Complexation with Diol Host Compounds. Part 7.† Structures and Thermal Analysis of 1,1,2,2-Tetraphenylethane-1,2-diol with Lutidine Guests

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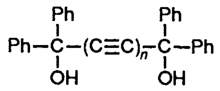
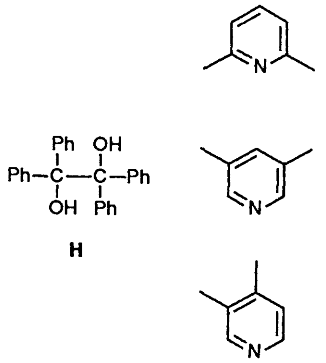
Structures of the inclusion compounds of 1,1,2,2-tetraphenylethane-1,2-diol with 2,6-lutidine (**1**), 3,5-lutidine (**2**) and 3,4-lutidine (**3**) have been determined. Crystal data: (**1**) $C_{26}H_{22}O_2{\cdot}C_7H_9N$, $M_r = 473.62$, triclinic, $P\bar{1}$, $a = 9.414(7)$, $b = 11.191(4)$, $c = 13.328(18)$ Å, $\alpha = 82.81(7)$, $\beta = 70.78(12)$, $\gamma = 86.44(4)^\circ$, $V = 1315.2$ Å^3, $Z = 2$, $D_m = 1.17$, $D_c = 1.20$ g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, $\mu = 0.40$ cm^{-1}, $F(000) = 504$. (**2**) $C_{26}H_{22}O_2{\cdot}(C_7H_9N)_2$, $M_r = 580.77$, triclinic, $P\bar{1}$, $a = 12.099(4)$, $b = 17.869(5)$, $c = 17.873(10)$ Å, $\alpha = 64.65(3)$, $\beta = 87.32(4)$, $\gamma = 75.25(2)^\circ$, $V = 3368.4$ Å^3, $Z = 4$, $D_m = 1.12$, $D_c = 1.15$ g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, $\mu = 0.64$ cm^{-1}, $F(000) = 1240$. (**3**) $C_{26}H_{22}O_2{\cdot}(C_7H_9N)_2$, $M_r = 580.77$, triclinic, $P\bar{1}$, $a = 9.163(4)$, $b = 11.740(4)$, $c = 17.721(7)$ Å, $\alpha = 69.50(3)$, $\beta = 74.22(4)$, $\gamma = 73.09(4)^\circ$, $V = 1677.2$ Å^3, $Z = 2$, $D_m = 1.14$, $D_c = 1.15$ g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, $\mu = 0.38$ cm^{-1}, $F(000) = 620$. The final R values at 293 K were (**1**) 0.043, (**2**) 0.070 and (**3**) 0.067 for 3382, 8561 and 4828 unique reflections. Strong host–guest hydrogen bonding is observed in all structures, O ··· N distances are between 2.664 and 2.889 Å. Thermal analysis revealed the strength of binding of the guest molecules and a competition experiment showed that 3,5-lutidine is preferentially included over 2,6-lutidine.

Molecular inclusion chemistry has become an important technique for the separation of close structural isomers and for the optical resolution of chiral compounds.[1] Diol compounds have proved to be versatile hosts in the formation of inclusion compounds with a variety of guest molecules, usually with concomitant hydrogen bonding. Toda has recently reviewed these compounds[2] and their uses in the isolation of alcohols, amines and alkali-metal hydroxides from aqueous solution, as well as how they can be employed in controlling guest reactions in clathrates.[3] We have studied the clathrating properties of selected tetraphenyl diols (**I**). We have reported[4] the structure of 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol in its non-porous α-form and the kinetics for the complexation reaction with acetone vapour. We have also investigated[4] the kinetics of the solid–solid reaction between this host and benzophenone and reported the crystal structure of the final product. We have described[5] the structure of the related host 1,1,2,2-tetraphenylethane-1,2-diol and that of its molecular inclusion complex with dimethyl sulphoxide. We now present the results of the enclathration behaviour of this host compound with the three isomers 2,6-lutidine, 3,5-lutidine and 3,4-lutidine. The thermal analysis of the molecular complexes is discussed and competition experiments between two of the guests are reported.



$Ph_2C(OH){-}(C{\equiv}C)_n{-}C(OH)Ph_2$

Ia; $n = 2$; **b**; $n = 1$; **c**; $n = 0$



1 = H·2,6-lutidine; **2** = H·2-(3,5-lutidine); **3** = H·2-(3,4-lutidine)

