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Hydrogen Bonding in Diphenylmethanols, RCPh$_2$OH: Structures of Monomeric (4-Biphenyl)diphenylmethanol and Diphenyl(2-pyridyl)methanol, Dimeric 1,1,3-Triphenylpropyn-1-ol, Trimeric 2-Methyl-1,1-diphenylpropan-1-ol, Tetrameric Diphenyl(2-thienyl)methanol, Hexameric Bis(pentafluorophenyl)methanol (at 293 and 173 K) and Polymeric Diphenylmethanol

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Abstract

(4-Biphenyl)diphenylmethanol (1), $C_{25}H_{20}O$, orthorhombic, $P2_12_12_1$, $a = 8.3580(11)$, $b = 13.8976(17)$, $c = 15.5915(12)$ Å, $Z = 4$, $R = 0.032$ for 1146 observations [$I > 3\sigma(I)$]: the structure contains isolated monomers with no hydrogen bonding. Diphenyl(2-pyridyl)methanol (2), $C_{18}H_{15}NO$, monoclinic, $P2_1/c$, $a = 8.1899(8)$, $b = 14.855(2)$, $c = 11.6069(15)$ Å, $\beta = 96.344(8)°$, $Z = 4$, $R = 0.049$ for 879 observations [$I > 3\sigma(I)$]: the structure consists of isolated monomers in which the intramolecular O—H···N hydrogen-bond motif has graph set $S(5)$. 1,1,3-Triphenylpropyn-1-ol (3), $C_{21}H_{16}O$, monoclinic, $P2_1/c$, $a = 5.9794(12)$, $b = 9.953(3)$, $c = 26.420(3)$ Å, $\beta = 91.365(12)°$, $Z = 4$, $R = 0.039$ for 971 observations [$I > 2\sigma(I)$]: the structure contains centrosymmetric dimers held together by O—H···π(arene) hydrogen bonds involving one of the phenyl groups, rather than the propargyl group. 2-Methyl-1,1-diphenylpropan-1-ol (4), $C_{16}H_{18}O$, trigonal, $P31c$, $a = 13.9232(17)$, $c = 12.0200(19)$ Å, $Z = 6$, $R = 0.031$ for 763 observations [$I > 3\sigma(I)$]: the structure consists of cyclic hydrogen-bonded trimers with crystallographic threefold symmetry and disordered hydroxyl H atoms in a motif with graph set $R_3^3(6)$: the O···O distance in the trimers is 2.864 (7) Å. Diphenyl(2-thienyl)methanol (5), $C_{17}H_{14}OS$, rhombohedral, $R\bar{3}$, $a = 19.20(1)$, $c = 26.48(1)$ Å, $Z = 24$: this compound is isomorphous and isostructural with triphenylmethanol, Ph$_3$COH, and forms hydrogen-bonded tetrahedral tetramers. Bis(pentafluorophenyl)methanol (6), $C_{13}H_2F_{10}O$, rhombohedral, $R\bar{3}$, $a = 26.113(3)$, $c = 9.788(3)$ Å (at 293 K), $R = 0.068$ for 1214 observations [$I > 2\sigma(I)$]; $a = 26.006(4)$, $c = 9.5941(11)$ Å (at 173 K), $R = 0.072$ for 1889 observations [$I > 2\sigma(I)$], $Z = 18$; the structure consists of coaxial stacks of cyclic hydrogen-bonded hexamers, each of $\bar{3}$ symmetry, and with a hydrogen-bond motif of graph set $R_6^6(12)$. Within the hexamers, the molecules are disordered over two orientations in the ratio 0.779 (3):0.221 (3) at 293 K and 0.776 (2):0.224 (2) at 173 K: the O···O distance is 2.702 (4) Å at 293 K and 2.683 (4) Å at 173 K. Diphenylmethanol (7), $C_{13}H_{12}O$, orthorhombic, $P22_12_1$, $a = 5.1300(10)$, $b = 18.650(5)$, $c = 21.168(6)$ Å, $Z = 8$, $R = 0.035$ for 1487 observations [$I > 3\sigma(I)$]: there are two molecules in the asymmetric unit and the molecules are linked by hydrogen bonds into spiral chains having graph set $C(4)$ and lying parallel to the a-axis; the O···O distances within the chains are 2.826 (3) and 2.878 (3) Å.

Introduction

Substituted diphenylmethanols RCPh$_2$OH exhibit a very wide range of hydrogen-bonding patterns. When the substituent R is a hydrocarbon group containing no other functionality, both intra- and intermolecular hydrogen bonding can occur. Thus, when $R = C_2H_5$, the hydrogen bonding is intramolecular, of O—H···π(arene) type, and the compound C_2H_5CPh$_2$OH is monomeric (Sultanov, Shnulin & Mamedov, 1985*a*), while (Ph$_2$C=CHCMe$_2$CH$_2$)CPh$_2$OH forms monomers containing intramolecular hydrogen bonds of OH···π(C=C) type involving the C=C double bond in the R substituent (Zimmerman & Zuraw, 1989). (PhCH$_2$)CPh$_2$OH forms dimers containing two OH···π(arene) hydrogen bonds (Ferguson, Gallagher, Glidewell & Zakaria, 1994), while (ferrocenyl)CPh$_2$OH forms dimers containing two O—H···O hydrogen bonds (Ferguson, Gallagher, Glidewell & Zakaria, 1993). Tetramers based on

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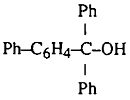
O—H···O hydrogen bonds are formed when $R = CH_3$ or Ph; CH_3CPh_2OH forms cyclic tetramers of S_4 symmetry (Sultanov, Shnulin & Mamedov, 1985*b*), while $PhCPh_2OH$ (*i.e.* Ph_3COH) forms tetrahedral tetramers (Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992).

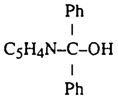
On the other hand, if the substituent *R* in $RCPh_2OH$ contains potential hydrogen-bond acceptors such as F, O or N atoms, different hydrogen-bonding patterns can then occur. Such compounds may crystallize as monomers with intramolecular hydrogen bonds (McClure & Schlemper, 1978; Tacke, Strecker, Sheldrick, Ernst, Heeg, Berndt, Knapstein & Niedner, 1980; Tacke, Lange, Sheldrick, Lambrecht, Moser & Mutschler, 1983) as dimers which may contain hydrogen bonds either of type O—H···N (Pyshnograeva, Setkina, Batsanov & Struchkov, 1985; Armesto, Barnes, Horspool & Langa, 1990) or of O—H···F type (DesMarteau, Xu & Witz, 1992), as single chains (Lindner & von Gross, 1973; Lewis, Duesler, Kress, Curtin & Paul, 1980; Glidewell & Ferguson, 1994), as double chains (Stora, 1971; Katritzky, Fan, Koziol & Palenik, 1987), or as infinite two-dimensional nets (Lewis, Curtin & Paul, 1979).

As part of a further systematic study of the structures of both functionalized and unfunctionalized diphenylmethanols $RCPh_2OH$, we have now determined the structures of (4-biphenyl)diphenylmethanol, $4\text{-}PhC_6H_4CPh_2OH$ (1) and diphenyl(2-pyridyl)methanol, $(2\text{-}C_5H_4N)CPh_2OH$ (2), which both prove to be monomeric in the solid state; 1,1,3-triphenylpropyn-1-ol, $PhC{\equiv}CCPh_2OH$ (3), which is dimeric; 1,1-diphenyl-2-methylpropan-1-ol, $(CH_3)_2CHCPh_2OH$ (4), which is trimeric; diphenyl(2-thienyl)methanol, $C_4H_3SCPh_2OH$ (5), which is isomorphous with triphenylmethanol and hence forms tetramers; bis(pentafluorophenyl)methanol, $HC(C_6F_5)_2OH$ (6), which is hexameric in the solid state; and the parent compound diphenylmethanol, $HCPh_2OH$ (7), which crystallizes in the form of extended polymer chains.



