Complexation with Hydroxy Host Compounds. Part 1. Structures and Thermal Analysis of a Suberol-derived Host and its Host–Guest Complexes with Dioxane and Acetone

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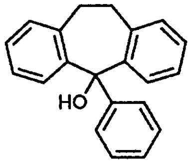
The title host compound, 10,11-dihydro-5-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol **1**, crystallizes in the non-porous α-phase without hydrogen bonding. The β-phases of its dioxane **2** and acetone **3** complexes are stabilized by hydrogen bonds between host and guest. Thermal analysis of the two inclusion compounds gives qualitative correlation with their structures and a relative measure of their stabilities.

To date, many organic hosts which form crystalline inclusion compounds with other organic guests are known.[1] Some are true clathrates[2] in which the host-guest aggregate is stabilized by steric factors alone. Relevant examples are the clathrates formed between 9,9′-bianthryl and benzene, 1:1[3a] and between 1,1,2,2-tetraphenylethane-1,2-diol and *p*-chlorotoluene, 1:0.5.[3b] More ubiquitous are coordinatoclathrates[2] so named because they demonstrate a certain degree of coordinative participation. Frequently, it is the hydrogen bond which forms the link between host and guest.[4] With these inclusion compounds or complexes, high selectivity of a given host to a particular guest, although rare, is also known.[5]



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2 = **1** • dioxane, 2:1
3 = **1** • acetone, 1:1

Our preliminary investigations of the host 10,11-dihydro-5-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol **1** show that it has clathrating ability for a great variety of guests [with: MeCN (2:1), DMF (1:1), DMSO (1:1), THF (3:1), morpholine (1:1), piperidine (1:1) and pyridine (1:1)][6] and we are currently working on the crystallographic and thermal analyses of some twenty of these compounds with a view to understanding selectivity and stability. Owing to the asymmetry of the host we also intend to investigate the possibilities of its inclusion compounds having non-linear optical properties.[7]

We report here our findings for the host **1** alone, and its dioxane **2** and acetone **3** complexes.

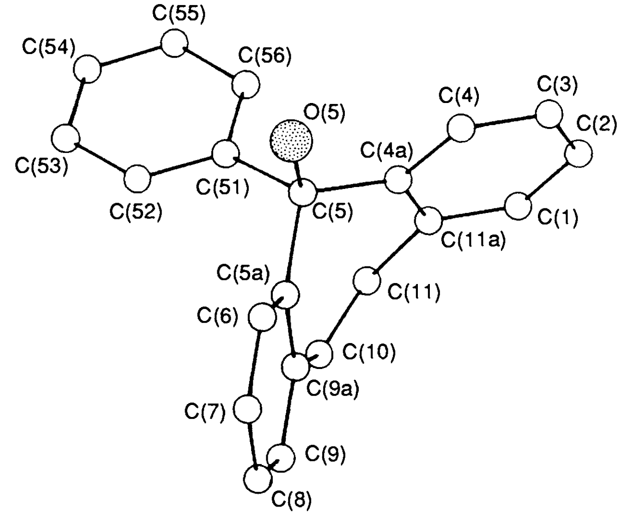

Fig. 1 A perspective view of a single host molecule $C_{21}H_{18}O$, with atomic numbering

Results and Discussion

Crystal data are given in Table 1; atomic coordinates are listed in Table 2. A single host molecule **1** with atomic numbering is illustrated in Fig. 1. Selected bond lengths and angles are reported in Table 3. Complete lists of bond lengths and bond angles, fractional atomic coordinates of the calculated hydrogen atom positions and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).* For the host in the α-phase **1** (non-complexed) and in each of its β-phase complexes (**2** and **3**), most of the bond lengths and angles are similar and lie within expected ranges.[8] Interestingly, C(10)–C(11) for **1** and **2** are similar at 1.384(8) and 1.418(5) Å, respectively, but differ significantly from C(10)–C(11) in **3**, which is 1.502(6) Å. Also noteworthy is the dihedral angle C(9a)–C(10)–C(11)–C(11a) which is 21(1) and 23.3(6)° for **1** and **2** but 39.8(7)° for **3**. We believe that these differences should be explained in terms of the high temperature factors observed for C(10) and C(11) in **3** (possibly indicative of slight disorder), and by the fact that **3** is not as well determined as **1** and **2**, having greater crystal decay and higher residuals R and R_w. Hence, despite the fact that the host molecule has some degree of conformational lability, it adopts an essentially similar shape in all three structures. This is particularly interesting against the background of significantly different packing between the host and complex structures. The former has no H-bonding while the latter two have H-bonding between the host and guest resulting