Experimental

The inclusion compounds **1**–**3** were obtained by dissolving the host compound **H** in a minimum amount of diethyl ether and adding an excess of the appropriate lutidine. Single crystals suitable for X-ray diffraction were obtained by slow evaporation over a period of 10 days. Preliminary cell dimensions and space-group symmetry were determined photographically. X-Ray diffraction data were then measured on a Nonius CAD4 diffractometer using graphite-monochromated radiation and the $\omega - 2\theta$ technique. Measurements were made at room temperature and the crystal stabilities were checked by monitoring three reference reflections periodically. Crystal data are listed in the abstract. Some experimental conditions are summarized in Table 1. All data were corrected for Lorentz polarization and an absorption correction[6] was applied to **1** and **3**. Final refinements were based only on those observations that satisfied the condition $I > 2\sigma(I)$. The structures were solved by direct methods using SHELXS-86.[7] Structures **1** and **3** were refined by full-matrix least squares while **2** was refined by large block least squares, using the SHELX76 program system.[8] Non-hydrogen atoms were treated anisotropically and non-hydroxy hydrogens were constrained to 1.00 Å from their parent atoms. The phenyl rings of the host in **2** were refined as rigid hexagons to avoid a too-low data-to-parameter ratio. Approximate positions for the hydroxy hydrogen atoms of **2** and **3** were found in difference Fourier maps but only one of the two hydroxy hydrogens in **1** could be found. The hydroxy hydrogens were fixed at set lengths from their parent oxygens according to a function of O ··· N *vs.* O–H distance.[9] They were then allowed to refine with this bond length constraint but with independent isotropic temperature factors. From the O ··· O distance of 2.664(4) Å in **1** we can infer an

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† Part 6 is ref. 4.

Table 1 Experimental conditions

	1	2	3
Crystal size/mm	0.30 × 0.55 × 0.50	0.40 × 0.40 × 0.30	0.45 × 0.35 × 0.50
2θ limit/°	22	22	23
Scan width/°	$(0.95 + 0.35 \tan\theta)$	$(0.95 + 0.35 \tan\theta)$	$(0.95 + 0.35 \tan\theta)$
Max. h, k, l	±9, ±11, +14	±11, ±17, +17	±10, ±12, +19
N (measured)	3382	8561	4828
N (observed)	2501	4561	2927
R_F	0.043	0.070	0.067
R_w	0.048	0.082	0.071
w^a	0.002	0.02	0.001
Absorption correction			
Min. trans. (%)	91.65		82.60
Max. trans. (%)	99.97		99.71
Av. trans. (%)	95.69		92.26

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

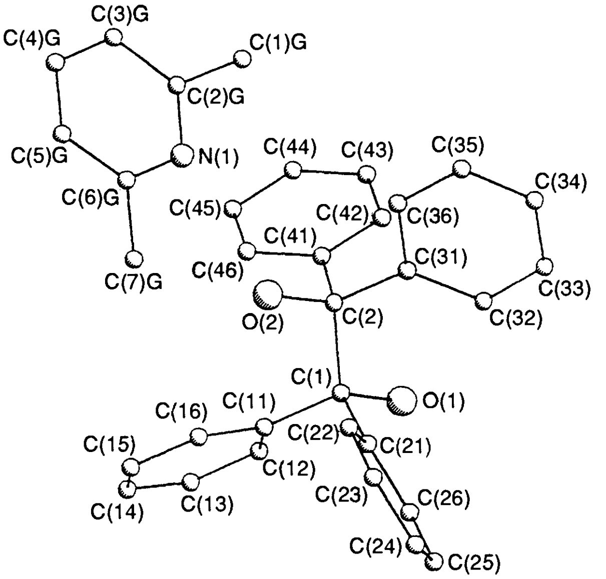

Fig. 1 Crystallographic numbering system used for the host and guest species. In compounds **2** and **3**, the independent guest molecules are labelled with the suffices A–D.

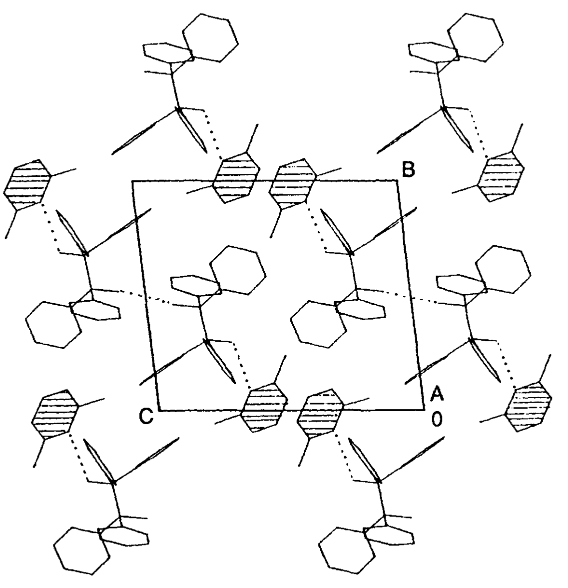

Fig. 2 Projection of **1** viewed along [100]. Guest molecules are shaded and hydrogen bonds indicated by broken lines.

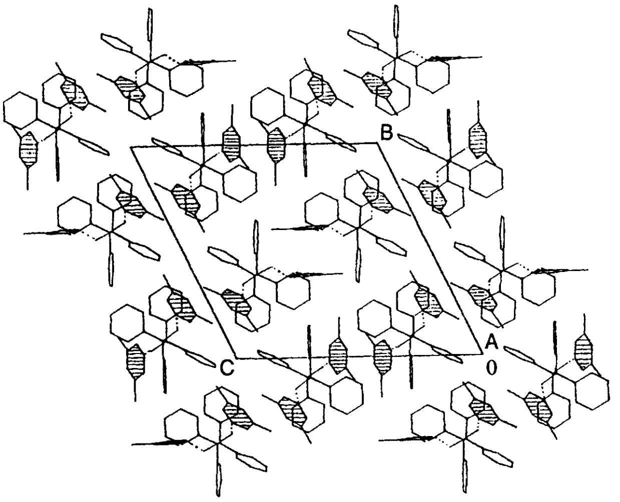

Fig. 3 Projection of **2** viewed along [100]. Guest molecules are shaded and hydrogen bonds indicated by broken lines.

