lists of bond lengths, angles, anisotropic thermal parameters and coordinates of calculated hydrogen positions have been desposited.*

Table 5 Fractional atomic coordinates ($\times 10^4$) with esds in parentheses for compound **4**

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Si(1)	979(0)	7 424(0)	8 303(0)
O(1)	1 558(1)	6 140(1)	7 433(1)
C(10)	1 018(2)	8 384(2)	7 521(1)
C(11)	−121(2)	9 074(2)	7 615(2)
C(12)	−182(2)	9 826(2)	7 066(2)
C(13)	902(3)	9 868(2)	6 390(2)
C(14)	2 114(2)	9 189(2)	6 256(1)
C(15)	3 261(3)	9 225(2)	5 560(2)
C(16)	4 426(3)	8 590(2)	5 452(2)
C(17)	4 540(2)	7 884(2)	6 045(2)
C(18)	3 449(2)	7 810(2)	6 713(2)
C(19)	2 194(2)	8 451(1)	6 833(1)
C(20)	2 160(2)	8 144(2)	9 647(1)
C(21)	2 798(2)	9 242(2)	9 925(2)
C(22)	3 667(2)	9 858(2)	10 939(2)
C(23)	3 895(2)	9 363(2)	11 668(2)
C(24)	3 277(2)	8 234(2)	11 439(2)
C(25)	3 491(3)	7 710(3)	12 201(2)
C(26)	2 910(3)	6 631(3)	11 971(2)
C(27)	2 061(3)	5 995(2)	10 957(2)
C(28)	1 810(2)	6 481(2)	10 208(2)
C(29)	2 410(2)	7 611(2)	10 418(2)
C(30)	−912(2)	7 294(2)	8 733(1)
C(31)	−1 245(2)	7 940(2)	9 870(2)
C(32)	−2 637(2)	7 914(2)	10 268(2)
C(33)	−3 710(2)	7 224(2)	9 523(2)
C(34)	−3 450(2)	6 538(2)	8 349(2)
C(35)	−4 568(2)	5 811(2)	7 562(2)
C(36)	−4 308(2)	5 161(2)	6 436(2)
C(37)	−2 945(3)	5 211(2)	6 018(2)
C(38)	−1 842(2)	5 906(2)	6 747(2)
C(39)	−2 056(2)	6 581(2)	7 942(2)
O(1G)	620(2)	3 982(1)	7 271(2)
O(2G)	2 347(2)	2 160(2)	5 904(2)
C(1G)	1 373(4)	3 318(2)	7 745(3)
C(2G)	1 683(3)	2 843(3)	7 075(3)
C(3G)	1 632(4)	2 836(3)	5 459(2)
C(4G)	304(4)	3 262(2)	6 078(3)

Molecular Structure.—The five host molecules have a common feature: each has a tetrahedral atom (C or Si) bonded to a hydroxy group and shielded by at least two bulky aromatic moieties. This is the feature which makes these compounds difficult to crystallize in their non-porous α-phase without a guest molecule and which renders them good hosts which can include a wide variety of guests. The central carbon atom of the host in **1** was found to be disordered and was modelled by two carbons with site occupancies of 0.7 and 0.3. The dioxane, which lies on a centre of inversion, was also disordered, with the oxygens located on either side of the plane formed by the four carbon atoms. The oxygens were modelled with site occupancies of 0.8 and 0.2. A similar disorder was shown by one of the dioxanes in **5**, labelled guest B, in which the oxygens were modelled with site occupancies of 0.7 and 0.3.

The bond lengths and angles in the five host structures show good agreement with those found in similar structures.[14–16] The carbon atoms bonded to the hydroxy moieties are tetrahedral and the angles all fall within the limits of 105–114°. The ordered dioxanes in the structures adopt the chair conformation, with C–O bond lengths varying from 1.410 to 1.438 Å and C–C bond lengths varying from 1.419 to 1.493 Å.

Crystal Packing and Host–Guest Interactions.—All five

---

* For details of the deposition scheme see 'Instructions for Authors', *J. Chem. Soc. Perkin Trans 2*, 1991, issue 1.