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* For details, see 'Instructions for Authors' (1990), *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

Table 1 Details of crystals, data collections and final refinements

	1	**2**	**3**
Molecular formula	$C_{21}H_{18}O$	$C_{21}H_{18}O{\cdot}0.5(C_{11}H_8O_2)$	$C_{21}H_{18}O{\cdot}C_3H_6O$
M_r	286.37	330.43	344.45
Guest	—	dioxane	acetone
Host:guest	—	1:0.5	1:1
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	8.769(1)	9.626(3)	9.83(1)
b/Å	9.057(2)	8.666(2)	8.80(1)
c/Å	10.836(2)	21.308(3)	21.67(3)
α/°	74.57(2)	90	90
β/°	86.37(1)	96.05(2)	94.8(1)
γ/°	67.00(2)	90	90
V/Å^3	762.8(3)	1767.6(7)	1866
Z	2	4	4
D_c	1.25	1.24	1.23
$F(000)$	304	704	736
μ(Mo–$K\alpha$)/cm^{-1}	0.70	0.72	0.41
Crystal dimensions/mm	0.30 × 0.40 × 0.42	0.44 × 0.44 × 0.50	0.28 × 0.30 × 0.48
Range scanned (θ)/°	1–25	1–25	1–25
Range of indices	h: ±10; k: ±10; l:0,25	h: ±11; k:0,10; l:0,25	h: ±11; k:0,10; l:0,25
Crystal decay (%)	0.9	0.6	3
Scan mode		$\omega - 2\theta$	
Scan width/°ω		$(0.85 + 0.35 \tan\theta)$	
Aperture width/mm		$(1.12 + 1.05 \tan\theta)$	
Scan speed		variable, max. time 40 s	
No. reflections collected	2400	2719	2825
No. reflections observed, N (with $I_{rel} > 2\sigma I_{rel}$)	1972	2195	2184
No. parameters	203	243	246
R	0.076	0.058	0.094
R_w	0.076	0.055	0.095
w	unity	$(\sigma^2 F)^{-1}$	$(\sigma^2 F + 0.001F^2)^{-1}$
S	0.77	3.80	6.27
Max. parameter shift/esd	0.08	0.001	0.5
Max/min residual electron density/eÅ^{-3}	0.40/−0.35	0.35/−0.43	0.38/−0.44

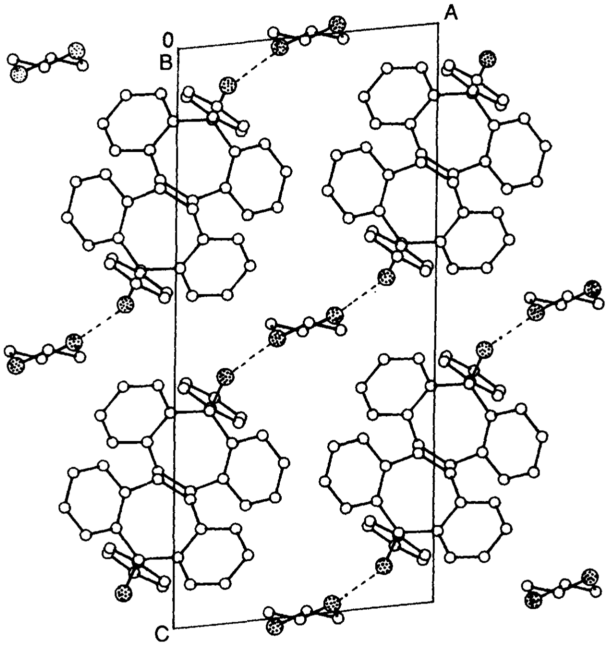

Fig. 2 Packing diagram of the dioxane complex; O atoms shaded and H-bonding represented by dotted lines

in a rearrangement of the host molecules to include the guests in channels running parallel to the b axis. Using OPEC,[9] approximate dimensions of the channel were obtained. It is at its narrowest at b = 0.5, when its a and c dimensions are 2.9 and 3.2 Å, respectively, and widens to a maximum of 4.9 and 7.6 Å in a and c, respectively, at b = 0.2. The two complex structures are similar with a single dioxane exchanged for two acetone molecules around the centre of symmetry and linking two host molecules. Fig. 2 shows the H-bonding and packing for the dioxane complex **2**. The channels are clearly illustrated in Fig. 3 which is the acetone complex **3** (host atoms drawn with Van der Waals' radii and guest molecules omitted).

