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INCLUSION COMPOUNDS OF HYDROXY HOSTS. 6. STRUCTURES AND THERMAL ANALYSIS OF 1,2,3,4,5-PENTAPHENYLCYCLOPENTA-2,4-DIEN-1-OL WITH METHANOL AND ETHANOL

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The crystal and molecular structures of the methanol and ethanol inclusion compounds of 1,2,3,4,5-pentaphenylcyclopenta-2,4-dien-1-ol have been elucidated. (I) $C_{35}H_{26}O \cdot CH_4O$ is triclinic, $P\bar{1}$, $a = 10{\cdot}377$, $b = 10{\cdot}778$, $c = 14{\cdot}537$ Å, $\alpha = 102{\cdot}66(2)$, $\beta = 90{\cdot}26(2)$, $\gamma = 117.33(2)^\circ$, $V = 1398(15)$ Å^3, $Z = 2$; (II) $(C_{35}H_{26}O)_2 \cdot C_2H_6O$ is triclinic, $P\bar{1}$, $a = 10{\cdot}901(2)$, $b = 13{\cdot}498(2)$, $c = 19{\cdot}037(3)$Å, $\alpha = 101{\cdot}88(1)$, $\beta = 93{\cdot}76(1)$, $\gamma = 90{\cdot}84(1)$, $V = 2734(8)$ Å^3, $Z = 2$. The structures were refined to final residuals of 0·127 for 2207 reflections and 0·073 for 4720 reflections. Thermal analysis of the complexes confirmed the crystallographic results and gave information about their thermal decompositions.

INTRODUCTION

Hydroxy-containing compounds, particularly those with a rigid structure, have been shown to act as excellent hosts in inclusion compounds. They have been shown to separate isomers and to resolve racemates[1]. Some hydroxy hosts include guests in topologically favourable positions and thus control their reactivity.[2]

We have studied the clathrating behaviour of a number of host compounds which contain one or two hydroxyl moieties. Thus, we have shown that 1,1,2,2-tetraphenylethane-1,2-diol forms inclusion compounds with various lutidines and have demonstrated preferential inclusion of 3,5-lutidine over 2,6-lutidine.[3] We have also reported the structure of the related host compound 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol in its non-porous α-form and the kinetics of the complexation reaction with acetone vapour.[4] In a recent paper, we compared the structures of a series of hydroxy hosts with the same guest, 1,4-dioxane, and discussed their stabilities.[5]

We have been studying the inclusion behaviour of the host 1,2,3,4,5-pentaphenylcyclopenta-2,4-dien-1-ol and have recently published the structures of this host in its non-porous α-phase and its inclusion compounds with water and dimethyl sulphoxide.[6] We now present the structures of the methanol and ethanol inclusion compounds of this host.

EXPERIMENTAL

The preparation of the host compound has been described.[6] The inclusion compounds of methanol (**I**) and ethanol (**II**) were obtained by making a concentrated solution of the host in the alcohol and allowing it to evaporate slowly at room temperature.

X-ray analyses. Suitable single crystals were mounted in Lindemann tubes with mother liquor to prevent the desorption of the guest. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation ($\lambda = 0{\cdot}7107$ Å). Accurate cell parameters were obtained by least-squares analysis of the setting angles of 24 reflections in the range $16 < \theta < 17^\circ$. Data were collected with variable scan width and scan speed, using the $\omega - 2\theta$ scan mode. Three reference reflections were monitored periodically for intensity and orientation control. The data were corrected for Lorentz polarization effects. Compound **I** decayed by 48% during data collection, hence a linear decay correction was applied to these data. Further details of the crystals and of data collection are given in Table 1.

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Table 1. Crystal data, details of data collection and final refinement

