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Complexation with Diol Host Compounds. 4. 1:1 Molecular Complexes of 1,1-Bis(4-hydroxyphenyl)cyclohexane* with Water and Ethanol

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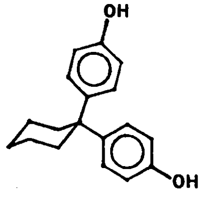
Abstract. Compound (1), 1,1-bis(4-hydroxyphenyl)cyclohexane–water (1/1), $C_{18}H_{20}O_2.H_2O$, M_r = 286·37, monoclinic, $P2_1$, a = 10·779 (3), b = 6·499 (5), c = 10·962 (2) Å, β = 97·54 (2)°, V = 761·3 (6) Å^3, Z = 2, D_x = 1·25 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·78 cm^{-1}, $F(000)$ = 308, T = 294 K, R = 0·036 for 1354 reflections. Compound (2), 1,1-bis(4-hydroxyphenyl)cyclohexane–ethanol (1/1), $C_{18}H_{20}O_2.C_2H_6O$, M_r = 314·43, triclinic, $P\bar{1}$, a = 6·292 (1), b = 10·864 (3), c = 13·425 (3) Å, α = 84·76 (3), β = 77·95 (2), γ = 78·95 (2)°, V = 879·6 (4) Å^3, Z = 2, D_x = 1·19 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·73 cm^{-1}, $F(000)$ = 340, T = 294 K, R = 0·049 for 2729 reflections. The cyclohexane ring of the host molecule is an almost perfect chair in both compounds with a mean absolute torsion angle of 55·70 (7)° in (1) and 55·90 (7)° in (2). The host–guest intermolecular associations in both structures are characterized by an efficient triangular donor–acceptor hydrogen-bonding arrangment with O···O distances ranging from 2·588 (3)–2·774 (3) Å.

Introduction. Recently we have reported the molecular inclusions of a range of cyclic aliphatic and aromatic ketones by the host complex *trans*-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (Bond, Nassimbeni & Toda, 1989*a*,*b*). As a continuation of our study of host–guest interactions we now report the molecular inclusions of water (1) and ethanol (2) by another dihydroxy host, 1,1-bis(4-hydroxyphenyl)cyclohexane (*H*). This host compound readily forms crystalline adducts with a variety of alcohols (Toda, 1987), as do many other diol host systems (Tanaka, Toda & Mak, 1984; Shin, Toda & Jhon, 1987; Toda, Tanaka & Mak, 1985). The isolation of ethanol from aqueous solution by a cost-effective crystal inclusion method may be of potential value in industry in deriving inexpensive energy from the fermentation of biomass (Toda, 1987). This study aims to understand the modes and strengths of the molecular association in the crystalline state which will provide insight as to the feasibility of the isolation process.



(*H*)

Experimental. The host compound, 1,1-bis(4-hydroxyphenyl)cyclohexane, was prepared as described by Goldberg, Stein, Kai & Toda (1987) and by Goldberg, Stein, Tanaka & Toda (1988). The 1:1 inclusion complexes were obtained by slow evaporation of dilute solutions of the host in the guest.

Compound (1). A needle crystal, 0·09 × 0·13 × 0·56 mm, was mounted in a glass capillary. 1544 profile-fitted intensities were recorded on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation to a $2\theta_{\max}$ of 50°. Accurate cell parameters were refined from 2θ values of 24 reflections in the range 16–17°. An ω–2θ scan mode was employed with variable scan and aperture widths and variable scan speeds with a maximum recording time of 40 s. The intensities of three standard reflections were checked every hour (with 1% variation) and recentring carried out every 200 measured reflections. Merging equivalents gave 1354 unique reflections ($R_{\rm int}$ = 0·018, index ranges after merging h − 12 to 12, k 0 to 7, l 0 to 13) of which 1180 with $F > 4\sigma(F)$ were considered observed. Data were corrected for Lorentz and polarization effects. The structure was solved using the direct-methods package *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least-squares