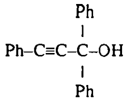
$\mathrm{Ph{-}C_6H_4{-}\underset{Ph}{\overset{Ph}{C}}{-}OH}$

(1)



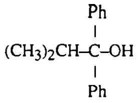
$\mathrm{C_5H_4N{-}\underset{Ph}{\overset{Ph}{C}}{-}OH}$

(2)



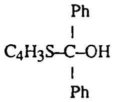
$\mathrm{Ph{-}C{\equiv}C{-}\underset{Ph}{\overset{Ph}{C}}{-}OH}$

(3)



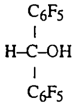
$\mathrm{(CH_3)_2CH{-}\underset{Ph}{\overset{Ph}{C}}{-}OH}$

(4)



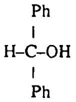
$\mathrm{C_4H_3S{-}\underset{Ph}{\overset{Ph}{C}}{-}OH}$

(5)



$\mathrm{H{-}\underset{C_6F_5}{\overset{C_6F_5}{C}}{-}OH}$

(6)



$\mathrm{H{-}\underset{Ph}{\overset{Ph}{C}}{-}OH}$

(7)

Experimental

Synthesis

(1), (2), (4) and (5) were prepared by reaction of phenyl-lithium with 4-benzoylbiphenyl, 2-benzoylpyridine, isobutyrophenone and 2-benzoylthiophene, respectively. ^{13}C NMR spectra ($CDCl_3$ solution): (1) 81.9 (*s*), 126.6 (*d*), 127.0 (*d*), 127.3 (*d*), 127.9_1 (*d*), 127.9_3 (*d*), 128.0 (*d*), 128.4 (*d*), 128.7 (*d*), 140.0 (*s*), 140.6 (*s*), 145.9 (*s*), 146.8 (*s*); (2) 80.9 (*s*), 122.3 (*d*), 122.9 (*d*), 127.3 (*d*), 127.9 (*d*), 128.2 (*d*), 136.4 (*d*), 146.1 (*s*), 147.8 (*d*), 163.3 (*s*); (4) 18.0 (*q*), 35.8 (*d*), 81.3 (*s*), 126.6 (*d*), 127.1 (*d*), 128.9 (*d*), 147.4 (*s*); (5) 80.1 (*s*), 125.6 (*d*), 126.5 (*d*), 126.9 (*d*), 127.2 (*d*), 127.7 (*d*), 128.4 (*d*), 146.6 (*s*), 153.3 (*s*). Samples of (3), (6) and (7) were obtained from Aldrich. Crystals of (1)–(7) were grown by slow evaporation of solutions in nitromethane, (1) and (7); diethyl ether, (2); methanol, (3) and (6); light petroleum (b.p. 313–333 K), (4) and (5).

Data collection, structure solution and refinement

Details of cell data, data collection and refinement are summarized in Table 1.* For (1), the space group was uniquely determined as $P2_12_12_1$ from the systematic absences ($h00$ absent if $h = 2n + 1$; $0k0$ absent if $k = 2n + 1$; $00l$ absent if $l = 2n + 1$); for (2) and (3), the space group $P2_1/c$ was uniquely determined from the systematic absences ($h0l$ absent if $l = 2n + 1$; $0k0$ absent if $k = 2n + 1$); for (4), the systematic absences ($hh2\bar{h}l$ absent if $l = 2n + 1$) permit the space group to be either $P31c$ or $P\bar{3}1c$. The former was chosen on the basis of the likely density of the compound, and confirmed by the analysis. For both (5) and (6), the conditions governing the reflection (hkl present only when $-h + k + l = 3n$) and Laue symmetry $\bar{3}$ allow the space group to be $R3$ or $R\bar{3}$. $R\bar{3}$ was in each case indicated by the *E* statistics and confirmed by the analysis. For (7), the space group was uniquely determined as $P22_12_1$ from the systematic absences ($0k0$ absent if $k = 2n + 1$; $00l$ absent if $l = 2n + 1$). All structures were solved by direct methods (Gabe, Le Page, Charland, Lee & White, 1989). In all structures, H atoms were all clearly visible in difference maps at intermediate stages of refinement. H atoms bonded to carbon were positioned on geometric grounds (C—H, 0.95 Å) and coordinates for hydroxyl H atoms were obtained from difference maps; all H atoms were included in the refinements as riding atoms. In the refinement of (4), the hydroxyl H atoms were disordered equally over two sites, as established from a difference map. In the refinement of (6), the C_6F_5 groups in the minor orientation were constrained to have planar rings

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* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB0331). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Summary of crystal data, data collection and refinement details*

	(1)	(2)	(3)	(4)	(6*a*)	(6*b*)	(7)
(*a*) Crystal data							
Empirical formula	$C_{25}H_{20}O$	$C_{18}H_{15}NO$	$C_{21}H_{16}O$	$C_{16}H_{18}O$	$C_{13}H_2F_{10}O$	$C_{13}H_2F_{10}O$	$C_{13}H_{12}O$
Molar mass	336.43	261.32	284.35	226.32	364.15	364.15	184.24
Colour, habit	Colourless, block	Colourless, plate	Colourless, needle	Colourless, needle	Colourless, rhomb	Colourless, rhomb	Colourless, plate
Crystal size (mm)	0.35 × 0.32 × 0.25	0.39 × 0.39 × 0.11	0.28 × 0.14 × 0.10	0.35 × 0.25 × 0.22	0.35 × 0.35 × 0.35	0.30 × 0.30 × 0.30	0.38 × 0.34 × 0.19
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Trigonal	Trigonal	Trigonal	Orthorhombic
a (Å)	8.3580 (11)	8.1899 (8)	5.9794 (12)	13.9232 (17)	26.113 (3)	26.006 (4)	5.1300 (10)
b (Å)	13.8976 (17)	14.855 (2)	9.953 (3)	13.9232 (17)	26.113 (3)	26.006 (4)	18.650 (5)
c (Å)	15.5915 (12)	11.6069 (15)	26.420 (3)	12.0200 (19)	9.788 (3)	9.5941 (11)	21.168 (6)
α (°)	90	90	90	90	90	90	90
β (°)	90	96.344 (8)	91.365 (12)	90	90	90	90
γ (°)	90	90	90	120	120	120	90
V (Å^3)	1811.0 (4)	1403.5 (3)	1571.9 (5)	2018.0 (4)	5780 (2)	5619 (1)	2025 (1)
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P31c$	$R\bar{3}$	$R\bar{3}$	$P22_12_1$
Z	4	4	4	6	18	18	8
$F(000)$	712	552	600	732	3204	3204	784
d_{calc} (g cm^{-3})	1.234	1.237	1.202	1.117	1.883	1.937	1.208
μ (mm^{-1})	0.07	0.07	0.07	0.06	0.22	0.22	0.07
(*b*) Data acquisition*							
Temperature (K)	293	293	293	293	293	173	293
Unit-cell reflections (2θ range°)	25 (24–39)	25 (21–39)	25 (21–37)	24 (19–24)	25 (19–24)	25 (10–50)	23 (30–39)
$2\theta_{max}$ (°) for reflections	53.8	49.7	49.8	53.7	53.7	59.9	49.9
hkl range of reflections	0–10; 0–17; 0–19	−9–9; 0–17; 0–13	−7–7; 0,11; 0–31	0–15; 0–15; 0–15	−33–33; 0–33; 0–12	0–36; −40–0; 0–13	0–6; 0–22; 0–25
Decay in 3 standard reflections (%)	<1	<1	<1	13	12	<1	<1
Reflections measured	2246	2614	3020	4619	3676	3956	2090
Unique reflections	2246	2432	2750	1474	2262	3641	2090
R_{int}	–	0.028	0.012	0.013	0.017	0.035	–
Reflections with $I > n\sigma(I), n$	1146, 3.0	879, 3.0	971, 2.0	763, 3.0	1214, 2.0	1889, 2.0	1487, 3.0
(*c*) Refinement†							
Refinement on	F	F	F^2	F	F^2	F^2	F
No. of variables in LS	236	181	217	154	257	257	253
k in $w = 1/(\sigma^2F_o + kF_o^2)$	0.0008	0.0008	0.0	0.0008	0.0	0.0	0.0008
R, wR, g.o.f.	0.032, 0.040, 1.09	0.049, 0.058, 1.46	0.039, 0.069, 1.17	0.031, 0.040, 1.13	0.068, 0.238, 1.09	0.072, 0.208, 1.03	0.035, 0.052, 1.61
Density range in final Δ-map (e Å^{-3})	−0.12, 0.10	−0.15, 0.16	−0.12, 0.11	−0.09, 0.08	−0.27, 0.23	−0.28, 0.35	−0.14, 0.01
Final shift/error ratio	0.000	0.000	0.007	0.000	0.002	0.000	0.001

* Data collection on an Enraf–Nonius CAD-4 diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å).

† All calculations were done on a Silicon Graphics 4D-35TG computer system with the *NRCVAX* system of programs (Gabe, Le Page, Charland, Lee & White, 1989) for refinement on F, and *SHELXL93* (Sheldrick, 1993) for refinement on F^2. The R-values are for observed data. The wR-values are for observed data where the refinement was on F, and for all data where the refinement was on F^2.

with C—C 1.37 and C—F 1.34 Å, and all bond angles 120.0°, and the site occupation factors for the two orientations were refined. The diagrams were prepared using *ORTEP*II (Johnson, 1976). Final fractional coordinates are presented in Table 2 and selected dimensions in Table 3. No attempt was made to determine the absolute configurations of compounds crystallizing in chiral space groups.