The host-guest ratios of the two inclusion compounds **2** and **3** were confirmed by thermogravimetry (TG) and the enthalpy of the guest-release reaction was determined by differential scanning calorimetry (DSC). The thermograms are shown in Fig. 4, and for each compound the percentage weight loss, reported in Table 4, shows good agreement between theoretical and experimental values for the dioxane complex (difference of 1.3%) but poorer agreement for the acetone adduct (difference of 3.6%). This is due to the highly volatile nature of acetone which desorbs from the crystals the moment the latter are removed from their mother liquor. For both compounds, the TG curves show that the loss of guest molecules is a single step process accompanied by a corresponding endotherm. This is followed by a second sharper endotherm at 156.6 °C which corresponds to the m.p. of the host compound.[6]

The objective of carrying out thermal analysis on these compounds is to reconcile thermodynamics with structure. Thus it should in principle be possible to find a relation between the measured enthalpies of the guest-release reactions and the host-guest interactions as revealed by the crystal structure. In this study however the strengths of the O–H ⋯ O hydrogen

Table 2 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms of **1**–**3** (esds in parentheses)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Compound **1** $C_{21}H_{18}O$			
C(1)	3 280(6)	5 439(6)	6 235(5)
C(2)	2 965(6)	4 179(6)	7 113(6)
C(3)	2 847(6)	4 208(6)	8 383(6)
C(4)	3 046(5)	5 468(5)	8 729(4)
C(4a)	3 384(4)	6 730(5)	7 863(4)
C(5)	3 589(4)	8 078(5)	8 328(3)
C(5a)	2 166(4)	9 773(5)	7 762(4)
C(6)	1 138(5)	10 601(5)	8 582(4)
C(7)	−179(5)	12 118(6)	8 139(5)
C(8)	−487(6)	12 783(6)	6 845(5)
C(9)	520(6)	11 977(6)	6 024(5)
C(9a)	1 861(5)	10 455(5)	6 442(4)
C(10)	2 854(10)	9 720(7)	5 442(6)
C(11)	3 800(8)	8 057(7)	5 546(5)
C(11a)	3 488(6)	6 715(5)	6 566(4)
C(51)	5 312(4)	8 176(5)	8 122(3)
C(52)	5 540(5)	9 546(5)	8 220(4)
C(53)	7 102(6)	9 618(6)	8 164(4)
C(54)	8 461(5)	8 231(6)	8 018(4)
C(55)	8 252(5)	6 870(6)	7 923(5)
C(56)	6 684(5)	6 801(5)	7 971(4)
O(5)	3 439(3)	7 738(4)	9 709(3)
Compound **2** $C_{21}H_{18}O{\cdot}(0.5C_4H_8O_2)$			
C(1)	−2 381(3)	1 798(4)	1 630(2)
C(2)	−2 841(3)	829(4)	1 146(2)
C(3)	−1 973(3)	460(4)	695(2)
C(4)	−633(3)	1 084(3)	739(1)
C(4a)	−154(3)	2 058(3)	1 231(1)
C(5)	1 344(3)	2 714(3)	1 265(1)
C(5a)	2 211(3)	2 089(3)	1 857(1)
C(6)	3 377(3)	1 178(4)	1 785(2)
C(7)	4 198(3)	574(4)	2 300(2)
C(8)	3 876(3)	882(4)	2 899(2)
C(9)	2 732(3)	1 780(4)	2 978(2)
C(9a)	1 874(3)	2 386(4)	2 467(1)
C(10)	622(4)	3 274(5)	2 632(2)
C(11)	−623(3)	3 504(5)	2 225(2)
C(11a)	−1 038(3)	2 424(4)	1 688(1)
C(51)	1 368(3)	4 476(3)	1 220(1)
C(52)	2 464(3)	5 314(3)	1 518(1)
C(53)	2 547(3)	6 905(4)	1 433(2)
C(54)	1 518(3)	7 661(4)	1 048(2)
C(55)	425(3)	6 831(4)	751(2)
C(56)	343(3)	5 249(4)	834(1)
O(5)	1 923(2)	2 161(2)	708(1)
O(2)	3 896(3)	932(3)	5 148(1)
C(21)	4 873(5)	−1 580(6)	5 067(2)
C(22)	3 657(4)	−561(6)	4 887(2)
Compound **3** $C_{21}H_{18}O{\cdot}C_3H_6O$			
C(1)	2 159(4)	1 573(5)	8 355(2)
C(2)	2 550(4)	529(5)	8 818(2)
C(3)	1 671(4)	171(5)	9 246(2)
C(4)	381(4)	814(5)	9 214(2)
C(4a)	−35(4)	1 847(4)	8 748(2)
C(5)	−1 483(4)	2 502(5)	8 715(2)
C(5a)	−2 298(4)	1 856(4)	8 129(2)
C(6)	−3 455(4)	995(5)	8 209(2)
C(7)	−4 244(4)	370(6)	7 704(2)
C(8)	−3 865(4)	624(6)	7 116(2)
C(9)	−2 736(4)	1 458(5)	7 033(2)
C(9a)	−1 904(4)	2 093(5)	7 532(2)
C(10)	−663(5)	2 904(6)	7 345(2)
C(11)	491(4)	3 367(5)	7 805(2)
C(11a)	868(4)	2 218(4)	8 311(2)
C(51)	−1 500(3)	4 237(4)	8 741(2)
C(52)	−2 486(4)	5 101(5)	8 401(2)
C(53)	−2 535(4)	6 654(5)	8 465(2)
C(54)	−1 596(5)	7 395(5)	8 868(2)
C(55)	−622(4)	6 553(5)	9 211(2)
C(56)	−578(4)	5 010(5)	9 151(2)
O(5)	−2 085(3)	2 010(3)	9 262(1)
C(21)	−5 245(7)	2 213(8)	10 250(3)
C(22)	−5 525(4)	3 250(6)	9 710(2)
O(22)	−4 704(3)	3 447(5)	9 342(2)
C(23)	−6 879(5)	4 009(6)	9 652(2)