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* Alternative nomenclature: 4,4′-(cyclohexylidene)diphenol.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	*y*	*z*	U_{eq}
Compound (1)				
C(1)	7803 (2)	1905	8882 (2)	40 (1)
C(2)	7709 (3)	3804 (6)	9707 (3)	46 (1)
C(3)	6815 (3)	3531 (7)	10663 (3)	55 (1)
C(4)	7174 (3)	1664 (8)	11479 (3)	62 (1)
C(5)	7263 (3)	−241 (7)	10706 (3)	55 (1)
C(6)	8167 (2)	77 (7)	9753 (3)	45 (1)
C(11)	8809 (2)	2261 (6)	8024 (2)	39 (1)
C(12)	8920 (3)	4154 (7)	7446 (3)	49 (1)
C(13)	9789 (2)	4495 (7)	6642 (3)	49 (1)
C(14)	10579 (2)	2913 (6)	6397 (3)	43 (1)
C(15)	10484 (3)	1028 (6)	6927 (3)	51 (1)
C(16)	9609 (3)	707 (7)	7735 (3)	48 (1)
O(14)	11432 (2)	3308 (6)	5599 (2)	56 (1)
C(21)	6565 (2)	1483 (6)	8029 (2)	37 (1)
C(22)	5728 (3)	3054 (7)	7647 (3)	50 (1)
C(23)	4653 (3)	2708 (7)	6830 (3)	52 (1)
C(24)	4380 (2)	763 (6)	6373 (2)	41 (1)
C(25)	5201 (2)	−827 (6)	6716 (3)	45 (1)
C(26)	6279 (2)	−439 (7)	7534 (3)	44 (1)
O(24)	3297 (2)	504 (6)	5582 (2)	55 (1)
O(99)	2825 (2)	6651 (6)	5001 (2)	63 (1)
Compound (2)				
C(1)	3028 (3)	8029 (2)	8922 (2)	35 (1)
C(2)	1090 (3)	7995 (2)	9845 (2)	38 (1)
C(3)	1429 (4)	6848 (2)	10580 (2)	43 (1)
C(4)	3562 (4)	6747 (2)	10964 (2)	51 (1)
C(5)	5501 (4)	6764 (2)	10081 (2)	48 (1)
C(6)	5131 (3)	7927 (2)	9369 (2)	40 (1)
C(11)	3292 (3)	6965 (2)	8198 (2)	33 (1)
C(12)	5184 (3)	6709 (2)	7443 (2)	42 (1)
C(13)	5446 (4)	5795 (2)	6756 (2)	47 (1)
C(14)	3794 (2)	5116 (2)	6799 (2)	40 (1)
C(15)	1884 (4)	5351 (2)	7524 (2)	42 (1)
C(16)	1657 (3)	6268 (2)	8213 (2)	40 (1)
O(14)	4098 (3)	4213 (1)	6097 (1)	56 (1)
C(21)	2561 (3)	9282 (2)	8305 (2)	34 (1)
C(22)	3893 (4)	10190 (2)	8155 (2)	42 (1)
C(23)	3398 (4)	11303 (2)	7586 (2)	46 (1)
C(24)	1562 (4)	11532 (2)	7154 (2)	41 (1)
C(25)	185 (4)	10654 (2)	7297 (2)	41 (1)
C(26)	706 (3)	9546 (2)	7862 (2)	40 (1)
O(24)	1128 (3)	12647 (1)	6600 (1)	55 (1)
O(90)	−1760 (4)	12786 (2)	5457 (2)	97 (1)
C(90)	−1595 (6)	11990 (3)	4653 (2)	80 (1)
C(91)	−3430 (7)	11262 (4)	4847 (3)	102 (2)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and geometrical hydrogen-bonding parameters* (Å,°) *with e.s.d.'s in parentheses*