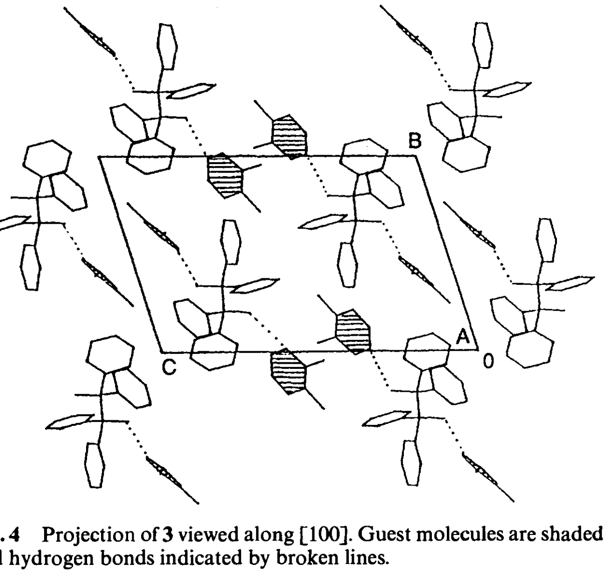

Fig. 4 Projection of **3** viewed along [100]. Guest molecules are shaded and hydrogen bonds indicated by broken lines.

intermolecular hydrogen bond which occurs across a centre of inversion. Close examination of the difference map of this region, however, did not reveal the position of the hydrogen atom, and the latter was therefore not included in the final model. The final difference Fourier maps for the three structures gave no indication of incorrectly placed or missing atoms. The crystallographic atom labelling scheme used for the host and

Table 2 Fractional atomic coordinates (× 10^4) with esds in parentheses for compounds **1**, **2** and **3**