	Compound	
Parameter	I	II
Molecular formula	$C_{35}H_{26}O \cdot CH_4O$	$(C_{35}H_{26}O)_2 \cdot C_2H_6O$
Mass (g mol^{-1})	470·442	971·253
Space group	$P\bar{1}$	$P\bar{1}$
a(Å)	10·377(2)	10·901(2)
b(Å)	10·778(3)	13·498(2)
c(Å)	14·537(4)	19·037(3)
α(°)	102·66(2)	101·88(1)
β(°)	90·26(2)	93·76(1)
γ(°)	117·33(2)	90·84(1)
Volume (Å)	1398(15)	2734(8)
Z	2	2
F(000)	524	1028
μ(Mo Kα) (cm^{-1})	0·38	0·37
Crystal dimensions (mm)	0·25 × 0·25 × 0·31	0·28 × 0·31 × 0·34
D_c (g cm^{-3})	1·21	1·18
D_m (g cm^{-3})	1·20	1·16
θ range scanned (°)	1–25	1–23
Range of h,k,l	±12, ±12, 17	±12, ±14, 20
Number of reflections collected	5060	7969
Number of reflections with $I_{rel} > 2\sigma I_{rel}$	2207	4720
Number of parameters	342	678
Max./min. residual electron density (e Å^{-3})	0·23/−0·21	0·53/−0·53
Max. LS shift to e.s.d.	0·17	0·24
R	0·127	0·073
R_w	0·127	0·073
w	1	1
S	2·19	1·56

Structure solution and refinement. The structures were solved by direct methods using SHELXS-86[7] and refined using SHELX76.[8] In the final refinement of **I** and **II**, the non-hydrogen atoms of the host were treated anisotropically. The phenyl hydrogens were placed in calculated positions and linked to a common isotropic temperature factor. The hydroxyl hydrogens were located in difference maps and constrained to ride at 1·00(2) Å from the hydroxyl oxygen. The two guests were modelled isotropically. No hydrogens were placed on the methanol carbon but the ethanolic hydrogens were placed in calculated positions and linked to a common temperature factor. The hydroxyl hydrogens of the guests were modelled as described for those of the host. Further details of the structure refinements are given in Table 1.

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 weights were *ca* 4–5 mg. The temperature range was 30–220 °C at 10 °C min^{-1}. The purge gas was dry nitrogen at a flow-rate of 40 ml min^{-1}.

RESULTS

Fractional coordinates of **I** and **II** are given in Tables 2 and 3. A perspective view of the host, with atomic labelling, is shown in Figure 1. A comparison of the three host molecules shows that the molecular structure is rather rigid. The double bonds in the cyclopentadiene ring are easily identified as C(2)—C(3) and C(4)—C(5) as these bond lengths are between 1·30(1) and 1·361(7) Å. Other bonds in this ring are between 1·508(7) and 1·54(1) Å. The bond joining the cyclopentadiene ring to the hydroxyl oxygen is 1·430(6)–1·44(2) Å. Bonds from the cyclopentadiene ring to the phenyl rings are in the range 1·453(8)–1·62(2) Å and the phenyl C—C bond lengths are between 1·36(3) and 1·41(7) Å. Bond angles differ by less than 5% for similarly defined angles in the three molecules.

The guest molecules in both structures were not as well defined as the hosts. Their bond lengths were generally poorer, with higher standard deviations, owing to the relatively high thermal motion of the guest molecules. This is a well known effect in clathrate structures, particularly when the guest molecules are highly volatile. The oxygen atoms of the guests, in both struc-

Table 2. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$) with e.s.d.s in parentheses for compound **I**

Atom	x/a	y/b	z/c	$U_{\text{iso}}/U_{\text{equiv}}$(*)
O(1)	828(8)	1263(11)	4151(6)	68(5)*
C(1)	772(11)	1305(14)	3168(8)	57(6)*
C(2)	1984(11)	1141(13)	2671(8)	53(6)*
C(3)	1474(10)	21(11)	1954(8)	43(5)*
C(4)	−201(11)	−718(13)	1920(8)	49(6)*
C(5)	−565(11)	26(13)	2605(9)	53(6)*
C(11)	836(11)	2837(14)	3159(8)	49(5)*
C(12)	691(14)	3040(17)	2243(10)	74(8)*
C(13)	701(17)	4349(20)	2217(12)	90(11)*
C(14)	776(18)	5289(26)	3000(15)	126(17)*
C(15)	961(16)	5131(18)	3907(12)	95(9)*
C(16)	926(13)	3738(17)	3904(9)	73(9)*
C(21)	3583(12)	2271(14)	2979(8)	59(6)*
C(22)	4156(13)	2902(16)	3925(9)	85(8)*
C(23)	5600(14)	3919(18)	4175(11)	108(10)*
C(24)	6496(14)	4285(18)	3480(12)	102(9)*
C(25)	5956(15)	3699(19)	2552(11)	119(11)*
C(26)	4501(13)	2684(18)	2265(10)	100(10)*
C(31)	2238(11)	−523(12)	1280(8)	52(6)*
C(32)	1935(12)	−840(13)	305(9)	60(6)*
C(33)	2646(14)	−1391(14)	−315(9)	70(6)*
C(34)	3735(15)	−1670(15)	13(13)	87(9)*
C(35)	4032(13)	−1366(15)	989(12)	79(9)*
C(36)	3327(11)	−822(14)	1623(10)	64(7)*
C(41)	−1098(11)	−2065(13)	1219(8)	51(5)*
C(42)	−870(11)	−3265(13)	1044(9)	58(7)*
C(43)	−1703(14)	−4534(18)	388(11)	92(9)*
C(44)	−2895(14)	−4645(17)	−160(11)	87(8)*
C(45)	−3152(14)	−3441(18)	26(11)	83(9)*
C(46)	−2345(11)	−2225(15)	674(9)	66(7)*
C(51)	−2089(12)	−441(16)	2951(9)	68(8)*
C(52)	−2836(14)	−1859(18)	3035(11)	94(10)*
C(53)	−4204(15)	−2286(22)	3378(12)	116(13)*
C(54)	−4732(16)	−1307(25)	3620(13)	119(13)*
C(55)	−4005(15)	104(23)	3547(12)	108(12)*
C(56)	−2625(13)	518(17)	3175(10)	79(9)*
O(1G)	665(15)	−1289(15)	4310(9)	128(4)
C(1G)	1964(26)	−1016(25)	4407(16)	152(8)