	Compound (1)	Compound (2)
C(1)—C(2)	1·541 (4)	1·550 (3)
C(1)—C(6)	1·542 (4)	1·545 (3)
C(1)—C(11)	1·543 (3)	1·540 (4)
C(1)—C(21)	1·550 (3)	1·539 (3)
C(2)—C(3)	1·524 (5)	1·528 (3)
C(3)—C(4)	1·527 (6)	1·517 (4)
C(4)—C(5)	1·510 (6)	1·515 (3)
C(5)—C(6)	1·533 (5)	1·524 (3)
C(11)—C(12)	1·396 (6)	1·394 (3)
C(11)—C(16)	1·391 (5)	1·386 (3)
C(12)—C(13)	1·386 (5)	1·380 (4)
C(13)—C(14)	1·384 (5)	1·374 (4)
C(14)—C(15)	1·365 (5)	1·377 (3)
C(14)—O(14)	1·374 (4)	1·382 (3)
C(15)—C(16)	1·393 (5)	1·388 (4)
C(21)—C(22)	1·390 (5)	1·387 (3)
C(21)—C(26)	1·382 (6)	1·389 (3)
C(22)—C(23)	1·387 (4)	1·390 (3)
C(23)—C(24)	1·377 (6)	1·370 (4)
C(24)—C(25)	1·380 (5)	1·383 (4)
C(24)—O(24)	1·371 (3)	1·374 (3)
C(25)—C(26)	1·394 (4)	1·385 (3)
O(90)—C(90)		1·419 (4)
C(90)—C(91)		1·488 (6)
C(11)—C(1)—C(21)	106·1 (2)	107·5 (2)
C(6)—C(1)—C(21)	111·5 (2)	111·4 (2)
C(6)—C(1)—C(11)	110·5 (2)	110·5 (2)
C(2)—C(1)—C(21)	112·2 (2)	108·2 (2)
C(2)—C(1)—C(11)	110·1 (2)	113·0 (2)
C(2)—C(1)—C(6)	106·5 (2)	106·4 (2)
C(1)—C(2)—C(3)	114·0 (3)	113·9 (2)
C(2)—C(3)—C(4)	111·2 (3)	111·2 (2)
C(3)—C(4)—C(5)	110·7 (3)	110·8 (2)
C(4)—C(5)—C(6)	111·4 (3)	111·4 (2)
C(1)—C(6)—C(5)	113·1 (3)	112·8 (2)
C(1)—C(11)—C(16)	122·4 (3)	123·0 (2)
C(1)—C(11)—C(12)	121·2 (2)	120·4 (2)
C(12)—C(11)—C(16)	116·3 (3)	116·5 (2)
C(11)—C(12)—C(13)	122·3 (4)	122·1 (2)
C(12)—C(13)—C(14)	119·3 (3)	119·8 (2)
C(13)—C(14)—O(14)	117·7 (3)	118·4 (2)
C(13)—C(14)—C(15)	120·2 (3)	120·0 (3)
C(15)—C(14)—O(14)	122·1 (3)	121·6 (2)
C(14)—C(15)—C(16)	120·0 (4)	119·4 (3)
C(11)—C(16)—C(15)	121·9 (4)	122·2 (2)
C(1)—C(21)—C(26)	121·8 (2)	119·3 (2)
C(1)—C(21)—C(22)	121·7 (3)	124·0 (2)
C(22)—C(21)—C(26)	116·3 (3)	116·6 (2)
C(21)—C(22)—C(23)	122·0 (4)	121·6 (3)
C(22)—C(23)—C(24)	120·3 (3)	120·3 (3)
C(23)—C(24)—O(24)	117·8 (3)	118·5 (2)
C(23)—C(24)—C(25)	119·3 (3)	119·7 (3)
C(25)—C(24)—O(24)	122·9 (3)	121·8 (2)
C(24)—C(25)—C(26)	119·3 (3)	119·3 (3)
C(21)—C(26)—C(25)	122·7 (4)	122·4 (2)
O(90)—C(90)—C(91)		111·7 (3)

Compound (1)			
O(14)···O(24^{i})	2·715 (4)	O(14)—H(14)···O(24^{i})	175 (3)
O(24)···O(99^{ii})	2·617 (6)	O(24)—H(24)···O(99^{ii})	177 (4)
O(99)···O(14^{iii})	2·768 (5)	O(99)—H(991)···O(14^{iii})	135 (3)

Symmetry code: (i) $x + 1, y, z$; (ii) $x, y - 1, z$; (iii) $x - 1, y, z$.

Compound (2)			
O(14^{i})···O(24)	2·706 (2)	O(14^{i})—H(14^{i})···O(24)	170 (3)
O(24)···O(90)	2·588 (3)	O(24)—H(24)···O(90)	174 (3)
O(90)··O(14^{ii})	2·774 (3)	O(90)—H(90)···O(14^{ii})	176 (2)

Symmetry code: (i) $x, y + 1, z$; (ii) $x - 1, y + 1, z$.

methods on *F*, *SHELX*76 (Sheldrick, 1976). Non-hydrogen atoms were refined anisotropically, hydrogen atoms isotropically using a riding model, with C—H = 1·0 Å, except for the hydroxy hydrogens. The O—H lengths of the hydroxy groups of the host and guest molecules were constrained to values chosen as representing the typical hydrogen-bonding geometry extrapolated from a graph depicting O—H *versus* O···O distances (Shuster, Zundel & Sandorfy, 1976). The weighting scheme was $w^{-1} = \sigma^2(F) + 0{\cdot}002(F)^2$. The final R value was 0·036 for 207 parameters, $wR = 0{\cdot}039$, $S = 0{\cdot}94$, max. shift/e.s.d. = 0·01, max. $\Delta\rho$ was within $\pm 0{\cdot}20$ e Å^{-3}. Atomic scattering factors for non-hydrogen atoms were from Cromer & Mann (1968), for hydrogen atoms from Stewart, Davidson & Simpson (1965). Molecular parameters were obtained from *PARST* (Nardelli, 1983) and drawings with *PLUTO* (Motherwell, 1974). Computations were carried out on the VAX/VMS (version 4.7) system of the University of Cape Town's Computer Centre.