Results and discussion

Structures and molecular packing

Structures showing no O—H···O *hydrogen bonding.* (1) and (2) are both monomeric in the solid state. Crystals of (1) are orthorhombic, with the non-centrosymmetric space group $P2_12_12_1$: the structure comprises isolated molecules (Fig. 1) with no hydrogen bonding, either inter- or intramolecular (Fig. 2). In the solid state the molecules of (1) are chiral (Fig. 1), although effective (or averaged) mirror symmetry is observed in solution. The molecular packing (Fig. 2) is dominated by antiparallel strings of molecules along the *b*-direction: the action of the 2_1 screw axes ensures that there are no close O···O contacts. In (2), the N atom in the pyridyl ring provides a potential hydrogen-bond acceptor site in addition to the hydroxyl O atom. This compound crystallizes in the centrosymmetric monoclinic space group $P2_1/c$, and the molecular structure is such that the 2-pyridyl ring is oriented with N12 rather than C16, nearer to the oxygen; similarly, the hydroxyl H atom is directed towards the N atom of the pyridyl substituent R, rather than away from the substituent R as in (1). Thus, rather than forming centrosymmetric dimers *via* intermolecular O—H···N hydrogen bonds, the compound crystallizes as isolated molecules containing an intramolecular O—H···N hydrogen bond (Fig. 3). The molecules are arranged in pairs about centres of inversion (Fig. 4): the closest

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
(1)				
O1	0.9564 (3)	0.56095 (17)	0.32603 (17)	0.0563 (14)
C1	0.8819 (4)	0.6386 (2)	0.2784 (2)	0.0428 (18)
C11	0.7846 (4)	0.5970 (2)	0.2041 (2)	0.0414 (17)
C12	0.8327 (5)	0.5131 (2)	0.1636 (3)	0.056 (2)
C13	0.7481 (6)	0.4763 (3)	0.0942 (3)	0.071 (3)
C14	0.6159 (6)	0.5231 (3)	0.0647 (2)	0.066 (3)
C15	0.5669 (5)	0.6054 (3)	0.1032 (2)	0.063 (2)
C16	0.6489 (4)	0.6418 (3)	0.1735 (2)	0.052 (2)
C21	0.7762 (4)	0.6960 (2)	0.34033 (19)	0.0397 (17)
C22	0.6566 (4)	0.6480 (3)	0.3849 (2)	0.054 (2)
C23	0.5621 (5)	0.6951 (3)	0.4437 (2)	0.063 (2)
C24	0.5830 (5)	0.7908 (4)	0.4586 (2)	0.063 (2)
C25	0.6990 (5)	0.8399 (3)	0.4148 (2)	0.063 (2)
C26	0.7965 (4)	0.7927 (3)	0.3556 (2)	0.050 (2)
C31	1.0221 (4)	0.6989 (2)	0.2444 (2)	0.0397 (17)
C32	1.1615 (4)	0.7069 (3)	0.2907 (2)	0.0472 (19)
C33	1.2882 (4)	0.7625 (3)	0.2623 (2)	0.0479 (19)
C34	1.2809 (4)	0.8105 (2)	0.1839 (2)	0.0416 (17)
C35	1.1395 (4)	0.8025 (3)	0.1381 (2)	0.050 (2)
C36	1.0117 (4)	0.7488 (3)	0.1679 (2)	0.0508 (19)
C41	1.4211 (4)	0.8652 (2)	0.1514 (2)	0.0449 (18)
C42	1.5212 (4)	0.9142 (3)	0.2073 (2)	0.051 (2)
C43	1.6567 (5)	0.9599 (3)	0.1784 (3)	0.065 (2)
C44	1.6937 (5)	0.9594 (3)	0.0928 (3)	0.074 (3)
C45	1.5957 (5)	0.9130 (3)	0.0369 (3)	0.071 (3)
C46	1.4587 (5)	0.8662 (3)	0.0643 (2)	0.058 (2)
(2)				
O1	0.6805 (5)	0.9544 (3)	0.1351 (3)	0.065 (3)
C1	0.6144 (7)	0.9629 (4)	0.2443 (5)	0.046 (4)
C11	0.4299 (8)	0.9749 (4)	0.2201 (5)	0.048 (4)
N12	0.3619 (7)	0.9396 (4)	0.1200 (5)	0.070 (4)
C13	0.1991 (11)	0.9463 (6)	0.0952 (7)	0.082 (6)
C14	0.0974 (10)	0.9842 (7)	0.1664 (9)	0.094 (7)
C15	0.1710 (11)	1.0224 (6)	0.2675 (8)	0.088 (6)
C16	0.3365 (9)	1.0178 (5)	0.2945 (6)	0.068 (5)
C21	0.6539 (8)	0.8749 (4)	0.3124 (5)	0.048 (4)
C22	0.7811 (9)	0.8226 (5)	0.2872 (6)	0.057 (4)
C23	0.8222 (9)	0.7448 (5)	0.3482 (7)	0.071 (5)
C24	0.7362 (11)	0.7202 (5)	0.4378 (7)	0.074 (5)
C25	0.6106 (10)	0.7719 (6)	0.4662 (6)	0.073 (5)
C26	0.5686 (9)	0.8498 (5)	0.4041 (6)	0.061 (4)
C31	0.6946 (8)	1.0447 (4)	0.3029 (5)	0.049 (4)
C32	0.6844 (10)	1.1256 (5)	0.2453 (7)	0.077 (5)
C33	0.7534 (12)	1.2002 (6)	0.2946 (9)	0.101 (7)
C34	0.8400 (10)	1.2001 (6)	0.4036 (8)	0.087 (6)
C35	0.8520 (9)	1.1200 (5)	0.4610 (6)	0.069 (5)
C36	0.7816 (8)	1.0427 (5)	0.4131 (5)	0.056 (4)
(3)				
O1	0.2999 (3)	0.0294 (2)	0.40658 (7)	0.0568 (5)
C1	0.5134 (4)	−0.0242 (2)	0.39348 (8)	0.0416 (6)
C2	0.6693 (4)	0.0895 (2)	0.38561 (8)	0.0460 (7)
C3	0.7822 (4)	0.1854 (3)	0.37968 (8)	0.0472 (7)
C11	0.4757 (4)	−0.1002 (2)	0.34379 (9)	0.0421 (6)
C12	0.2794 (5)	−0.0911 (3)	0.31559 (11)	0.0665 (8)
C13	0.2487 (7)	−0.1633 (4)	0.27178 (13)	0.0906 (11)
C14	0.4112 (7)	−0.2484 (4)	0.25552 (12)	0.0901 (12)
C15	0.6094 (7)	−0.2576 (3)	0.28245 (11)	0.0862 (11)
C16	0.6401 (5)	−0.1831 (3)	0.32613 (10)	0.0679 (8)
C21	0.5921 (4)	−0.1196 (2)	0.43514 (8)	0.0368 (6)
C22	0.4453 (4)	−0.2179 (2)	0.45097 (9)	0.0506 (7)
C23	0.5056 (5)	−0.3084 (3)	0.48825 (9)	0.0586 (8)
C24	0.7165 (5)	−0.3022 (3)	0.51052 (9)	0.0578 (7)
C25	0.8649 (5)	−0.2059 (3)	0.49528 (9)	0.0534 (7)
C26	0.8033 (4)	−0.1152 (2)	0.45740 (8)	0.0451 (7)
C31	0.9121 (4)	0.3057 (2)	0.37299 (8)	0.0417 (6)
C32	0.8390 (5)	0.4261 (3)	0.39295 (9)	0.0578 (7)
C33	0.9636 (6)	0.5421 (3)	0.38742 (10)	0.0704 (9)
C34	1.1574 (6)	0.5389 (3)	0.36114 (10)	0.0704 (9)
C35	1.2300 (5)	0.4210 (3)	0.34128 (10)	0.0647 (8)
C36	1.1105 (4)	0.3054 (3)	0.34725 (9)	0.0532 (7)