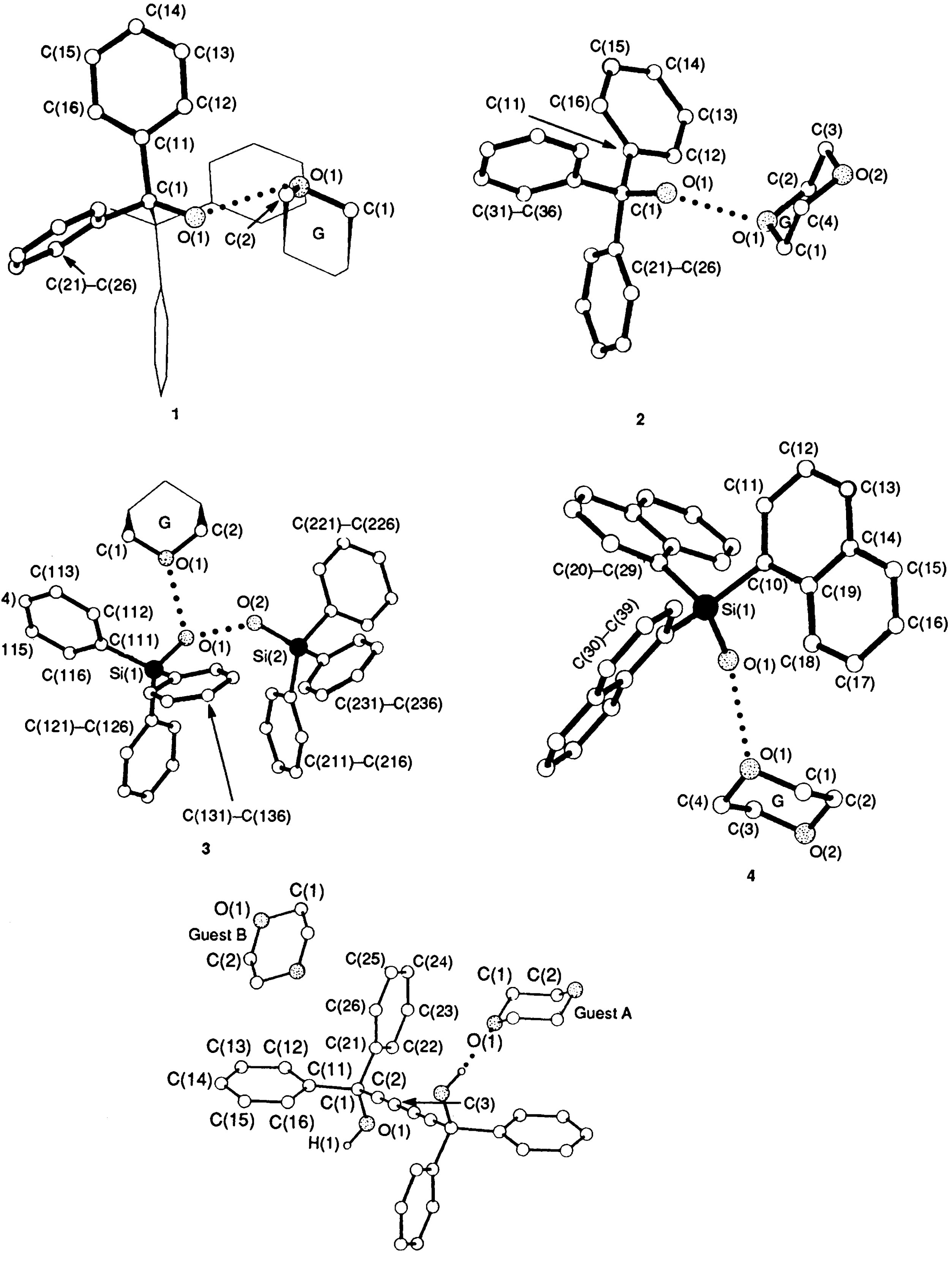


Fig. 1 Perspective diagrams of hosts, H1–H5, showing the atom labelling used

structures exhibit hydrogen bonding between the hydroxy moiety and the dioxane oxygen, as has been observed in similar structures.[4,5] Different hydrogen bonding patterns are observed in each of these compounds. Details of the hydrogen bonds are given in Table 7.

In **1**, **H1** is located on a diad, while the dioxane is positioned at a centre of inversion at Wyckoff position *c*. Both hydroxy moieties are involved in hydrogen bonding giving rise to infinite chains of host and guest molecules running in the [1 0 1] direction, as shown in Fig. 2(*a*). This leads to a 1:1 stoichiometry for this compound.