Compound (2). A 0·47 × 0·28 × 0·25 mm crystal was sealed in a glass capillary surrounded by mother liquor. Data collection, structure solution and refinement were as for (1) with the following differences. 3235 reflections were measured, 2729 were unique ($R_{\rm int}$ = 0·014, index ranges h − 7 to 7, k − 12 to 12, l 0 to 15), 2172 were observed. Refinement to R = 0·049, wR = 0·058, 227 parameters, S = 1·01, max. shift/e.s.d. = 0·01, max. $\Delta\rho$ was within ± 0·27 e Å^{-3}.

Discussion. Final fractional atomic coordinates for compounds (1) and (2) are listed in Table 1.* Bond lengths and angles, which are in agreement with literature values (Tanaka *et al.*, 1984; Shin *et al.*, 1987, Toda *et al.*, 1985) are listed in Table 2. Perspective views of the host molecule with its associated guest are shown in Figs. 1(*a*) and 1(*b*) for compounds (1) and (2) respectively. Torsional asymmetry parameters (Duax & Norton, 1975) show that, in both crystal structures, the host cyclohexane ring has its preferred highly symmetrical chair conformation. All asymmetry parameters are below 3·5. Rotational symmetry dominates. In structure (1), ΔC_2^{2-3} = 0·81, ΔC_s^1 = 0·84 and ΔC_2^{1-2} = 2·58. The average dihedral angle in this ring is 55·70 (7)°. In structure (2), ΔC_2^{2-3} = 0·87, ΔC_s^1 = 1·77 and ΔC_2^{1-2} = 3·20. The average of the dihedral angles in the ring is 55·90 (7)°. In both structures the individual aromatic rings of the two phenol substituents are planar to within 0·01 Å and make dihedral angles of 79·70 (7)° with respect to each other in structure (1) and 85·23 (7)° in structure (2).

Stereoscopic views of the crystal packing of both structures are shown in Figs. 2(*a*) and 2(*b*). The host–guest intermolecular interactions form an extensive triangular-shaped hydrogen-bonding arrangement. In structure (1) the hydroxyl group

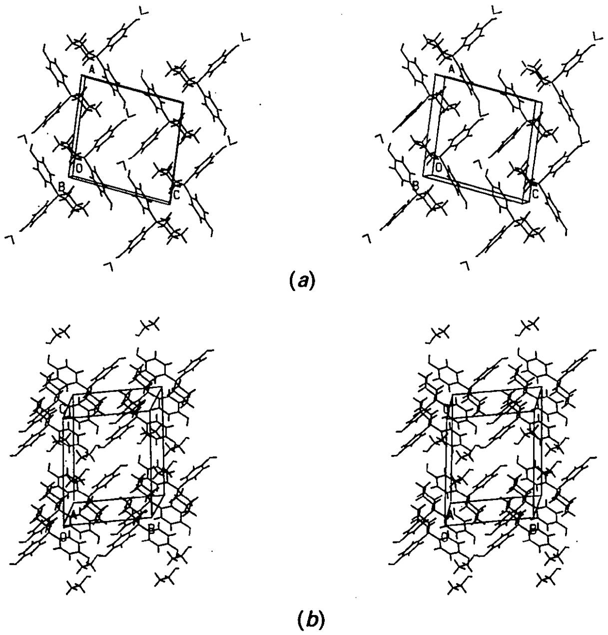

Fig. 1. Host–guest arrangements of structures (*a*) (1) and (*b*) (2), with atomic nomenclature.