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Compound **1**			
O(1)	4 491(2)	5 262(1)	1 007(1)
O(2)	1 937(2)	6 958(1)	3 035(1)
C(1)	3 336(2)	5 410(2)	2 005(2)
C(2)	3 222(2)	6 810(2)	2 131(2)
C(11)	1 850(3)	4 932(2)	1 988(2)
C(12)	1 742(3)	4 563(2)	1 060(2)
C(13)	421(4)	4 133(3)	1 036(3)
C(14)	−820(4)	4 060(3)	1 912(3)
C(15)	−741(3)	4 392(2)	2 859(3)
C(16)	588(3)	4 817(2)	2 898(2)
C(21)	3 834(2)	4 618(2)	2 850(2)
C(22)	3 490(3)	4 878(2)	3 897(2)
C(23)	3 932(3)	4 105(3)	4 635(2)
C(24)	4 721(3)	3 063(3)	4 352(2)
C(25)	5 060(3)	2 791(2)	3 326(2)
C(26)	4 619(3)	3 553(2)	2 577(2)
C(31)	4 614(2)	7 270(2)	2 319(2)
C(32)	6 045(3)	6 754(2)	1 975(2)
C(33)	7 242(3)	7 248(3)	2 146(2)
C(34)	7 056(3)	8 265(3)	2 646(2)
C(35)	5 644(3)	8 790(2)	2 991(2)
C(36)	4 439(3)	8 294(2)	2 840(2)
C(41)	2 984(2)	7 524(2)	1 135(2)
C(42)	4 142(3)	8 083(2)	306(2)
C(43)	3 859(4)	8 750(3)	−557(2)
C(44)	2 435(4)	8 850(3)	−623(2)
C(45)	1 274(4)	8 286(3)	187(3)
C(46)	1 546(3)	7 631(2)	1 052(2)
N(1)	306(2)	9 128(2)	3 544(2)
C(1G)	1 482(4)	10 578(3)	2 028(3)
C(2G)	210(3)	10 216(2)	3 025(2)
C(3G)	−1 018(4)	10 980(3)	3 409(3)
C(4G)	−2 116(4)	10 621(3)	4 341(3)
C(5G)	−2 004(3)	9 529(3)	4 880(2)
C(6G)	−787(3)	8 788(2)	4 459(2)
C(7G)	−649(3)	7 569(2)	5 017(2)
Compound **2**			
O(1)	2 506(3)	9 559(2)	6 728(2)
O(2)	4 917(3)	8 576(2)	8 222(2)
C(1)	3 046(4)	9 103(3)	7 536(3)
C(2)	4 350(4)	9 071(3)	7 415(3)
C(12)	1 283(3)	9 721(2)	8 070(2)
C(13)	680(3)	10 151(2)	8 517(2)
C(14)	1 269(3)	10 398(2)	8 986(2)
C(15)	2 462(3)	10 218(2)	9 009(2)
C(16)	3 066(3)	9 788(2)	8 562(2)
C(11)	2 476(3)	9 539(2)	8 093(2)
C(22)	2 629(3)	7 829(2)	7 422(2)
C(23)	2 523(3)	6 990(2)	7 770(2)
C(24)	2 696(3)	6 496(2)	8 626(2)
C(25)	2 975(3)	6 842(2)	9 137(2)
C(26)	3 082(3)	7 681(2)	8 790(2)
C(21)	2 909(3)	8 175(2)	7 934(2)
C(32)	3 770(2)	10 748(2)	6 705(2)
C(33)	4 083(2)	11 518(2)	6 421(2)
C(34)	5 234(2)	11 510(2)	6 467(2)
C(35)	6 072(2)	10 732(2)	6 797(2)
C(36)	5 759(2)	9 961(2)	7 081(2)
C(31)	4 608(2)	9 969(2)	7 034(2)
C(42)	4 644(2)	9 092(1)	5 987(2)
C(43)	5 022(2)	8 679(1)	5 478(2)
C(44)	5 541(2)	7 799(1)	5 830(2)
C(45)	5 682(2)	7 332(1)	6 691(2)
C(46)	5 304(2)	7 747(1)	7 200(2)
C(41)	4 785(2)	8 626(1)	6 848(2)
N(1A)	4 231(4)	6 202(3)	3 794(3)
C(1A)	4 048(7)	6 032(5)	5 982(5)
C(2A)	3 840(5)	6 163(3)	4 530(5)
C(3A)	4 532(5)	6 067(3)	5 184(4)
C(4A)	5 679(6)	6 003(3)	5 026(5)
C(5A)	6 091(5)	6 043(4)	4 277(5)
C(6A)	5 333(5)	6 154(4)	3 682(4)
C(7A)	7 389(6)	5 956(5)	5 884(6)
N(1B)	−156(4)	10 278(4)	3 626(4)
C(1B)	1 820(7)	8 095(5)	4 954(6)
C(2B)	330(5)	9 428(5)	4 014(4)
C(3B)	1 316(5)	9 075(4)	4 523(4)
C(4B)	1 830(5)	9 645(5)	4 597(4)
C(5B)	1 377(5)	10 496(4)	4 202(5)
C(6B)	402(5)	10 790(4)	3 714(5)
C(7B)	1 982(7)	11 102(5)	4 310(7)
O(1H)	−2 557(3)	14 315(2)	6 773(2)
O(2H)	−175(2)	13 501(2)	8 285(2)
C(1H)	−2 022(4)	13 921(3)	7 593(3)
C(2H)	−732(4)	13 969(3)	7 472(3)
C(12H)	−3 871(2)	14 646(2)	7 955(2)
C(13H)	−4 544(2)	15 105(2)	8 353(2)
C(14H)	−4 027(2)	15 332(2)	8 878(2)
C(15H)	−2 836(2)	15 099(2)	9 005(2)
C(16H)	−2 162(2)	14 640(2)	8 608(2)
C(11H)	−2 680(2)	14 413(2)	8 083(2)
C(22H)	−2 119(3)	12 522(2)	7 593(2)
C(23H)	−2 148(3)	11 665(2)	8 002(2)
C(24H)	−2 114(3)	11 267(2)	8 867(2)
C(25H)	−2 051(3)	11 725(2)	9 322(2)
C(26H)	−2 023(3)	12 582(2)	8 913(2)
C(21H)	−2 057(3)	12 980(2)	8 047(2)
C(32H)	−1 467(2)	15 635(2)	6 714(2)
C(33H)	−1 244(2)	16 440(2)	6 402(2)
C(34H)	−129(2)	16 503(2)	6 463(2)
C(35H)	763(2)	15 762(2)	6 833(2)
C(36H)	540(2)	14 958(2)	7 146(2)
C(31H)	−575(2)	14 894(2)	7 086(2)
C(42H)	−386(3)	13 997(1)	6 043(2)
C(43H)	44(3)	13 594(1)	5 533(2)
C(44H)	653(3)	12 732(1)	5 885(2)
C(45H)	829(3)	12 273(1)	6 745(2)
C(46H)	400(3)	12 676(1)	7 255(2)
C(41H)	−209(3)	13 538(1)	6 903(2)
N(1C)	2 647(4)	2 114(4)	1 560(3)
C(1C)	206(6)	4 029(5)	1 254(5)
C(2C)	1 992(5)	2 816(4)	1 595(4)
C(3C)	899(5)	3 210(4)	1 210(4)
C(4C)	501(5)	2 836(5)	776(4)
C(5C)	1 152(6)	2 109(5)	740(4)
C(6C)	2 233(5)	1 771(4)	1 136(4)
C(7C)	729(8)	1 680(5)	267(5)
N(1D)	2 264(4)	2 992(3)	8 508(3)
C(1D)	4 918(6)	1 253(6)	8 636(6)
C(2D)	3 003(5)	2 358(4)	8 411(4)
C(3D)	4 110(5)	2 022(5)	8 757(4)
C(4D)	4 449(5)	2 373(5)	9 229(4)
C(5D)	3 719(5)	3 034(4)	9 345(4)
C(6D)	2 648(5)	3 301(4)	8 979(4)
C(7D)	4 070(7)	3 427(5)	9 874(4)
Compound **3**			
O(1)	1 982(3)	2 020(3)	6 855(2)
O(2)	−1 003(3)	3 396(2)	8 259(2)
C(1)	1 100(4)	2 071(3)	7 643(2)
C(2)	−106(4)	3 357(3)	7 472(2)
C(11)	231(4)	1 011(3)	8 026(2)
C(12)	−399(4)	658(3)	8 863(2)
C(13)	−1 213(5)	−266(4)	9 207(3)
C(14)	−1 408(5)	−894(4)	8 731(4)
C(15)	−798(5)	−578(4)	7 907(4)
C(16)	11(5)	373(4)	7 554(3)
C(21)	2 205(4)	1 932(3)	8 205(2)
C(22)	2 051(5)	2 742(4)	8 647(2)
C(23)	3 155(6)	2 557(5)	9 111(3)
C(24)	4 389(5)	1 577(5)	9 149(3)
C(25)	4 535(5)	759(5)	8 730(3)
C(26)	3 448(5)	930(4)	8 265(3)
C(31)	−1 149(4)	3 371(3)	6 917(2)
C(32)	−2 555(4)	3 019(4)	7 264(3)