Although **2** and **4** have 1:1 stoichiometry, the structural units from which these structures are built consist of only one host and one guest molecule, leaving one dioxane oxygen free of hydrogen bonds. These structures are shown in Fig. 2(*b*) and (*d*).

Fig. 2(*c*) shows the packing for **3**. This is the only case which exhibits a host-to-host hydrogen bond. Here the host molecule has a hydroxy moiety acting both as a proton acceptor to the hydroxy of a second host and as a proton donor to the oxygen of a dioxane. The latter is located on a centre of inversion at Wyckoff position *f*, giving rise to a repeat of the structural unit and a stoichiometry of 4:1.

In **5**, the host molecule is located at a centre of inversion at Wyckoff position *d* while the two independent guest molecules are located on centres of inversion at Wyckoff positions *g* (guest A) and *c* (guest B). The oxygen atoms of guest A are hydrogen bonded to the hydroxy moieties of neighbouring host molecules, giving rise to hydrogen bonded ribbons of alternating host and guest molecules running parallel to [1 −1 0]. The second dioxane molecule, guest B, is not hydrogen bonded. The

Table 6 Fractional atomic coordinates ($\times 10^4$) with esds in parentheses for compound **5**

Atom	*x*/*a*	*y*/*b*	*z*/*c*
C(1)	3 159(4)	10 307(5)	7 447(4)
O(1)	3 560(3)	9 096(4)	6 432(3)
H(1)	2 839(54)	8 034(42)	6 287(46)
C(2)	3 968(5)	10 184(5)	8 577(4)
C(3)	4 625(5)	10 066(6)	9 485(4)
C(11)	1 279(4)	10 020(6)	7 434(4)
C(12)	336(5)	10 481(6)	6 621(4)
H(12)	884(5)	11 065(6)	6 096(4)
C(13)	−1 366(5)	10 134(6)	6 533(5)
H(13)	−2 034(5)	10 474(6)	5 942(5)
C(14)	−2 133(5)	9 339(6)	7 244(5)
H(14)	−3 359(5)	9 095(6)	7 176(5)
C(15)	−1 205(6)	8 871(7)	8 049(5)
H(15)	−1 758(6)	8 284(7)	8 572(5)
C(16)	490(5)	9 203(6)	8 138(5)
H(16)	1 153(5)	8 863(6)	8 731(5)
C(21)	3 847(5)	12 027(5)	7 368(4)
C(22)	4 490(5)	12 185(6)	6 342(4)
H(22)	4 555(5)	11 169(6)	5 654(4)
C(23)	5 044(6)	13 739(8)	6 269(6)
H(23)	5 474(6)	13 848(8)	5 515(6)
C(24)	5 008(7)	15 140(8)	7 228(7)
H(24)	5 432(7)	16 266(8)	7 177(7)
C(25)	4 375(7)	14 990(7)	8 262(6)
H(25)	4 343(7)	16 011(7)	8 957(6)
C(26)	3 811(6)	13 450(6)	8 329(5)
H(26)	3 366(6)	13 345(6)	9 078(5)
O(1AG)	8 445(4)	14 012(5)	4 540(3)
C(1AG)	9 119(8)	15 298(10)	4 072(7)
C(2AG)	10 863(8)	15 628(10)	4 229(6)
O(1GB)	316(20)	15 509(20)	8 985(16)
O(1BG)	−877(8)	15 894(8)	9 474(6)
C(1GB)	−847(11)	16 564(9)	10 139(8)
C(2GB)	−1 111(10)	14 256(9)	8 938(6)