Table 2 (*cont.*)

	x	*y*	*z*	U_{eq}
(4)				
O1	0.54263 (18)	0.3220 (2)	0.0	0.0650 (18)
C1	0.4420 (2)	0.3209 (3)	0.0306 (4)	0.048 (2)
C2	0.4026 (3)	0.2637 (3)	0.1439 (4)	0.053 (2)
C3	0.3623 (3)	0.1399 (3)	0.1393 (4)	0.072 (3)
C4	0.4906 (4)	0.3179 (4)	0.2349 (4)	0.076 (3)
C11	0.4678 (2)	0.4416 (3)	0.0294 (4)	0.050 (2)
C12	0.5324 (3)	0.5109 (3)	−0.0561 (4)	0.064 (3)
C13	0.5562 (4)	0.6198 (4)	−0.0602 (4)	0.080 (3)
C14	0.5151 (4)	0.6607 (3)	0.0176 (5)	0.083 (4)
C15	0.4504 (4)	0.5940 (4)	0.1010 (5)	0.082 (4)
C16	0.4268 (3)	0.4850 (3)	0.1082 (4)	0.067 (3)
C21	0.3550 (3)	0.2571 (3)	−0.0588 (4)	0.054 (2)
C22	0.3754 (3)	0.2101 (3)	−0.1499 (4)	0.066 (3)
C23	0.2937 (5)	0.1496 (3)	−0.2263 (4)	0.089 (4)
C24	0.1895 (5)	0.1358 (4)	−0.2138 (6)	0.103 (4)
C25	0.1672 (4)	0.1831 (4)	−0.1243 (6)	0.094 (4)
C26	0.2491 (3)	0.2440 (3)	−0.0478 (5)	0.071 (3)
(6*a*)				
O1	0.21915 (12)	0.63666 (10)	0.1482 (3)	0.0955 (9)
C1	0.1926 (2)	0.6458 (2)	0.0258 (4)	0.0692 (12)
C11	0.1644 (2)	0.5889 (2)	−0.0573 (6)	0.0610 (13)
C12	0.2015 (2)	0.5758 (2)	−0.1286 (6)	0.0701 (12)
C13	0.1833 (2)	0.5284 (2)	−0.2101 (5)	0.0832 (14)
C14	0.1241 (2)	0.4895 (2)	−0.2251 (5)	0.0804 (13)
C15	0.0843 (2)	0.5003 (2)	−0.1547 (5)	0.0814 (14)
C16	0.1060 (2)	0.5495 (2)	−0.0718 (4)	0.0735 (14)
F12	0.26015 (12)	0.61318 (15)	−0.1195 (4)	0.1102 (11)
F13	0.2210 (2)	0.5180 (2)	−0.2796 (4)	0.1429 (15)
F14	0.1035 (2)	0.44255 (14)	−0.3060 (3)	0.1259 (13)
F15	0.02654 (13)	0.46290 (14)	−0.1679 (4)	0.1246 (13)
F16	0.06412 (11)	0.5557 (2)	−0.0065 (4)	0.1170 (13)
C21	0.1514 (2)	0.6677 (2)	0.0687 (4)	0.064 (2)
C22	0.1156 (2)	0.6482 (2)	0.1826 (5)	0.0752 (12)
C23	0.0803 (2)	0.6695 (2)	0.2225 (5)	0.092 (2)
C24	0.0811 (3)	0.7135 (3)	0.1447 (7)	0.113 (3)
C25	0.1160 (3)	0.7366 (3)	0.0314 (6)	0.103 (2)
C26	0.1501 (2)	0.7122 (2)	−0.0016 (5)	0.0838 (14)
F22	0.11274 (14)	0.60407 (13)	0.2572 (3)	0.1073 (10)
F23	0.04573 (15)	0.6494 (2)	0.3314 (4)	0.1359 (15)
F24	0.0474 (2)	0.7372 (3)	0.1776 (5)	0.166 (2)
F25	0.1168 (3)	0.7815 (2)	−0.0365 (6)	0.172 (2)
F26	0.1847 (2)	0.73558 (15)	−0.1125 (3)	0.1113 (11)
C1*B*	0.1595 (4)	0.6131 (4)	0.0948 (9)	0.054 (3)
C11*B*	0.1607 (3)	0.5776 (3)	−0.0283 (6)	0.054 (6)
C12*B*	0.2129 (2)	0.5872 (2)	−0.0864 (6)	0.064 (6)
C13*B*	0.2121 (2)	0.5524 (3)	−0.1945 (5)	0.076 (6)
C14*B*	0.1590 (3)	0.5079 (3)	−0.2446 (5)	0.063 (6)
C15*B*	0.1068 (2)	0.4983 (2)	−0.1865 (6)	0.054 (5)
C16*B*	0.1076 (2)	0.5332 (3)	−0.0784 (6)	0.068 (7)
F12*B*	0.2648 (3)	0.6307 (3)	−0.0374 (8)	0.095 (4)
F13*B*	0.2631 (3)	0.5618 (4)	−0.2513 (7)	0.111 (4)
F14*B*	0.1581 (4)	0.4739 (3)	−0.3503 (7)	0.121 (4)
F15*B*	0.0548 (3)	0.4549 (3)	−0.2355 (8)	0.119 (4)
F16*B*	0.0566 (3)	0.5238 (4)	−0.0216 (8)	0.103 (4)
C21*B*	0.1440 (3)	0.6619 (3)	0.0709 (6)	0.067 (9)
C22*B*	0.1037 (3)	0.6661 (3)	0.1552 (7)	0.076 (5)
C23*B*	0.0898 (4)	0.7098 (4)	0.1322 (8)	0.113 (9)
C24*B*	0.1162 (4)	0.7492 (3)	0.0251 (8)	0.126 (10)
C25*B*	0.1565 (3)	0.7451 (3)	−0.0592 (7)	0.107 (6)
C26*B*	0.1704 (2)	0.7014 (2)	−0.0362 (6)	0.076 (5)
F22*B*	0.0779 (4)	0.6275 (4)	0.2600 (8)	0.113 (4)
F23*B*	0.0504 (5)	0.7139 (5)	0.2146 (11)	0.161 (9)
F24*B*	0.1027 (5)	0.7920 (4)	0.0027 (12)	0.230 (15)
F25*B*	0.1823 (4)	0.7837 (3)	−0.1640 (8)	0.117 (4)
F26*B*	0.2098 (3)	0.6973 (3)	−0.1186 (7)	0.085 (3)
(6*b*)				
O1	0.21902 (10)	0.63648 (10)	0.1519 (3)	0.0668 (8)
C1	0.19209 (14)	0.64502 (14)	0.0259 (4)	0.0425 (9)
C11	0.1639 (2)	0.5876 (2)	−0.0561 (5)	0.0375 (10)

Table 2 (*cont.*)