Table 2 (*continued*)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
C(33)	−3 500(5)	3 030(4)	6 763(3)
C(34)	−3 044(6)	3 385(4)	5 926(3)
C(35)	−1 658(5)	3 727(4)	5 578(3)
C(36)	−696(4)	3 723(3)	6 065(2)
C(41)	630(4)	4 508(3)	7 076(2)
C(42)	2 191(5)	4 496(4)	6 748(2)
C(43)	2 721(6)	5 580(5)	6 427(3)
C(44)	1 736(7)	6 720(5)	6 409(3)
C(45)	177(6)	6 758(4)	6 718(3)
C(46)	−370(5)	5 666(4)	7 046(3)
N(1A)	5 633(6)	111(5)	3 412(3)
C(1A)	2 015(11)	435(11)	5 030(6)
C(2A)	4 403(9)	−176(7)	3 957(4)
C(3A)	3 310(7)	736(6)	4 388(4)
C(4A)	3 722(6)	1 824(6)	4 145(3)
C(5A)	4 949(8)	2 124(6)	3 538(5)
C(6A)	5 838(8)	1 241(7)	3 222(5)
C(7A)	2 870(10)	2 873(8)	4 526(5)
N(1B)	6 249(4)	5 193(4)	8 473(3)
C(1B)	1 921(6)	6 107(6)	8 683(4)
C(2B)	4 791(5)	5 296(4)	8 434(3)
C(3B)	3 527(5)	6 057(4)	8 779(3)
C(4B)	3 797(5)	6 761(4)	9 195(3)
C(5B)	5 303(6)	6 664(5)	9 227(3)
C(6B)	6 481(6)	5 876(5)	8 874(4)
C(7B)	2 487(7)	7 615(6)	9 591(4)

guest molecules is shown in Fig.1. The final non-hydrogen atom coordinates for **1**, **2** and **3** are given in Table 2.*

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a Perkin-Elmer PC7 series system. In order to carry out the analysis, crystals were removed from their mother liquor, blotted dry on filter paper and crushed. Sample weight in each case was *ca.* 5 mg. The temperature range was typically 30–220 °C at a heating rate of 10 °C min^{-1}. A constant stream of nitrogen (flow rate 40 cm^3 min^{-1}) was passed over the samples.

Varying mole fractions of 2,6- and 3,5-lutidine were added to the host, which had been dissolved in ether. The solutions were left for several weeks until crystals formed. These were dissolved in acetone and analysed by gas chromatography using a Pye Unicam PU4500 chromatograph which was equipped with a flame ionizer detector; output was plotted on a pen recorder. Columns used were glass-tubing packed with 10% (w/w) squalane on Chromosorb W (80/100 mesh) at a temperature of 180 °C. Nitrogen was used as the carrier gas (30 cm^3 min^{-1}) and the flame of the detector was supported by an air–hydrogen mixture. The injector and detector temperatures were 250 °C and the sample aliquot was 5 mm^3. X-Ray powder diffraction studies were performed using a Philips vertical goniometer PW1050/80 with a Philips PW1394 motor control and PW1390 channel control.