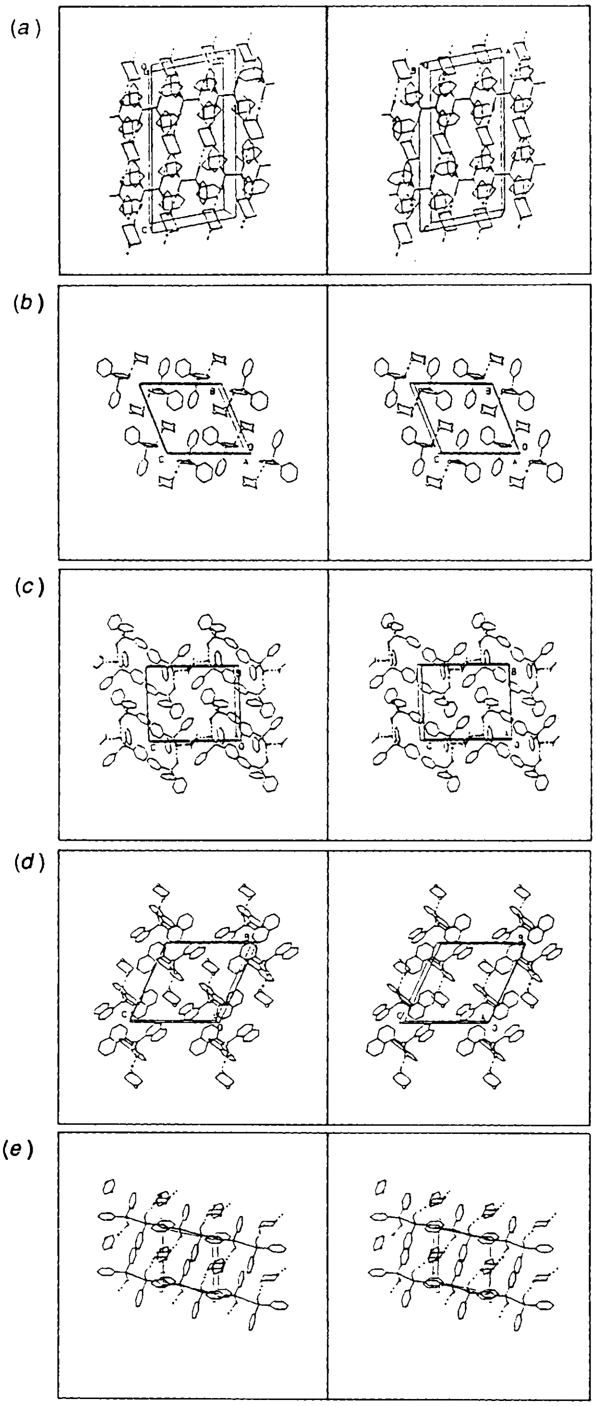


Fig. 2 Packing diagrams of compounds **1**–**5**. Hydrogen bonds are shown by dotted lines.

Table 7 Hydrogen bonding

Compound	Atom	O···O/Å	O–H/Å	O–H···O/°
1	O(1)···O(1G)	2.865(4)	1.05(4)	120.1(2.8)
2	O(1)···O(1G)	2.839(3)	0.95(2)	169.0(2.3)
3	O(2)···O(1)	2.789(2)	0.94(3)	164.7(4.2)
	O(1)···O(1G)	2.703(2)	0.92(3)	165.6(2.6)
4	O(1)···O(1G)	2.736(3)	0.90(3)	169.7(2.3)
5	O(1)···O(1G)	2.755(3)	0.97(4)	159.5(4.3)