	x	y	z	U_{eq}
C12	0.2018 (2)	0.5744 (2)	−0.1301 (5)	0.0430 (9)
C13	0.1826 (2)	0.5258 (2)	−0.2133 (4)	0.0505 (11)
C14	0.1228 (2)	0.4876 (2)	−0.2290 (4)	0.0472 (9)
C15	0.0833 (2)	0.4988 (2)	−0.1586 (4)	0.0456 (9)
C16	0.10442 (15)	0.5475 (2)	−0.0737 (4)	0.0417 (9)
F12	0.26070 (10)	0.61175 (12)	−0.1194 (3)	0.0676 (8)
F13	0.22085 (15)	0.5152 (2)	−0.2813 (3)	0.0893 (10)
F14	0.10260 (15)	0.43984 (12)	−0.3114 (3)	0.0769 (9)
F15	0.02505 (11)	0.46147 (11)	−0.1721 (3)	0.0751 (9)
F16	0.06277 (9)	0.55523 (12)	−0.0079 (3)	0.0718 (9)
C21	0.1507 (2)	0.6671 (2)	0.0693 (4)	0.039 (2)
C22	0.1144 (2)	0.6470 (2)	0.1860 (4)	0.0434 (9)
C23	0.0794 (2)	0.6691 (2)	0.2278 (4)	0.0527 (10)
C24	0.0803 (2)	0.7139 (2)	0.1513 (5)	0.0623 (15)
C25	0.1156 (2)	0.7379 (3)	0.0364 (5)	0.062 (2)
C26	0.1504 (2)	0.7133 (2)	−0.0019 (4)	0.0468 (9)
F22	0.11115 (10)	0.60189 (11)	0.2607 (3)	0.0638 (7)
F23	0.04458 (11)	0.64842 (13)	0.3400 (3)	0.0746 (8)
F24	0.0460 (2)	0.7367 (2)	0.1893 (4)	0.0962 (11)
F25	0.1177 (2)	0.7830 (2)	−0.0360 (4)	0.1009 (12)
F26	0.18521 (11)	0.73665 (11)	−0.1148 (3)	0.0618 (7)
C1*B*	0.1580 (4)	0.6120 (4)	0.0938 (8)	0.035 (2)
C11*B*	0.1597 (2)	0.5760 (2)	−0.0333 (5)	0.032 (5)
C12*B*	0.2123 (2)	0.5858 (2)	−0.0898 (5)	0.033 (4)
C13*B*	0.2120 (2)	0.5508 (2)	−0.1968 (4)	0.044 (4)
C14*B*	0.1593 (2)	0.5060 (2)	−0.2474 (4)	0.037 (4)
C15*B*	0.1067 (2)	0.4962 (2)	−0.1909 (5)	0.037 (3)
C16*B*	0.1070 (2)	0.5312 (2)	−0.0839 (5)	0.049 (5)
F12*B*	0.2639 (2)	0.6296 (2)	−0.0403 (7)	0.059 (3)
F13*B*	0.2634 (2)	0.5604 (3)	−0.2521 (6)	0.068 (3)
F14*B*	0.1591 (3)	0.4718 (2)	−0.3521 (5)	0.068 (3)
F15*B*	0.0551 (2)	0.4524 (2)	−0.2404 (6)	0.077 (3)
F16*B*	0.0556 (2)	0.5216 (3)	−0.0286 (6)	0.060 (2)
C21*B*	0.1438 (2)	0.6620 (2)	0.0697 (5)	0.043 (7)
C22*B*	0.1044 (2)	0.6670 (2)	0.1554 (5)	0.048 (3)
C23*B*	0.0906 (3)	0.7107 (3)	0.1322 (6)	0.087 (9)
C24*B*	0.1163 (3)	0.7494 (2)	0.0234 (6)	0.075 (8)
C25*B*	0.1557 (2)	0.7444 (2)	−0.0622 (5)	0.051 (3)
C26*B*	0.1695 (2)	0.7007 (2)	−0.0390 (5)	0.041 (3)
F22*B*	0.0792 (3)	0.6291 (3)	0.2618 (6)	0.069 (3)
F23*B*	0.0521 (3)	0.7156 (4)	0.2160 (8)	0.100 (5)
F24*B*	0.1029 (4)	0.7922 (3)	0.0008 (9)	0.119 (7)
F25*B*	0.1809 (3)	0.7823 (2)	−0.1686 (6)	0.071 (3)
F26*B*	0.2081 (2)	0.6958 (3)	−0.1228 (6)	0.050 (2)
(7)				
O1	0.6262 (4)	0.82853 (11)	0.02969 (10)	0.0510 (12)
C11	0.6534 (6)	0.80745 (16)	−0.03449 (14)	0.0422 (16)
C111	0.4510 (5)	0.84745 (15)	−0.07347 (13)	0.0380 (15)
C112	0.3299 (7)	0.90793 (17)	−0.05022 (14)	0.0516 (19)
C113	0.1504 (9)	0.94498 (18)	−0.08645 (18)	0.068 (2)
C114	0.0885 (8)	0.92206 (19)	−0.14634 (16)	0.061 (2)
C115	0.2088 (7)	0.86215 (18)	−0.16995 (15)	0.0534 (19)
C116	0.3897 (7)	0.82512 (16)	−0.13358 (15)	0.0503 (17)
C121	0.6358 (6)	0.72680 (16)	−0.04169 (13)	0.0401 (15)
C122	0.4411 (7)	0.68819 (17)	−0.01124 (16)	0.0533 (19)
C123	0.4283 (9)	0.61465 (19)	−0.01760 (17)	0.067 (2)
C124	0.6055 (9)	0.57905 (18)	−0.05471 (18)	0.067 (2)
C125	0.7951 (9)	0.6161 (2)	−0.08517 (18)	0.067 (2)
C126	0.8144 (7)	0.69016 (18)	−0.07789 (15)	0.0538 (19)
O2	0.1205 (4)	0.82919 (11)	0.08862 (9)	0.0492 (12)
C21	0.1335 (6)	0.80650 (15)	0.15285 (14)	0.0395 (15)
C211	−0.0764 (6)	0.84422 (15)	0.19039 (13)	0.0396 (15)
C212	−0.2142 (6)	0.90174 (15)	0.16595 (15)	0.0465 (17)
C213	−0.4007 (7)	0.93745 (16)	0.20174 (17)	0.056 (2)
C214	−0.4462 (7)	0.91661 (19)	0.26257 (18)	0.059 (2)
C215	−0.3127 (8)	0.8604 (2)	0.28786 (16)	0.062 (2)
C216	−0.1255 (7)	0.82423 (17)	0.25200 (14)	0.054 (2)
C221	0.1182 (6)	0.72494 (15)	0.15782 (14)	0.0404 (15)
C222	−0.0699 (7)	0.68782 (17)	0.12567 (17)	0.0563 (19)
C223	−0.0828 (8)	0.61339 (19)	0.12962 (19)	0.070 (2)
C224	0.0948 (9)	0.57696 (19)	0.1664 (2)	0.071 (2)
C225	0.2810 (8)	0.6137 (2)	0.1988 (2)	0.070 (2)
C226	0.2942 (7)	0.68771 (19)	0.19412 (17)	0.056 (2)

Table 3. *Selected molecular dimensions* (Å, °)

(1)			
C1—O1	1.451 (4)	C1—O1—H1	99
C1—C11	1.528 (5)	O1—C1—C11	109.6 (3)
C1—C21	1.533 (5)	O1—C1—C21	108.2 (3)
C1—C31	1.535 (5)	O1—C1—C31	104.8 (2)
C34—C41	1.486 (5)		
Shortest O···O	7.378 (4)		
(2)			
C1—O1	1.438 (5)	C1—O1—H1	100
C1—C11	1.517 (7)	O1—C1—C11	108.1 (4)
C1—C21	1.542 (7)	O1—C1—C21	107.4 (4)
C1—C31	1.508 (7)	O1—C1—C31	106.3 (4)
H1···N12	1.98	C1—C11—N12	115.1 (4)
O1···N12	2.605 (7)	C1—C11—C16	123.5 (5)
		N12—C11—C16	121.4 (5)
		O1—H1···N12	134
(3)			
C1—O1	1.433 (2)	C1—O1—H1	109
C1—C2	1.484 (3)	O1—C1—C2	108.4 (2)
C2—C3	1.181 (3)	O1—C1—C11	106.1 (2)
C3—C31	1.441 (3)	O1—C1—C21	108.6 (2)
C1—C11	1.527 (3)	C1—C2—C3	175.8 (3)
C1—C21	1.519 (3)	C2—C3—C31	177.7 (3)
H1···C25^{i}	2.57		
O1···C25	3.302 (3)		
(4)			
C1—O1	1.441 (4)	C1—O1—Ho1	112
C1—C2	1.534 (6)	C1—O1—Ho2	112
C2—C3	1.523 (5)	O1—C1—C2	109.0 (2)
C2—C4	1.530 (6)	O1—C1—C11	107.0 (2)
C1—C11	1.533 (4)	O1—C1—C21	108.1 (3)
C1—C21	1.529 (6)	C1—C2—C3	112.9 (3)
O1···O1^{ii}	2.864 (7)	C1—C2—C4	112.8 (3)
O1···O1^{iii}	2.864 (7)	C3—C2—C4	109.6 (3)
Ho1···O1^{iii}	2.18		
Ho2···O1^{ii}	2.37		
(6)			
(*a*) At 293 K			
C1—O1	1.462 (4)	C1—O1—Ho1	95
C1—C11	1.522 (5)	O1—C1—C11	108.4 (3)
C1—C21	1.508 (5)	O1—C1—C21	108.7 (3)
O1···O1^{iv}	2.702 (4)		
O1···O1^{v}	2.702 (4)		
Ho1···O1^{v}	1.80		
C—F range 1.323 (5)–1.348 (5), mean 1.337 (8)			
(*b*) At 173 K			
C1—O1	1.468 (4)	C1—O1—Ho1	93
C1—C11	1.513 (5)	O1—C1—C11	108.1 (3)
C1—C21	1.509 (4)	O1—C1—C21	108.4 (3)
O1···O1^{iv}	2.683 (4)		
O1···O1^{v}	2.683 (4)		
Ho1···O1^{v}	1.79		
C—F range 1.327 (4)–1.352 (5), mean 1.341 (7)			
(7)			
C11—O1	1.421 (4)	C11—O1—H1	102
C11—C111	1.522 (4)	O1—C11—C111	108.4 (2)
C11—C121	1.515 (4)	O1—C11—C121	111.4 (2)
C21—O2	1.426 (3)	C21—O2—H2	110
C21—C211	1.512 (4)	O2—C21—C211	109.3 (2)
C21—C221	1.527 (4)	O2—C21—C221	111.0 (2)
O1···O2	2.878 (3)		
O1···O2^{vi}	2.826 (3)		
O1···H2	1.90		
O2···H1^{vii}	1.87		

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $1-y, x-y, z$; (iii) $1-x+y, 1-x, z$; (iv) $\frac{2}{3}+x-y, \frac{1}{3}+x, \frac{1}{3}-z$; (v) $-\frac{1}{3}+y, \frac{1}{3}-x+y, \frac{1}{3}-z$; (vi) $1+x, y, z$; (vii) $-1+x, y, z$.

intermolecular contact across these centres is between H1 in the molecule at (x, y, z) and the N atom in the molecule at $(1-x, 2-y, -z)$ at a distance of 2.93 Å. The molecular volume V/Z is 350.9 (3) Å^3, significantly larger than the molecular volume 338.8 (3) Å^3 of the chain-forming isomer (4-pyridyl)diphenylmethanol (Glidewell & Ferguson, 1994), but still smaller than 360 (2) Å^3 of the isoelectronic triphenylmethanol (Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992).