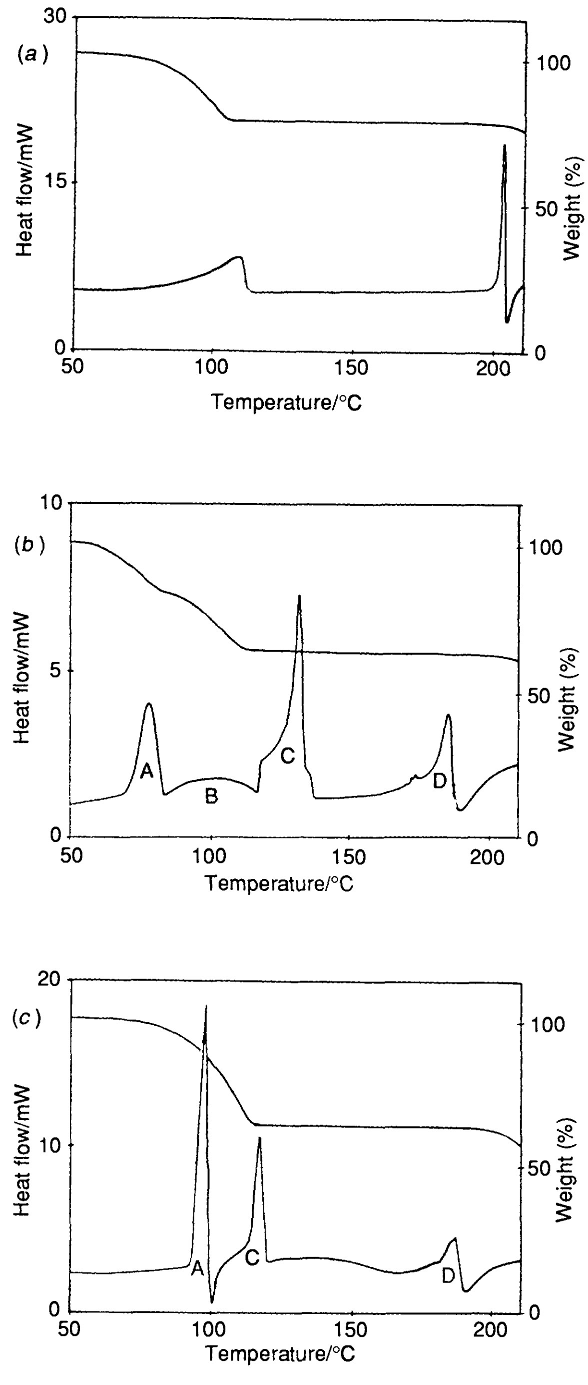

Fig. 5 Thermal analyses of (*a*) **1**; (*b*) **2**; (*c*) **3**

Results and Discussion

The host conformation is similar in the three structures. In each case the phenyl rings attached to a common carbon atom are almost perpendicular to each other, with dihedral angles ranging from 78.7 to 94.5°. The torsion angle O(1)–C(1)–C(2)–O(2) ranges from 171.7 to 179.1°, indicating the hydroxy moieties to be in the *trans* conformation. Selected bond lengths and angles are given in Table 3. The aromatic rings of the host molecules are planar; maximum deviations from their mean planes are listed in Table 4.

In compound **1** the host:guest ratio of 1:1 arises from the hydrogen bonding pattern. Thus there is a host–host hydrogen bond across the centre of inversion at Wyckoff position *e*, and each host is in turn hydrogen bonded to a guest molecule. Details of the hydrogen bonding are given in Table 5. Pairs of guest molecules lie in centrosymmetric cavities as shown in Fig. 2. The packing of compound **2** is shown in Fig. 3. There are two crystallographically independent host molecules in the cell, each of which is hydrogen bonded to two guest molecules, giving rise to four independent O–H ••• N hydrogen bonds (Table 5). The guest molecules lie in channels centred on $x = 0$ and $x = 0.5$, and running in the $[0\bar{1}1]$ direction. Compound **3** is structurally similar to compound **2**, in that each host is

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* Full lists of structure factors, anisotropic thermal parameters, atomic coordinates of calculated hydrogens, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. For details, see 'Instructions for Authors (1991)', *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

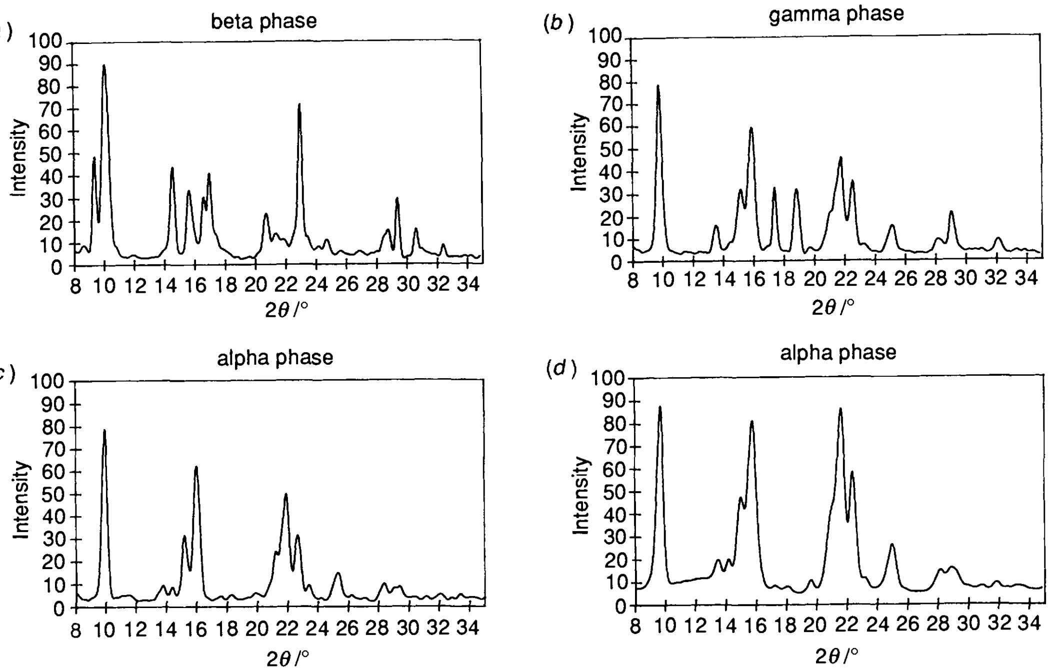

Fig. 6 Powder diffraction patterns of **2**. (*a*) Freshly removed from mother liquor; (*b*) maintained at 87 °C for 1 h; (*c*) dried at 120 °C for 24 h; (*d*) host powder recrystallised from diethyl ether.