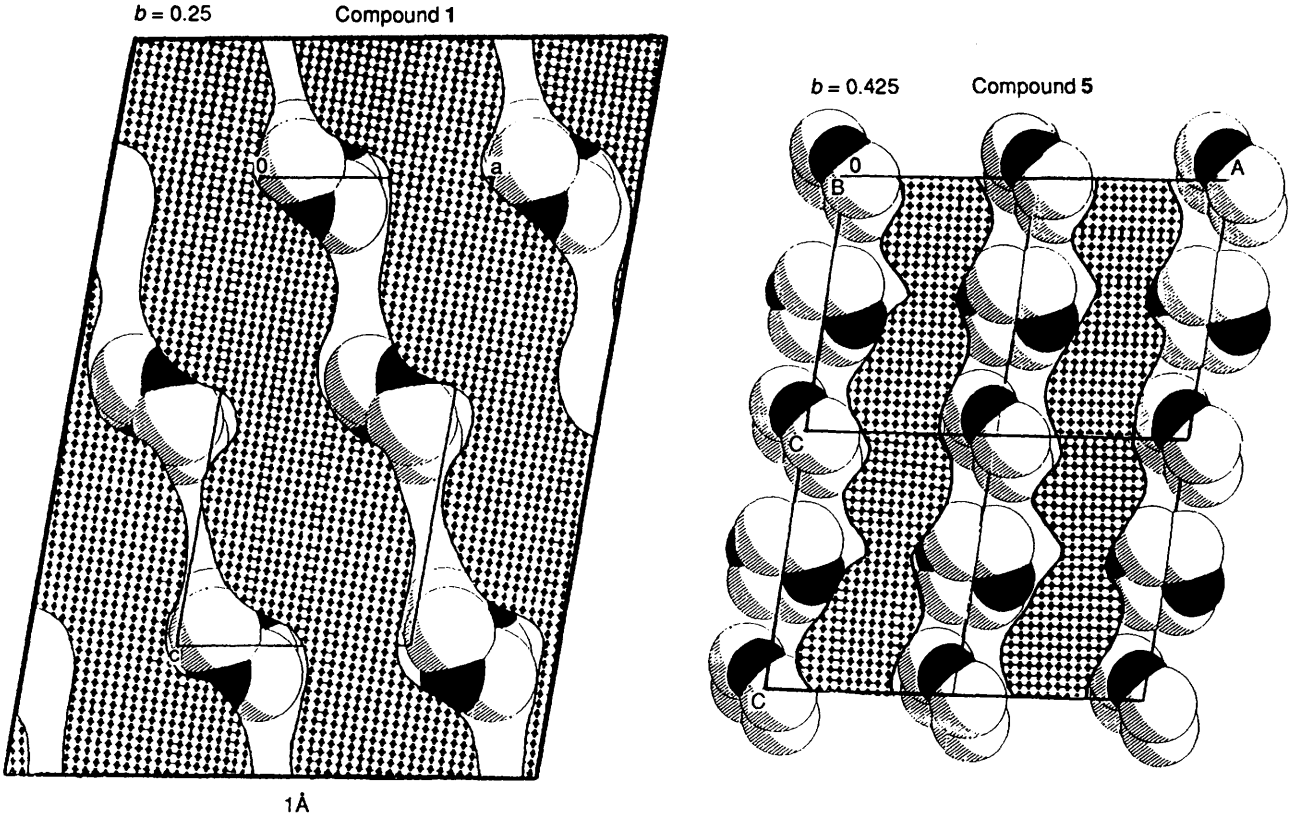


Fig. 3 OPEC mapped channels of (*a*) compound **1**, and (*b*) compound **5**. Space occupied by host atoms is shaded. Guest molecules are drawn with van der Waals radii, and oxygen atoms are shaded for clarity.

Table 8 Thermal analysis

Compound	H:G	TG weight loss (%) Calc.	TG weight loss (%) Obs.	ΔH/kJ mol^{-1}	U_{min}/kJ mol^{-1}
1	1:1	19.4	19.9	30.5	−75.1
2	1:1	25.3	23.9	49.4	−77.6
3	1:0.25	7.4	6.3	58.4	−87.3
4	1:1	17.1	16.8	58.2	−96.9
5	1:2	29.8	30.0	70.3	−93.2

packing is shown in Fig. 2(*e*), in which guest B is shaded, for clarity.

The topology of these compounds fall into two categories. **2**, **3** and **4** entrap the guest in pockets and can thus be classified as aediculates,[1] while **1** and **5** are tubulates, with the dioxane molecules lying in channels. These were mapped using the program OPEC[17] and are shown in Fig. 3. In **1** the channel has an hour-glass shape with approximately circular constrictions of *ca.* 2 Å, while in **5** the channel constrictions are less severe and measure *ca.* 4 Å.

Thermal Analysis.—Fig. 4 shows the DSC and TG traces for **1**–**5** and the results of the thermal analysis are summarized in Table 8. There is close agreement between the calculated and observed weight losses of the TG for all five compounds, thus confirming their host:guest ratios. The DSC curves of **1**–**4** are characterised by an initial endotherm corresponding to the guest release, followed by the second, sharper, endotherm due to the melting of the host compound. **5** however, displays only a single endotherm, with an onset temperature of 105 °C, which corresponds to the release of the guest with a concomitant dissolution of the host compound. This has been confirmed by visual observation of the decomposition. Crushed crystals of **5** were observed on a Linkam TH600 hotstage set on a Nikon SMZ-10 stereo microscope. The clear crystals, when heated at approximately 20 °C min^{-1}, started to melt at 112 °C. Small crystallites that remained in the melt were also liquid by 136 °C. The reason that **5** behaves differently from the other compounds is unclear, but we note that with a host:guest ratio of 1:2 it is considerably richer in guest than the others.