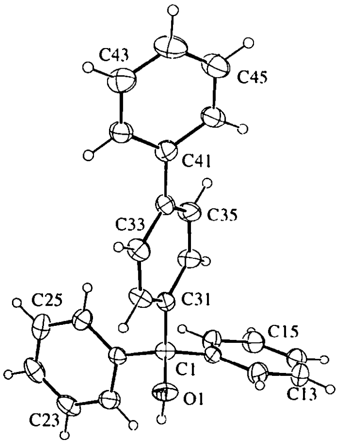

Fig. 1. View of the molecule (4-biphenyl)diphenylmethanol (1), showing the atom-labelling scheme. Thermal ellipsoids are drawn at the 30% level for non-H atoms; H atoms are shown as small spheres of an arbitrary size.

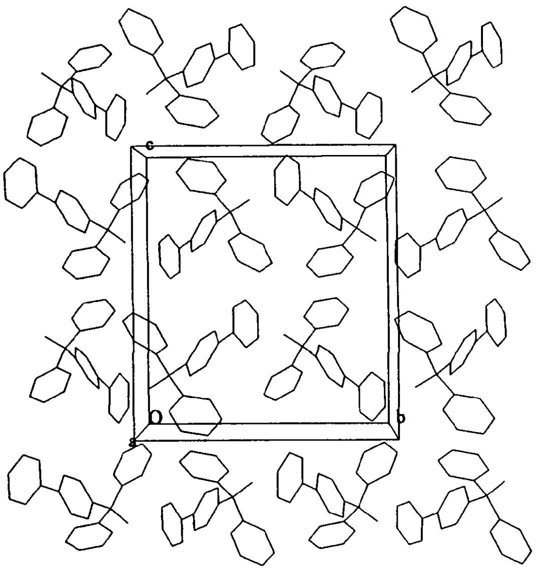

Fig. 2. Packing diagram of the unit-cell contents of (1), viewed along the a-direction; for the sake of clarity, H atoms bonded to C are not shown.

The acetylenic alcohol (3) crystallizes in space group $P2_1/c$ and forms centrosymmetric hydrogen-bonded dimers (Figs. 5 and 6), which lie across the inversion centres at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$. The hydrogen bonding is of the OH$\cdots\pi$(arene) type: the shortest O$\cdots$C interatomic distance between molecules is the O1$\cdots$C25 distance of 3.302 (3) Å, with a corresponding H1$\cdots$C25 distance of 2.57 Å. These distances are thus shorter than the closest intermolecular O$\cdots$C and H$\cdots$C distances [3.525 (4) and 2.73 (4) Å, respectively] observed in the dimer of 1,1,2-triphenylethanol (Ferguson, Gallagher, Glidewell & Zakaria, 1994), where again O—H$\cdots\pi$(arene) interactions provide the sole driving force towards dimer formation. In previously reported examples of intermolecular aggregation involving O—H$\cdots\pi$(arene) interactions, these have generally been accompanied, and presumably reinforced, either by O—H$\cdots$O hydrogen bonding, as in HO(SiPh$_2$)$_7$OH (Ovchinnikov, Shklover, Struchkov, Dement'ev, Frunze & Antipova, 1987), or by $\pi\cdots\pi$ facial interactions, as in (9-anthryl)CHC(CF$_3$)OH (Rzepa, Webb, Slawin & Williams, 1991).

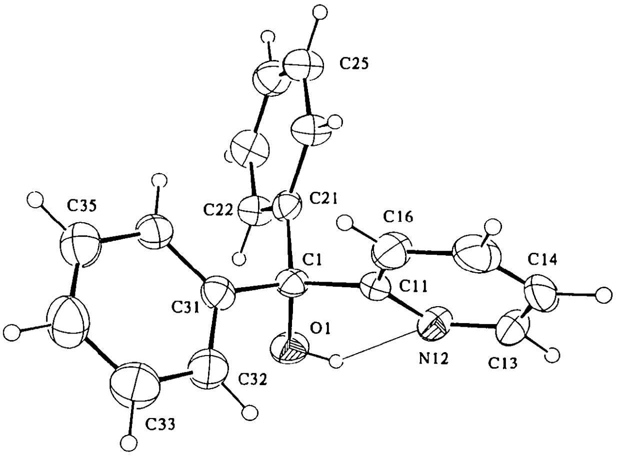

Fig. 3. View of the molecule diphenyl(2-pyridyl)methanol (2); atoms are depicted as in Fig. 1.

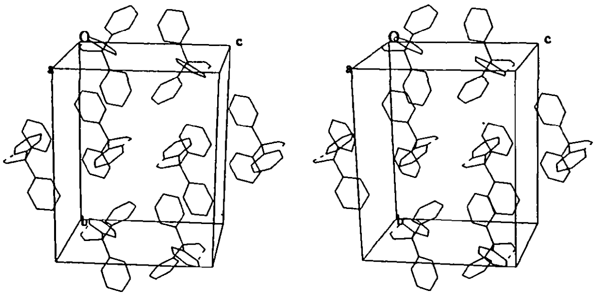

Fig. 4. Stereoview of the unit-cell contents of (2); the intramolecular hydrogen bond is shown as a dashed line; H atoms bonded to C are not shown.

Structures dominated by O—H···O *hydrogen bonding.* (4) crystallizes in the trigonal space group $P31c$ and forms hydrogen-bonded trimers (Figs. 7 and 8), with crystallographic threefold rotational symmetry and comprising the three molecules at (x, y, z), $(1-y, x-y, z)$ and $(1-x+y, 1-x, z)$. Of the series RCPh$_2$OH, having small alkyl groups as the substituent R, the first three members are a cyclic tetramer ($R = CH_3$), a monomer ($R = C_2H_5$) and a trimer ($R = Me_2CH$); the next member of this series, having $R = Me_3C$, is a liquid at room temperature, and all our attempts at low temperature crystallization have so far been unsuccessful, only glasses having been obtained. Within the trimers of (4) the hydroxyl H atoms are disordered over two sites with equal occupancies: both hydroxyl hydrogen sites are slightly displaced from the O_3 plane, by 0.144 and 0.276 Å, respectively. In several related systems, where the hydroxyl H atoms have been found from X-ray structure analysis to be disordered, including Ph_3COH (Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992), $[Fe(C_5H_4CPh_2OH)_2]$ (Ferguson, Gallagher, Glidewell & Zakaria, 1993) and $(PhCH_2)_3COH$ (Ferguson, Gallagher, Glidewell, Liles & Zakaria, 1993), subsequent study by variable-temperature ^{2}H NMR in the solid state has shown that even at the temperature of the structure analysis, the hydroxyl H atoms are mobile between the various sites found by X-ray methods (Aliev, Harris, Shannon, Glidewell & Zakaria, 1995); it is therefore possible (or probable) that similar mobility occurs in (4).

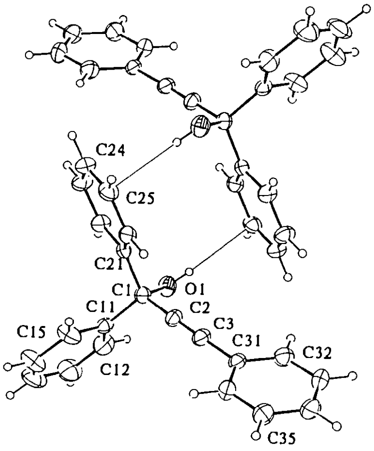

Fig. 5. View of the centrosymmetric dimeric aggregate in 1,1,3-triphenylpropyn-1-ol (3); atoms are depicted as in Fig. 1.