Table 3 Selected bond lengths (Å) and angles (°)

	1	$\mathbf{2}_{\mathrm{molecule\ 1}}$	$\mathbf{2}_{\mathrm{molecule\ 2}}$	**3**
Host				
O(1)–C(1)	1.453(3)	1.409(6)	1.427(6)	1.422(5)
O(2)–C(2)	1.417(3)	1.423(6)	1.425(6)	1.422(5)
C(1)–C(2)	1.590(3)	1.572(7)	1.583(7)	1.576(4)
$\mathrm{C_{central}}$–$\mathrm{C_{phenyl}}$	1.523(4)–1.542(4)	1.537(7)–1.561(6)	1.534(6)–1.555(6)	1.528(5)–1.544(6)
$\mathrm{C_{phenyl}}$–$\mathrm{C_{phenyl}}$	1.351(5)–1.391(4)	Fixed at 1.395	Fixed at 1.395	1.355(7)–1.396(4)
Guest				
N–C	1.336(3), 1.341(4)	1.347(9), 1.323(9)	1.330(10), 1.341(4)	1.311(9), 1.306(10)
$\mathrm{C_{ring}}$–$\mathrm{C_{methyl}}$	1.490(3), 1.497(5)	1.497(12), 1.493(9)	1.529(11), 1.537(15)	1.434(11), 1.523(12)
$\mathrm{C_{ring}}$–$\mathrm{C_{ring}}$	1.355(5)–1.388(4)	1.352(11)–1.396(11)	1.363(12)–1.387(13)	1.353(9)–1.375(14)
N–C		1.334(9), 1.329(11)	1.316(9), 1.344(11)	1.325(6), 1.332(10)
$\mathrm{C_{ring}}$–$\mathrm{C_{methyl}}$		1.557(10), 1.532(14)	1.565(13), 1.529(13)	1.509(8), 1.508(8)
$\mathrm{C_{ring}}$–$\mathrm{C_{ring}}$		1.343(9)–1.374(13)	1.353(9)–1.375(14)	1.367(8)–1.390(9)
Host				
Around C(1)	105.5(3)–114.7(3)	104.9(4)–115.3(5)	105.0(4)–114.0(5)	104.6(3)–114.5(3)
Around C(2)	105.5(3)–112.9(3)	105.6(4)–114.1(5)	104.9(4)–114.5(5)	108.9(3)–114.5(4)
Guest				
Around N	119.2(4)	118.3(6)	119.0(7)	117.7(7)
		117.4(7)	116.8(6)	116.7(5)

Table 4 Maximum deviation from the mean planes of the aromatic rings (Å)

	1	2 molecule 1	2 molecule 2	3
C(11)–C(16)	−0.011	0.000	0.000	0.007
C(21)–C(26)	−0.005	−0.001	−0.001	0.010
C(31)–C(36)	−0.008	0.001	−0.001	0.003
C(41)–C(46)	0.007	0.000	0.001	0.007
N(1A)–C(6A)	−0.010	0.016		0.030
N(1B)–C(6B)		0.016		0.007
N(1C)–C(6C)		−0.008		
N(1D)–C(1D)		−0.008		

hydrogen bonded to two guests (Table 5), and the latter lie in channels centred at $x = 0.5$ and running in the $[0\bar{1}1]$ direction, as shown in Fig. 4.

Table 5 Hydrogen bonding

			Bond length/Å		Bond angle/°
Compound	Donor	Acceptor	O–H	O···N	O–H···N
1	O(1)	O(1$^{\mathrm{i}}$)[a]		2.664(4)[b]	
	O(2)	N(1)	0.99(1)	2.825(3)	159.9(1.7)
2	O(1)	N(1B)	0.99(3)	2.861(6)	165.0(4.0)
	O(2)	N(1C)	0.99(2)	2.868(5)	161.4(5.2)
	O(1H)	N(1A)	0.96(7)	2.813(8)	155.4(5.5)
	O(2H)	N(1D)	1.07(2)	2.861(5)	150.4(3.4)
3	O(1)	N(1A)	0.87(4)	2.889(6)	167.2(3.8)
	O(2)	N(1B)	0.91(5)	2.808(4)	166.5(4.9)

[a] Related to O(1) by $-x + 1$, $-y + 1$, $-z$. [b] A hydrogen bond is implied by the short O···O contact although the hydrogen could not be located.