An important parameter to be considered in inclusion compounds is the energy of the structure as manifested by the host–guest interactions. These are of two kinds, van der Waals forces and hydrogen bonds. The potential energy environment of the guest molecules in the lattice made up of host molecules was evaluated using the method of atom–atom potentials. The program HEENY uses empirical atom pair potential curves to evaluate non-bonded van der Waals interactions. The coefficients of the atom–atom potentials are of the form given in eqn. (1) where r is the distance between any pair of atoms (in Å)

$$V(r) = a\exp[(-br)/r^{d} - c/r^{6}] \qquad (1)$$

and the coefficients a, b, c and d are those given by Giglio[18] and recently reviewed by Pertsin and Kitaigorodsky.[19] In addition, we have incorporated a hydrogen bonding potential into our calculations. This was a simplified version of that used by Vedani and Dunitz,[20] using the potential of eqn. (2) where θ is the donor–H $\cdots$ acceptor angle, which was allowed to scale

$$V_{\text{H-bond}} = (A/R^{12} - C/R^{10})\cos^{2}\theta \qquad (2)$$

the interaction with $\cos^2\theta$ for $90 \leqslant \theta \leqslant 180°$. R is the distance between the hydrogen and the acceptor. At $\theta = 180°$, the constants A and C are related to the well depth V_{min} and the equilibrium distance R_0 by $A = -5R_0^{12}\ V_{\text{min}}$ and $C = -6\ R_0^{10}\ V_{\text{min}}$. The program employed a mixing scheme

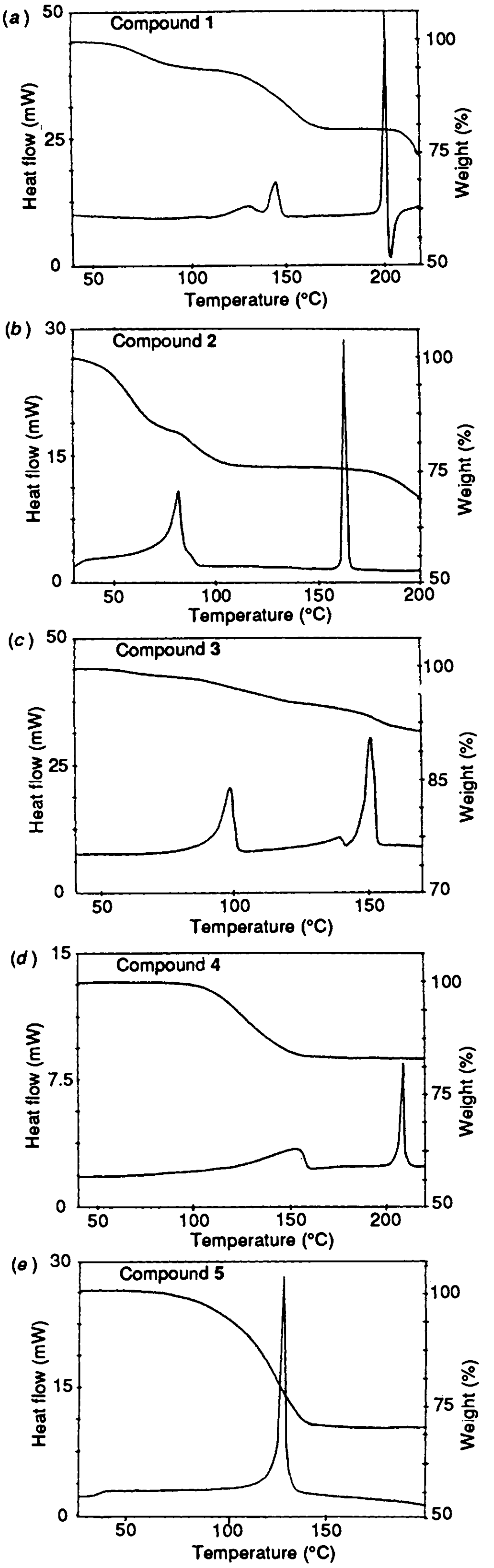


Fig. 4 Thermal analysis curves (TG and DSC) for compounds **1**–**5**

[eqn. (3)] so that the full non-bonded potential, V_{normal}, is

$$V_{\text{total}} = V_{\text{H-bond}} + (1 - \lambda)V_{\text{normal}};\ \lambda = \cos^2 \theta \quad (3)$$

progressively added as the angle deviates from the ideal hydrogen-bonding geometry.