$U^* = e^{-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)}$

Table 3. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$) with e.s.d.s in parentheses for compound **II**

Atom	x/a	y/b	z/c	$U_{\text{iso}}/U_{\text{equiv}}$(*)
O(11)	4003(4)	1038(3)	4093(2)	59(2)*
C(11)	4725(5)	1932(4)	4406(3)	51(2)*
C(12)	5662(5)	1786(4)	5014(3)	52(2)*
C(13)	6785(5)	1938(4)	4827(3)	52(2)*
C(14)	6740(5)	2217(4)	4099(3)	50(2)*
C(15)	5536(5)	2209(4)	3856(3)	50(2)*
C(111)	3829(5)	2776(4)	4672(3)	51(2)*
C(112)	2606(6)	2667(5)	4461(3)	74(3)*
C(113)	1811(6)	3466(6)	4664(4)	89(4)*
C(114)	2301(7)	4375(5)	5069(4)	84(4)*
C(115)	3523(7)	4477(5)	5285(3)	79(3)*
C(116)	4300(6)	3679(4)	5089(3)	69(3)*
C(121)	5238(5)	1558(4)	5689(3)	54(2)*
C(122)	5915(6)	1896(5)	6342(3)	67(3)*

continued

Table 3. (*Continued*)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{\mathrm{iso}}/U_{\mathrm{equiv}}$(*)
C(123)	5511(7)	1669(5)	6968(3)	78(3)*
C(124)	4463(7)	1089(5)	6953(4)	78(3)*
C(125)	3781(7)	770(5)	6312(4)	80(3)*
C(126)	4168(6)	1007(4)	5691(3)	67(3)*
C(131)	7991(5)	1893(5)	5228(3)	60(2)*
C(132)	8381(6)	981(5)	5380(3)	74(3)*
C(133)	9536(8)	930(8)	5723(4)	102(4)*
C(134)	10275(8)	1767(10)	5915(4)	117(5)*
C(135)	9906(8)	2676(8)	5787(4)	109(4)*
C(136)	8754(6)	2734(6)	5443(3)	84(3)*
C(141)	7812(5)	2383(4)	3718(3)	52(2)*
C(142)	8756(5)	1689(5)	3619(3)	65(3)*
C(143)	9741(6)	1849(6)	3250(4)	81(3)*
C(144)	9879(6)	2720(7)	2980(4)	87(3)*
C(145)	8949(7)	3415(6)	3072(4)	81(3)*
C(146)	7946(6)	3244(4)	3433(3)	63(2)*
C(151)	5046(5)	2319(4)	3138(3)	55(2)*
C(152)	4170(6)	3019(4)	3036(3)	70(3)*
C(153)	3702(7)	3065(6)	2353(4)	90(4)*
C(154)	4097(7)	2431(6)	1760(4)	90(3)*
C(155)	4945(6)	1731(6)	1848(3)	84(3)*