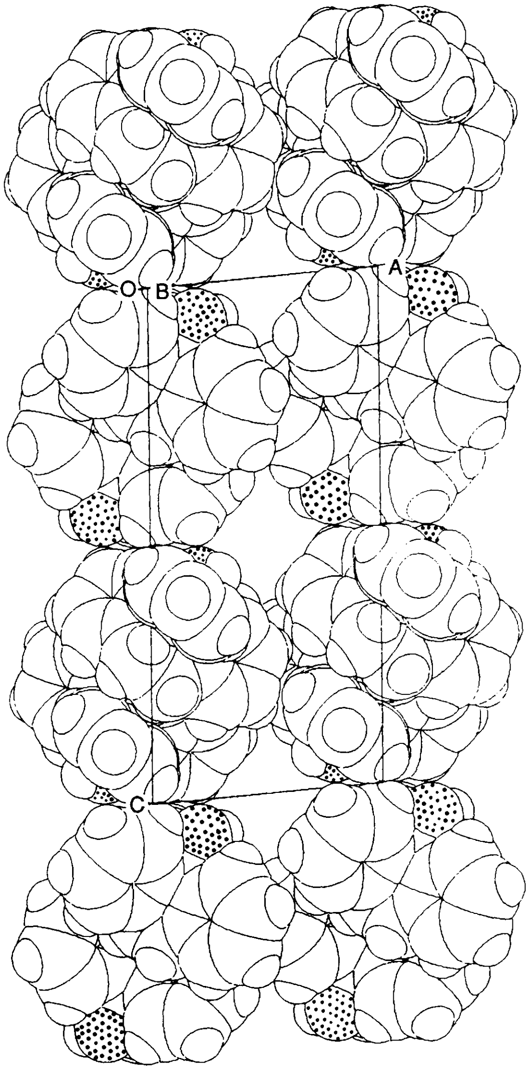

Fig. 3 Host packing in the acetone complex; O atoms shaded, host atoms drawn with Van der Waals' radii, guest atoms omitted

bonds as measured by the O ··· O distances are similar [2.870(3), 2.885(5) Å for **2** and **3**, respectively] and the measured changes in enthalpy of the guest-release reactions are correspondingly close.