For each compound, the guest molecule was completely surrounded by host molecules. The positions of the latter were held constant while the guest molecule was allowed to find its minimum energy environment by incremental translations and rotations. The final positions of the guest molecules were close to those obtained by the X-ray structural analyses. The minimum potential energies thus calculated are presented in Table 8, which also lists the enthalpies of the guest release reactions. The results of the thermal analysis bear comment. In a previous publication[5] we suggested that the functions $T_{\text{on}} - T_{\text{b}}$ or $T_{\text{on}}/T_{\text{b}}$, ($T_{\text{on}}$ = onset temperature and T_{b} = normal boiling point) may be useful parameters of compound stability. However, in our case the endotherms corresponding to the guest release reaction are never sharp, but are characterised by long initial tails which precluded a sensible definition of onset temperatures. We can see, however, that for **1**–**4**, there is a qualitative correlation between the minimum energy and the enthalpy of the guest release reaction, and we can infer the following stability pattern.

more stable ΔH $4 \approx 3 > 2 > 1$ *least stable*
U_{min} $4 > 3 > 2 > 1$

We did not include **5** in this comparison because its mode of decomposition is different from those of the other compounds.

References

1 E. Weber and H. P. Josel, *J. Incl. Phenom.*, 1983, **1**, 79.
2 F. Toda, *Molecular Inclusion and Molecular Recognition—Clathrates I*; *Topics in Current Chemistry Vol. 140*, Springer-Verlag, Berlin, Heidelberg, 1987, p. 43.
3 F. Toda, *Molecular Inclusion and Molecular Recognition—Clathrates II*; *Topics in Current Chemistry Vol. 149*, Springer-Verlag, Berlin, Heidelberg, 1988, p. 211.
4 E. Weber, N. Dörpinghaus and I. Csöregh, *J. Chem. Soc., Perkin Trans. 2*, 1990, 2167.
5 M. R. Caira, L. R. Nassimbeni, M. L. Niven, W.-D. Schubert, E. Weber and N. Dörpinghaus, *J. Chem. Soc., Perkin Trans. 2*, 1990, 2129.
6 D. R. Bond, M. R. Caira, G. A. Harvey, L. R. Nassimbeni and F. Toda, *Acta Crystallogr., Sect. B*, 1990, **46**, 771.
7 D. R. Bond, L. R. Nassimbeni and F. Toda, *J. Incl. Phenom. and Mol. Recog. in Chem.*, 1989, **7**, 623.
8 D. R. Bond, L. R. Nassimbeni and F. Toda, *J. Crystallogr. Spectrosc. Res.*, 1989, **19**, 847.
9 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta. Crystallogr., Sect. A*, 1968, **24**, 351.
10 *Program Decay*, Structure Determination Package, Enraf–Nonius, Delft, Holland, 1982.
11 G. M. Sheldrick, *SHELXS-86 Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985, p. 175.
12 G. M. Sheldrick, *SHELX76: A Program for Crystal Structure Determination*, University of Cambridge, England, 1976.
13 *The Hydrogen Bond II. Structure and Spectroscopy*, eds. P. Schuster, G. Zundel and C. Sanderfy, North-Holland Publishing Co., Amsterdam, 1976, ch. 8.
14 D. R. Bond, L. Johnson, L. R. Nassimbeni and F. Toda, *J. Solid State Chem.*, 1991, **92**, 68.
15 S. A. Bourne, L. R. Nassimbeni and F. Toda, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1335.
16 S. A. Bourne, L. R. Nassimbeni, K. Skobridis and E. Weber, *J. Chem. Soc., Chem. Commun.*, 1991, 282.
17 A. Gavezzotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220.
18 E. Giglio, *Nature*, 1969, **222**, 339.
19 A. J. Pertsin and A. I. Kitaigorodsky, *The Atom–Atom Potential Method, Chemical Physics 43*, Springer-Verlag, Berlin, Heidelberg, 1987, chapter 3.
20 A. Vedani and J. D. Dunitz, *J. Am. Chem. Soc.*, 1985, **107**, 7653.

Paper 1/03231C
Received 28*th June* 1991
Accepted 18*th July* 1991