C(156)	5428(6)	1671(5)	2531(3)	70(3)*
O(21)	−1289(4)	5684(3)	620(2)	62(2)*
C(21)	−1516(5)	6500(4)	1207(3)	51(2)*
C(22)	−2250(5)	7346(4)	960(3)	48(2)*
C(23)	−1578(5)	8210(4)	1145(3)	48(2)*
C(24)	−357(5)	8025(4)	1504(3)	47(2)*
C(25)	−333(5)	7036(4)	1547(3)	48(2)*
C(211)	−2233(5)	6074(4)	1736(3)	47(2)*
C(212)	−2665(5)	5083(4)	1603(3)	65(3)*
C(213)	−3339(6)	4727(5)	2093(4)	82(3)*
C(214)	−3631(6)	5358(6)	2721(4)	80(3)*
C(215)	−3194(6)	6348(5)	2859(4)	75(3)*
C(216)	−2520(5)	6705(4)	2376(3)	63(3)*
C(221)	−3512(5)	7185(4)	651(3)	52(2)*
C(222)	−4437(5)	7835(5)	927(3)	69(3)*
C(223)	−5637(6)	7681(5)	649(4)	80(3)*
C(224)	−5960(7)	6866(6)	94(4)	91(4)*
C(225)	−5060(7)	6232(6)	−181(4)	86(3)*
C(226)	−3872(6)	6372(4)	93(3)	72(3)*
C(231)	−1942(5)	9219(4)	1032(3)	51(2)*
C(232)	−2462(6)	9345(5)	373(3)	67(2)*
C(233)	−2798(7)	10289(5)	266(4)	84(3)*
C(234)	−2582(7)	11124(5)	820(4)	92(3)*
C(235)	−2076(6)	11015(5)	1470(4)	79(3)*
C(236)	−1738(5)	10078(4)	1581(3)	63(2)*
C(241)	609(5)	8805(4)	1769(3)	50(2)*
C(242)	1097(5)	8947(4)	2481(3)	57(2)*
C(243)	1969(5)	9704(4)	2750(3)	64(2)*
C(244)	2368(6)	10323(5)	2326(4)	68(2)*
C(245)	1907(6)	10184(5)	1619(3)	71(3)*
C(246)	1032(5)	9430(4)	1344(3)	60(2)*
C(251)	736(5)	6512(4)	1805(3)	58(2)*
C(252)	664(6)	6046(5)	2381(4)	79(3)*
C(253)	1720(8)	5616(6)	2642(4)	98(4)*
C(254)	2803(8)	5642(6)	2311(6)	107(4)*
C(255)	2852(7)	6062(6)	1733(6)	112(5)*
C(256)	1805(6)	6491(5)	1473(4)	89(3)*
O(1)	−241(5)	3819(4)	354(3)	111(2)
C(1)	178(12)	3416(10)	980(7)	194(5)
C(2)	643(12)	2583(9)	873(7)	216(6)

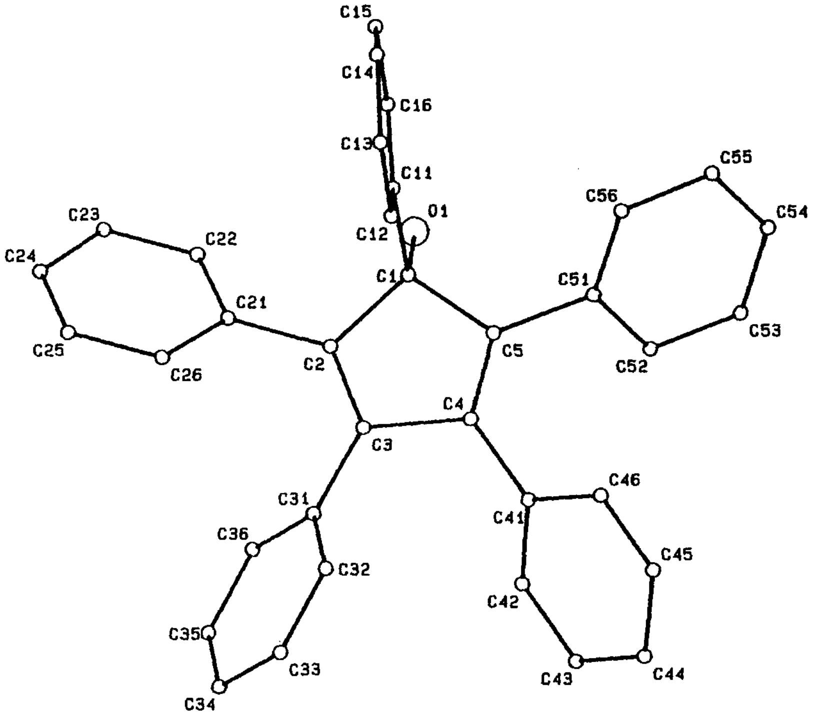

Figure 1. Perspective view of the host, showing the atomic nomenclature

tures, are involved in hydrogen bonding and were thus correctly identified.