Another parameter of thermal stability is the temperature characterizing the start of the endothermic guest-release reaction, the onset temperature T_{on}. For inclusion compounds of a given host with a variety of guests, the onset temperatures are clearly a function of both the host-guest interactions and of

Table 3 Selected molecular parameters for **1–3**

	1	**2**	**3**
Bond lengths/Å			
(*a*) Host C_{Ar}–C_{Ar}	1.345(9)–1.406(6)	1.367(5)–1.398(4)	1.355(6)–1.415(6)
C_{Ar}–C_{Alk}	1.479(8)–1.547(6)	1.500(5)–1.545(4)	1.498(7)–1.551(6)
C_{Alk}–C_{Alk}	1.384(8)	1.418(5)	1.502(6)
C_{Alk}–O	1.454(5)	1.446(3)	1.434(5)
(b) Guest C–C	—	1.484(7)	1.485(7), 1.491(8)
C–O	—	1.418(6)	1.193(6)
Bond angles/°			
(*a*) Host C_{Ar}–C_{Ar}–C_{Ar}	117.5(4)–123.2(4)	118.4(3)–122.2(3)	117.3(4)–121.5(5)
C_{Ar}–C_{Ar}–C_{Alk}	117.0(4)–125.6(4)	115.6(3)–125.7(3)	114.4(4)–128.1(5)
C_{Ar}–C_{Alk}–C_{ar}	110.4(3)–114.8(3)	109.4(2)–113.1(2)	108.3(4)–113.0(4)
C_{Ar}–C_{Alk}–C_{Alk}	120.9(5), 127.2(5)	121.2(3), 125.2(4)	115.2(4), 122.4(5)
C_{Ar}–C_{Alk}–O	104.1(3)–109.3(3)	105.6(2)–109.5(2)	105.4(4)–110.3(4)
(*b*) Guest C–C–C	—	—	116.6(5)
O–C–C	—	110.5(4)	121.5(6), 121.9(5)
C–O–C	—	109.8(4)	
Hydrogen bonding			
O(5) ··· O_{guest}		2.870(3)	2.885(5)
H(5) ··· O_{guest}		1.91(3)	1.90(3)
O(5)–H(5) ··· O_{guest}		163(2)	171(4)
Internal torsion angles of the seven-membered ring/°			
C(5)–C(5a)–C(9a)–C(10)	−2.6(7)	2.7(5)	2.9(8)
C(5a)–C(9a)–C(10)–C(11)	26.4(10)	22.1(6)	10.9(9)
C(9a)–C(10)–C(11)–C(11a)	20.6(10)	23.3(6)	39.8(7)
C(10)–C(11)–C(11a)–C(4a)	−50.7(8)	−53.8(5)	−65.4(6)
C(11)–C(11a)–C(4a)–C(5)	−0.5(7)	2.1(4)	4.0(7)
C(11a)–C(4a)–C(5)–C(5a)	65.0(5)	64.5(3)	66.6(6)
C(4a)–C(5)–C(5a)–C(9a)	−58.0(5)	−61.8(3)	−60.1(6)

Table 4 Thermal analysis of the dioxane **2** and acetone **3** complexes of the host compound $C_{21}H_{18}O$ **1**

Reaction	Calc. weight loss (%)	Measured weight loss (%)	Onset temp./°C	Δ*H*/J g^{-1}	Δ*H*/kJ mol^{-1}	T_{on}/T_b	$(T_{on} - T_b)$/°C
1·0.5 dioxane → **1** + 0.5 dioxane	13.3	12.0	122	57.3	18.9	1.056	21
1·acetone → **1** + acetone	16.9	13.5	66	68.4	23.6	1.030	10