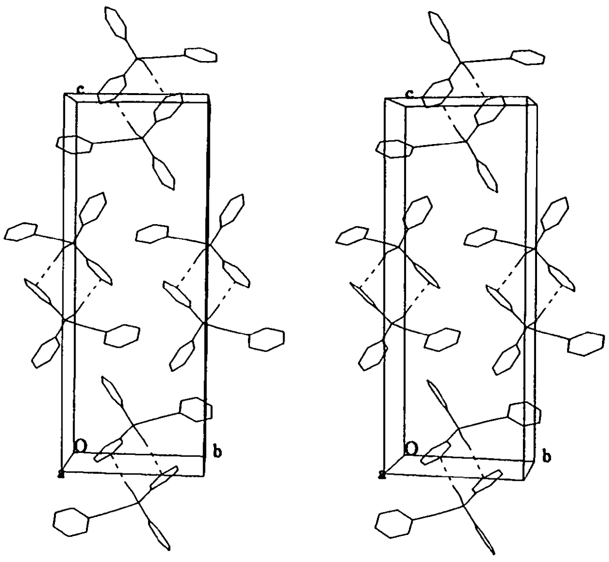

Fig. 6. Stereoview of the unit-cell contents of (3); the intermolecular hydrogen bonds are shown as dashed lines; H atoms bonded to C are not shown.

(5) crystallizes in the rhombohedral space group $R\bar{3}$, with $Z = 24$ in a unit cell of volume 8454 (5) Å^3; this compound is thus isomorphous with triphenylmethanol, $V = 8631$ (2) Å^3 (Ferguson, Gallagher, Glidewell, Low

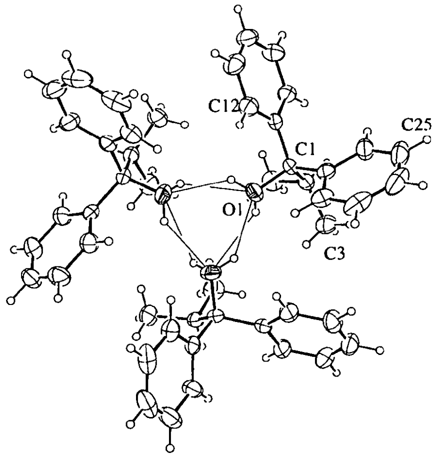

Fig. 7. View of the trimeric aggregate in 2-methyl-1,1-diphenylpropan-1-ol (4), showing the disorder of the hydroxyl H atoms; atoms are depicted as in Fig. 1.

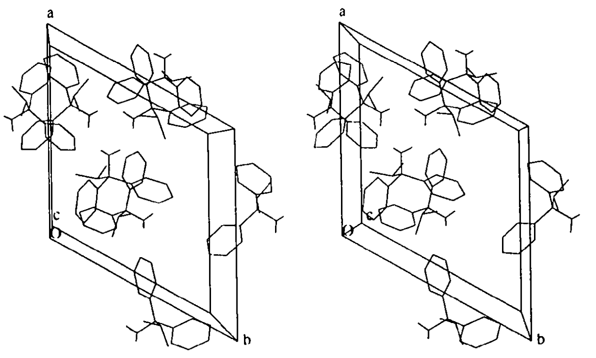

Fig. 8. Stereoview of the unit-cell contents of (4); H atoms bonded to C are not shown.

& Scrimgeour, 1992), which forms tetrameric, almost tetrahedral, aggregates lying on a crystallographic threefold axis, and having O···O distances of 2.884 (10) and 2.896 (11) Å. The structure of triphenylmethanol is characterized by two independent types of disorder: first, the orientation of the tetrameric aggregates is disordered with 29% inverted relative to the majority, and second, the four hydroxyl H atoms are shared between six O···O atom pairs. In (5), yet a third type of disorder must be present: in the space group $R3$ with $Z = 24$, one molecule must lie on the crystallographic threefold axis, giving rise to statistical distribution of two phenyl groups and one thienyl group in three symmetry-equivalent sites. The crystals of (5) did not diffract well at room temperature, and this may be because the thienyl group of the molecule in the general position is also disordered over several sites. It was therefore felt that pursuit of this analysis would be inappropriate at the present time.

Bis(pentafluorophenyl)methanol (6) crystallizes in the space group $R\bar{3}$, with $Z = 18$. Initial refinements using diffraction data collected at 293 K showed that the structure consisted of cyclic hexameric aggregates, of $\bar{3}$ symmetry, with the component molecules held together by O—H···O hydrogen bonds having an O···O distance of *ca* 2.7 Å. A difference map at this stage clearly showed, however, the presence of a second, minor orientation of the asymmetric unit, in the same volume element of space. In order to fully resolve and define the disorder, diffraction data were also collected at 173 K. From the low-temperature data set, the form of the disorder became apparent: the two orientations of the $H(C_6F_5)_2COH$ molecules share a common oxygen site, but have the opposite handedness at C1 (Fig. 9). Within each orientation, the hydroxyl hydrogens are fully ordered. The structures at 293 and 173 K are essentially identical, apart from the extent of the thermal motion, with the major:minor orientation ratio unchanged over this temperature range, and in the two different crystals employed the refined values for this ratio are 0.779 (3):0.221 (3) at 293 K and 0.776 (2):0.224 (2) at 173 K. The cyclic hexamers (Figs. 10 and 11) lie in ordered coaxial stacks parallel to the short c-axis. Three such stacks run through each unit cell with the stack axes at $(0, 0, z)$, $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, z)$. Both within and between the stacks the hexamers are separated only by intermolecular F···F contacts. Although there appears to be scope for channel formation along the stack axis, the fluorine atoms F12 lie inside the channel, and because of this, there is no free volume inside the stack, as calculated using *PLATON* (Spek, 1994).

Diphenylmethanol (7) crystallizes in the orthorhombic space group $P22_12_1$ with two molecules (labelled 1 and 2) in the asymmetric unit (Fig. 12). The molecules are linked by hydrogen bonds into chains parallel to the a-direction (Fig. 13); the two molecules of the asymmetric unit are linked by O—H···O hydrogen bonds and the chain is built up by repeated translation of the asymmetric unit along the a-direction. The molecular packing exhibits pseudosymmetry: molecule (1) at (x, y, z) and molecule (2) at $(1 - x, \frac{3}{2} - y, \frac{1}{2} + z)$ are related by an approximate inversion centre at $(\frac{3}{4}, \frac{3}{4}, z)$, where $z = ca$ 0.31; other pairs of molecules of types (1) and (2) are related by other such approximate inversions at $(\frac{1}{4}, \frac{3}{4}, z)$, $(\frac{3}{4}, \frac{3}{4}, \frac{1}{2} + z)$, $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2} + z)$, $(\frac{3}{4}, \frac{1}{4}, 1 - z)$, $(\frac{1}{4}, \frac{1}{4}, 1 - z)$, $(\frac{3}{4}, \frac{1}{4}, \frac{1}{2} - z)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2} - z)$. The space group for (7) is uniquely determined, and these inversion relationships are only approximate; however, if they were precise, and z were 0.25 rather than *ca* 0.31, the space group would become *Pnaa* (No. 56). Four hydrogen-bonded chains run through the unit cell, but the 2_1 screw axes parallel to the b- and c-directions play no part in

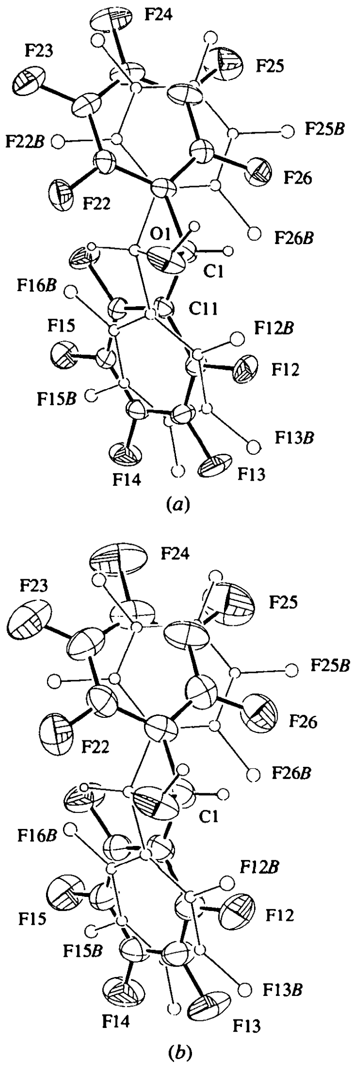

Fig. 9. Comparison of the asymmetric units in bis(pentafluorophenyl)-methanol (6) at (*a*) 293 and (*b*) 173 K. For the major orientation the atoms are depicted as in Fig. 1; for the minor orientation the atoms are drawn as small spheres of arbitrary size.

their generation. This may be contrasted, for example, with the crystallization behaviour of 7-acenaphthol $C_{12}H_9OH$ (Gupta & Gupta, 1975), where the molecules are linked by O—H···O hydrogen bonds into spirals generated by the 2_1 axis in $P2_1/a$, and with that of 1-ferrocenylethanol $[(C_5H_5)Fe(C_5H_4)]CH(OH)CH_3$ (Ferguson, Glidewell, Klar, Lightfoot & Zakaria, 1995), where the O—H···O hydrogen bonding takes the form of spirals around the 4_1 axis in $I4_1cd$.