The packing of structure **I**, viewed along [100], is shown in Figure 2. A cyclic system of hydrogen bonds, involving two hosts and two guests, is present. O···O distances are 2·73(2) and 2·74(2) Å. The cell parameters and packing of this structure are very close to those found in the host · H_2O structure.[6]

A projection down [100] of structure **II** is shown in Figure 3. Although a similar cyclic hydrogen bonding pattern between two hosts and two guests is observed [O···O distances are 2·745(7) and 2·749(7) Å], the packing of this structure is made more complex by the presence of an additional host molecule in the asymmetric unit. This molecule is not involved in hydrogen bonding.

Thermal analysis curves of **I** and **II** are shown in Figures 4 and 5. TG yielded a weight loss of 6·06% for **I**, which is close to the calculated value of 6·47%. For **II**, the measured weight loss of 4·90% also agrees well with the calculated value of 4·67%. TG thus confirmed the stoichiometries found crystallographically for these compounds.

The DSC of **II** was straightforward. An initial skewed endotherm between 106 and 137 °C corresponds to the weight loss in the TG and is caused by the desorption of the ethanol from the crystal. A second, sharp, endotherm occurs at onset 178 °C and is indicative of the melting of the host.

The DSC of compound **I** has an unusual feature. The first endotherm, marked A, occurring between 112 and 130 °C is due to the loss of the methanol. This reasoning is confirmed by the weight loss in the TG which occurs over the same temperature range. This is followed almost immediately by an exotherm (labelled B) between 135 and 152 °C. Finally, the host melts at 178 °C (endotherm C), as expected. An exotherm as seen here may imply the rearrangement of the compound to a more stable form. This heating process was followed visually on a Linkam TH600 hot stage set on a Nikon SMZ-10 stereo microscope. The clear, yellow crystals when heated at *ca* 10 °C min^{-1} showed the appearance of bubbles at 110–125 °C. This was vigorous and by 128 °C the crystals appeared to have melted. Between 140 and 150 °C, fine yellow needles appeared in the liquid and these finally melted at 178 °C. Hence it seems probable that the exotherm B in Figure 4 is caused by the rearrangement of the host molecules that remain once the methanol has been lost.

The objective of carrying out thermal analysis in these compounds is to reconcile thermodynamics with structure. Thus it should be possible, in principle, to

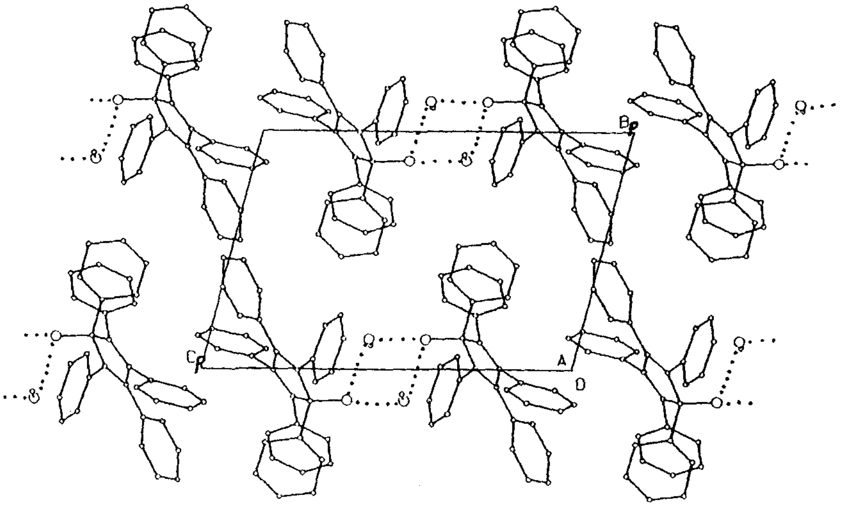

Figure 2. Projection of compound **I** down [100]. Hydrogen bonds are shown by dotted lines