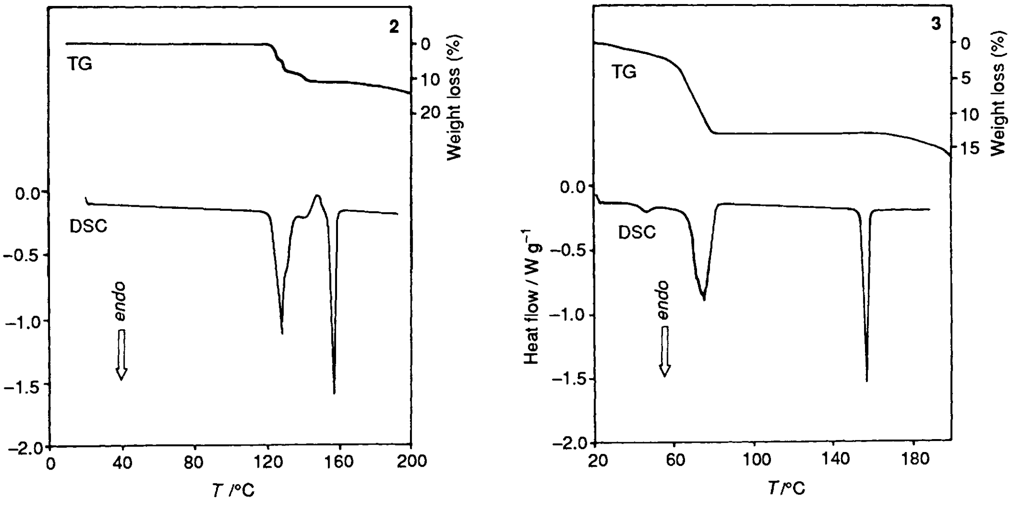

Fig. 4 Thermal analyses of complexes **2** and **3**

the intrinsic physical properties of the guest itself. In particular, the normal b.p. T_b of the guest compound is important; we suggest that a useful parameter for the measurement of the relative stabilities of inclusion compounds may be the ratio of the onset temperature to the normal b.p. T_{on}/T_b or their difference $T_{on} - T_b$. Using these criteria, the dioxane compound is more stable than its acetone analogue. This corresponds to the result of a solvent competition experiment using a 1:1 mixture (v/v) of dioxane and acetone for recrystallization of **1**. In this case, dioxane is enclathrated with high preference (50:1) over acetone. Dioxane in the vapour state is also absorbed highly specifically from a vaporous solvent mixture of dioxane and acetone by solid **1** to form the dioxane complex. There is reason to believe that a memory-effect is present since solvent-free **1** recovered by decomposition of the dioxane complex absorbs vaporous dioxane faster than **1** obtained by recrystallization from a non-clathrating solvent. Moreover, we found that on treatment of the solid acetone complex **3** with vaporous dioxane, it is readily converted to the dioxane complex within a few hours. Thus **1** is useful for sequestering dioxane in the liquid and vapour phase. With this in view, we are extending our study of this host compound with a variety of guest molecules (see above) and we are also analysing compounds made from a variety of hydroxy hosts with the same guest molecules.[6]

Experimental

Synthesis and Crystal Preparation.—The synthesis of the host compound 10,11-dihydro-5-phenyl-5*H*-dibenzo[*a,d*]cyclohepten-5-ol **1**, has been reported previously.[6] The dioxane and acetone complexes (**2** and **3**, respectively) were formed by dissolving host **1** (*ca.* 0.1 g) in the respective guest (4 cm^3) at room temperature. Dioxane inclusion crystals formed after being allowed to stand for 6 days and acetone inclusion crystals formed overnight. For the X-ray determinations of the complexes, single crystals were mounted with mother liquor in Lindemann tubes because of decomposition in air.

X-Ray Structure Determinations.—For **1**–**3** single crystals were irradiated with Mo-$K\alpha$ ($\lambda = 0.7107$ Å) radiation on an Enraf-Nonius CAD4 diffractometer. Accurate cell parameters were obtained by least-squares refinement on the setting angles of 24 reflections ($16° \leq \theta \leq 17°$). Data were collected with variable scan width, aperture width and speed. In each case, three reference reflections were monitored for intensity and orientation control; the data were corrected for Lorentz-polarization but not for absorption. Further details of the crystals and data collections are reported in Table 1.

Structure Solution and Refinement.—All three structures were solved by direct methods using SHELXS-86 [10] and refined using SHELX-76.[11] In the final refinements all non-hydrogen atoms were treated anisotropically. For **1** all hydrogen atoms were treated isotropically with a single temperature factor; H of CH_2, and CH were placed in calculated positions and the hydroxyl hydrogen, once located, was constrained at 1.00(1) Å from the parent oxygen. For **2** and **3**, the host hydrogen atoms were modelled the same way as for **1**. For **2** the hydrogen atoms on the dioxane were placed in calculated positions with a single temperature factor. For **3** the methyl groups of acetone were treated as rigid groups with the hydrogen atoms again having a single temperature factor. For each structure, appropriate weighting schemes were employed. Complex neutral atom scattering factors were taken from Cromer and Mann[12] for non-hydrogen atoms and from Stewart, Davidson and Simpson[13] for H, with dispersion corrections from Cromer and Liberman.[14] Molecular parameters were calculated using PARST[15] and drawings obtained using PLUTO.[16] All computations were performed on a VAX computer at the University of Cape Town. Final fractional atomic coordinates for all three structures are reported in Table 2. Full details of the structure solution and refinement are given in Table 1.

Thermal Analyses.—TG and DSC experiments were carried out in a Dupont 9900 thermal system at a heating rate of 5 °C min^{-1}; the TG runs were carried out with the sample under a stream of dry nitrogen flowing at 30 cm^3 min^{-1}.

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