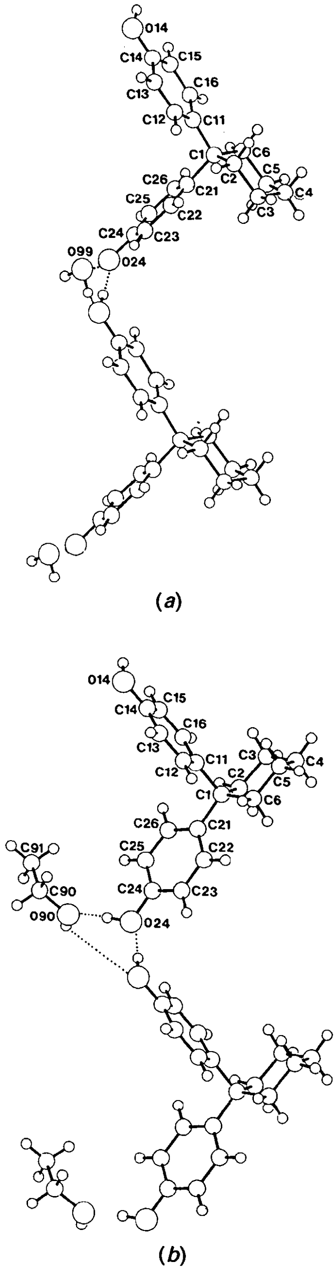

Fig. 2. Packing of structures (*a*) (1) and (*b*) (2).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53210 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

O(14) donates its proton H(14) to the neighbouring host O(24) hydroxyl oxygen atom. This oxygen atom in turn donates its proton, H(24) to the acceptor oxygen O(99) of the water guest molecule. The water proton H(991) is then donated to the hydroxy oxygen atom of the adjacent host O(14) atom. Both structures show a remarkable similarity in the complexation of their guest molecules, the host-to-guest interactions being dominated by the triangular arrangement of O—H···O=C hydrogen bonds (detailed in Table 2). The O···O distances, and hence their strengths of interaction are similar in both structures. In both structures the O(guest)···O(24)(host) interaction is particularly strong.

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Structure of an Antipyrine–Monophosphoric Acid Complex

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Abstract. 1,2-Dihydro-1,5-dimethyl-2-phenyl-3*H*-pyrazol-3-one–phosphoric acid (2/1), $2C_{11}H_{12}N_2O.H_3PO_4$, $M_r = 474{\cdot}454$, monoclinic, $C2/c$, $a = 25{\cdot}14\ (2)$, $b = 11{\cdot}393\ (7)$, $c = 18{\cdot}55\ (2)$ Å, $\beta = 116{\cdot}07\ (7)°$, $V = 4773\ (15)$ Å^3, $Z = 8$, $D_x = 1{\cdot}321$ Mg m^{-3}, $\lambda(\text{Ag}\ K\alpha) = 0{\cdot}5608$ Å, $\mu = 0{\cdot}095$ mm^{-1}, $F(000) = 2000$, room temperature, final $R = 0{\cdot}053$ for 2859 reflections. The main building unit of this arrangement is a centrosymmetrical complex (antipyrine)$_4$(H_3PO_4)$_2$ made up of a central cluster of two H_3PO_4 groups connected by hydrogen bonds to four neighbouring antipyrine molecules. The hydrogen-bond scheme is described.

Introduction. This work is part of an investigation of the interactions of phosphoric acids with various organic compounds: amines, amino alcohols and amino acids. The present work is the first study of such an interaction with an organic molecule containing a ketone function.

Experimental. The present compound is readily prepared by the action of monophosphoric acid on an aqueous solution of antipyrine at room temperature. By slow evaporation, at room temperature, of such a solution corresponding to the stoichiometry antipyrine/H_3PO_4 = 2, large stout monoclinic prisms (up to 25 mm) can be grown within 2–3 weeks.

Crystal size: 0·40 × 0·40 × 0·32 mm. Density not measured. Nonius CAD-4 diffractometer, graphite monochromator. 21 reflections ($10{\cdot}0 < \theta < 13{\cdot}5°$) for refining unit-cell dimensions. $\omega/2\theta$ scan, scan width 1·20°, scan speed 0·02° s^{-1}. Total background measuring time: 28 s. θ range: $2 < \theta < 35°$, $\pm h,k,l$, $h_{\max} = 42$, $k_{\max} = 16$, $l_{\max} = 27$.

Two orientation and intensity control reflections, $\overline{16},\bar{6},7$ and $\bar{1}7\bar{4}$, were measured every 3 h without any significant variation. 3958 reflections were obtained after averaging Friedel pairs ($R_{\text{int}} = 0{\cdot}04$). Lorentz and polarization corrections, no absorption correction.