find a relationship between the onset temperature characterizing the guest-release reaction and the strength of the hydrogen bonding interactions. For inclusion compounds of a given host with different guests, the onset temperatures, T_{on}, are a function of both the host–guest interactions and the intrinsic physical properties of the guest. In particular, the normal boiling point, T_b, of the guest is important, and we suggest that the temperature difference, $T_{on} - T_b$ is a measure of the thermal stability of the inclusion compound. For **I** and **II**, these temperature differences are +52 and +27 °C, respectively, which are considerably higher than the value for the dimethyl sulphoxide[6] inclusion compound, for which $T_{on} - T_b = -74$ °C. This shows that the methanol and ethanol guests are tightly held by the host compound. Such high positive temperature differences are unusual but not unknown, and Weber and Czugler[9] list three inclusion compounds of the host 1,1′-binaphthyl-2,2′-dicarboxylic acid which exibit $T_{on} - T_b > 50$ °C.

Attempts to form inclusion compounds with higher alcohols, acetonitrile and methyl ethyl ketone all failed.

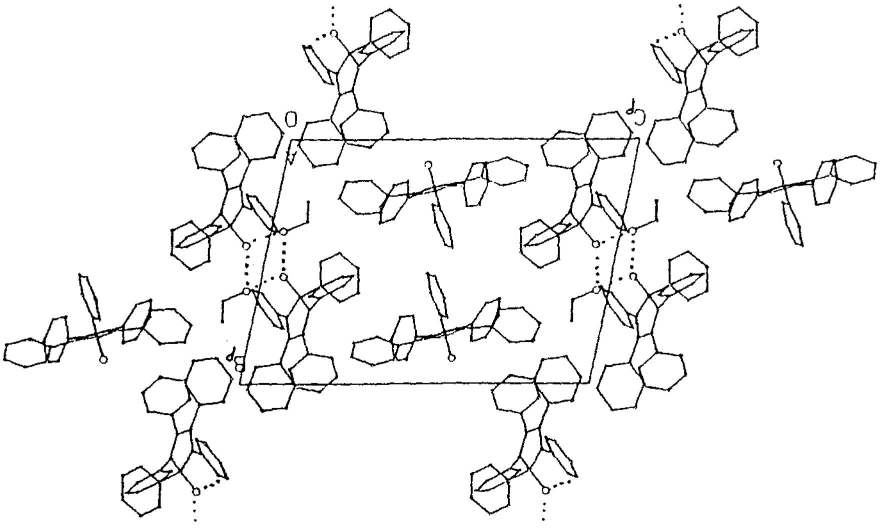

Figure 3. Projection of compound **II** down [100]. Hydrogen bonds are shown by dotted lines

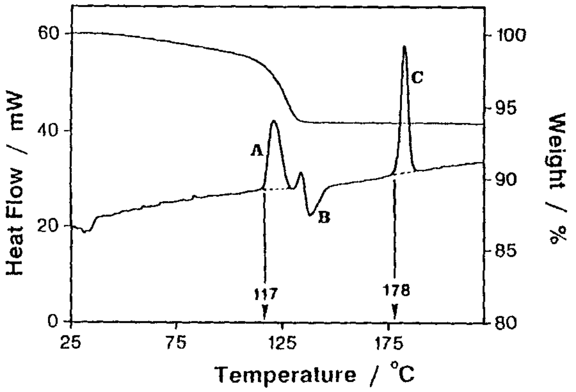

Figure 4. Thermal analysis curves of compound **I**

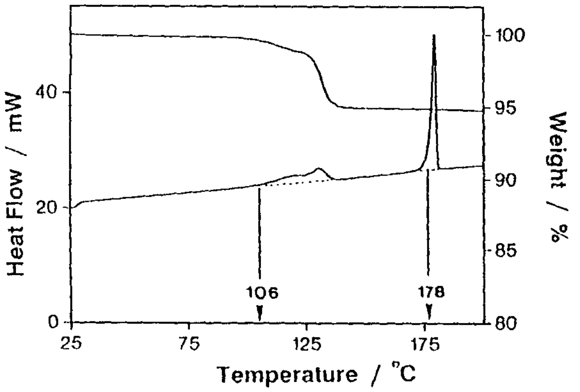

Figure 5. Thermal analysis curves of compound **II**

Hence it seems that the bulkiness of the phenyl groups surrounding the hydroxyl moiety of this host prevents the close approach of many of the guest molecules which might be expected to be included.

Supplementary material

Tables of bond lengths and angles, anisotropic temperature factors and structure factors are available from the author on request.

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