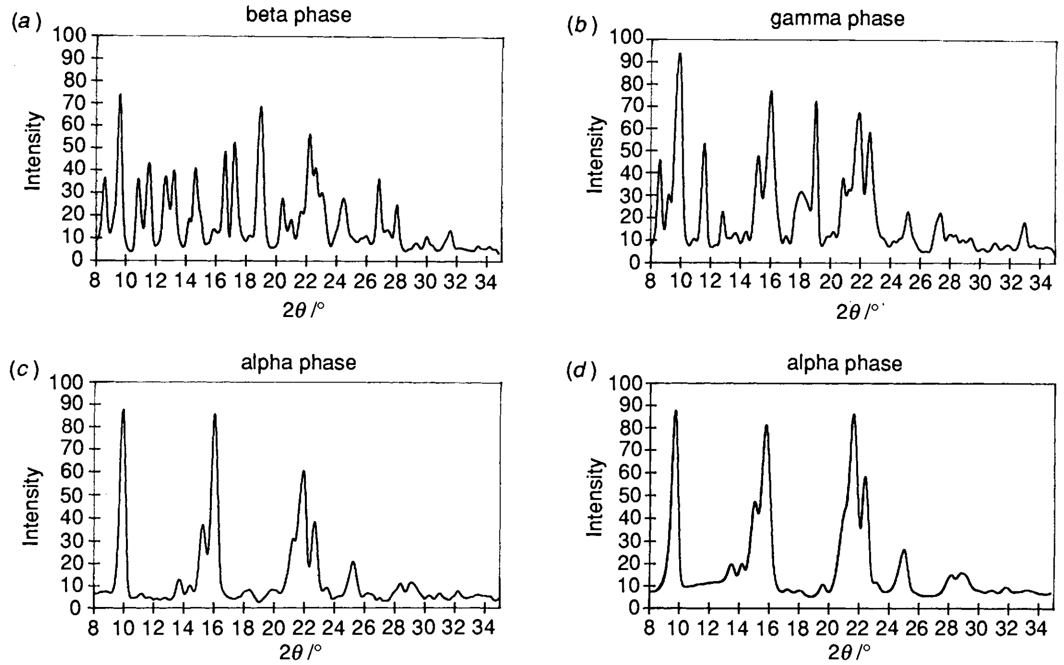

Fig. 7 Powder diffraction patterns of 3. (*a*) Freshly removed from mother liquor, (*b*) maintained at 87 °C for 1 h, (*c*) dried at 120 °C for 24 h; (*d*) host powder recrystallised from diethyl ether.

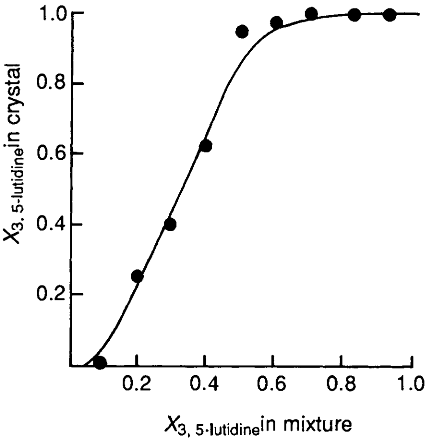

Fig. 8 Separation of 2,6-lutidine and 3,5-lutidine by inclusion formation

The results of the thermal analysis are shown in Fig. 5. For all three compounds the thermal gravimetric (TG) curves show experimental weight losses which are in excellent agreement with calculated values (differences $<1\%$). The DSC curve of **1**, shown in Fig. 5(*a*), shows a skewed endotherm with no definitive onset temperature, but which corresponds to the weight loss in the TG curve. This is followed by the melting endotherm of the host at 198 °C. We have carried out X-ray powder photography of **1** before and after guest loss, and have shown that the inclusion compound (β-phase), reverts to the non-porous α-phase. Compound **2**, however, displays a different decomposition pattern. Fig. 5(*b*) shows an inflection in the TG which, with its concomitant endotherms in the DSC labelled A and B corresponds to a complex guest loss reaction. This is followed by a third endotherm, C, which is caused by a structural phase change occurring between 118 and 137 °C. The fourth endotherm, D, is associated with the melting of the host compound. We confirmed this by visual observation of the decomposition. Crystals of **2** were observed on a Linkam TH600 hotstage set on a Nikon SMZ-10 stereo microscope fitted with a 35 mm camera. The clear crystals, when heated at 10 °C min^{-1}, showed the appearance of bubbles at 60–75 °C and discoloured to brown. This corresponds to endotherms A and B. Between 120 and 140 °C feather-like crystallites appear on the surface of the crystal, corresponding to endotherm C. The melting is observed at *ca.* 190 °C, with further discolouration and decomposition. The powder diffraction patterns, shown in Fig. 6, show the various phases of the host·3,5-lutidine complex (**2**) after it had been: (*a*) freshly removed from its mother liquor and crushed (β-phase); (*b*) crushed and maintained at 87 °C *in vacuo* for 1 h; (*c*) crushed and maintained at 120 °C *in vacuo* for 24 h, which yields essentially the same pattern as Fig. 6(*d*) which is the pattern obtained from the pure host crystallised from diethyl ether, which is known to yield the non-porous α-phase. The X-ray powder pattern shown in Fig. 6(*b*) is different from the other patterns, and corresponds to a new structure, which we have labelled the γ-phase. The decomposition of **3** is similar to that of **2** in that we again have the endotherm C [Fig. 5(*c*)] which corresponds to a structural phase change. This was also confirmed by visual observation of feather-like crystals growing between 105 and 120 °C. Powder diffraction patterns shown in Fig. 7 again show the presence of a new γ-phase which occurs after the guest loss, but before the reversion to the α-phase.

2,6-Lutidine and 3,5-lutidine are very similar in shape and size. A competition experiment was carried out to determine which of the two isomers would be most readily included. The result is shown in Fig. 8. 3,5-Lutidine is preferentially included; at compositions of $X_{3,5\text{-lutidine}} \geq 0.5$ it is the only guest species included in the host lattice. X-Ray powder diffraction studies showed that only two phases are possible in this series: those of compounds **1** and **2**. For $X_{3,5\text{-lutidine}} = 0$ to 0.3, the crystals exist in the same phase as **1** while from $X_{3,5\text{-lutidine}} = 0.4$ to 1, the phase is the same as that of **2**.

Acknowledgements

We thank the University of Cape Town and Foundation for Research Development (Pretoria) for research grants.

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Paper 1/01733K
Received 15*th April* 1991
Accepted 23*rd April* 1991