Molecular dimensions and conformations

Within the molecular components, the C—O bond lengths, measured at 293 K, range from 1.421 (4) Å in one of the molecules of (7) to 1.462 (4) Å in the major orientation of (6), with an overall ordering, in terms of increasing C—O distance, thus: (7) < (3) ≈ $Ph_2CC{=}CHCMe_2CH_2CPh_2OH$ (Zimmerman & Zuraw, 1989) ≈ $PhCHFCPh_2OH$ (DesMarteau, Xu & Witz, 1992) < Ph_3COH (Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992) ≈ (2) ≈ (4) ≈ $[(C_5H_5)Fe(C_5H_4)]CPh_2OH$ (Ferguson, Gallagher, Glidewell & Zakaria, 1993) < $(PhCH_2)CPh_2OH$ (Ferguson, Gallagher, Glidewell & Zakaria, 1994) < (1) < (6). Clear placing within this series of CH_3CPh_2OH (Sultanov, Shnulin & Mamedov, 1985*b*) and $C_2H_5CPh_2OH$ (Sultanov, Shnulin & Mamedov, 1985*a*) is not possible because of the limited metrical precision of these structure determinations. In general, in monoalcohols the C—O bond length increases with increasing substitution at C1 (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), a trend most simply interpreted in terms of increasing steric stress at C1. This simple reasoning provides an entirely satisfactory rationalization of the C—O bond-length order noted above, and indicates that in molecules RCPh$_2$OH, the local steric demands of the groups R increase in the order H < C≡CPh ≈ CHFPh ≈ $CH_2CMe_2CH{=}CPh_2$ < Ph

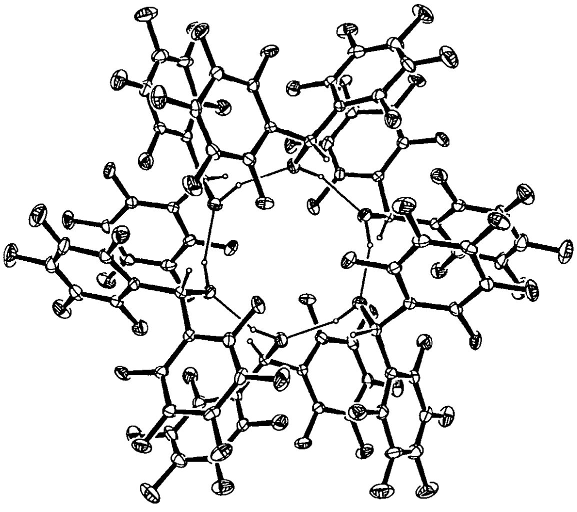

Fig. 10. View of the hexameric aggregate of bis(pentafluorophenyl)methanol (6) at 293 K, showing only the major orientation. Thermal ellipsoids are drawn at the 10% level for non-H atoms; H atoms are shown as small spheres of an arbitrary size.

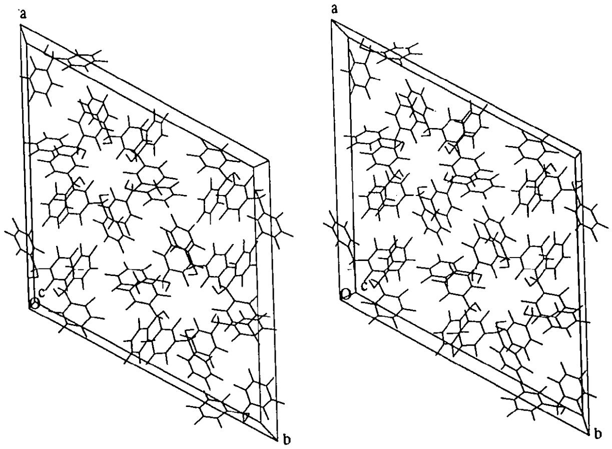

Fig. 11. Stereoview of the unit-cell contents of (6).

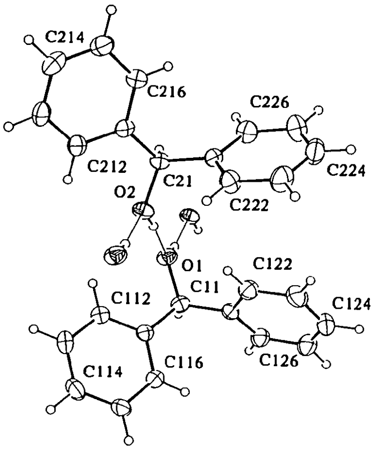

Fig. 12. View of the asymmetric unit of diphenylmethanol (7), together with two further hydroxyl groups which form part of the infinite hydrogen-bonded chain.

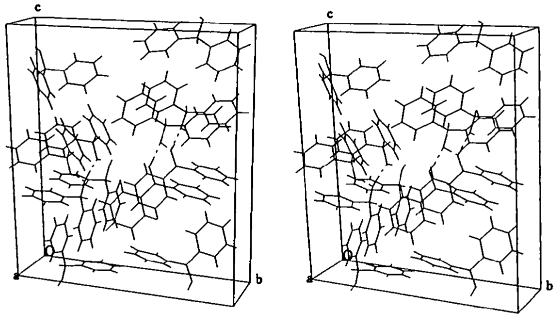

Fig. 13. Stereoview of the unit-cell contents of (7); intermolecular hydrogen bonds are shown as dashed lines.

$\approx$ (2-pyridyl) $\approx$ $CHMe_2$ $\approx$ $[(C_5H_5)Fe(C_5H_4)]$ < CH_2Ph < (4-biphenyl). The $C(sp^3)$—C(aryl) bond lengths span the range 1.508 (7)–1.542 (7) Å, with both extremes found in (2), but this range is typical of those observed when $C(sp^3)$ is fully substituted. For compounds $RCPh_2OH$ with R = organic, the mean value for (1)–(4) each does not differ, within experimental error, from 1.527 Å, the reported mean value for such bonds (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), while the $C(sp^3)$—C(aryl) bonds in (6) and (7) are somewhat shorter with mean values, at 293 K, of 1.515 in (6) and 1.519 Å in (7). The C(aryl)—C(aryl) distance in (1), and the C≡C and ≡C—C(aryl) distances in (2) are all, within experimental uncertainty, identical with the mean values reported for distances of these types.

In (1), the conformation about C1 and O1 appears to shield the hydroxyl hydrogen against both inter- and intramolecular hydrogen-bonding interactions; the three torsional angles O1—C1—C*n*1—C*n*2 (n = 1, 2, 3) are −32.0 (4), −57.0 (4) and −32.4 (4)°, respectively, and the H1—O1—C1—C31 torsional angle is 171°. It is noteworthy that in both (1) and triphenylmethanol, Ph_3COH, the primary coordination around the unique $C(sp^3)$ atom is the same (three aryl groups), yet (1) is monomeric and Ph_3COH is tetrameric (Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992). The twist angle C33—C34—C41—C42 in the biphenyl fragment of (1) is −35.1 (4)°, and it is primarily this feature which renders the molecules chiral in the solid state. There is an interesting conformational difference between (3) and 1,1,2-triphenylethanol, which both form dimers, on the one hand, and (1) which does not, on the other. In both dimers, the OH bond takes up a conformation almost exactly *trans* to one of the phenyl groups, with a torsional angle H1—O1—C1—C11 of −174° in (3), whereas in (1) the OH is *trans* not to a phenyl group, but to the 4-biphenyl substituent.

Associated with the intramolecular hydrogen bond in (2) is the tilt of the 2-pyridyl ring relative to the C1—C11 bond, shown by the two angles C1—C11—N12, 115.1 (4), and C1—C11—C16, 123.5 (5)°, and indicative of an attractive N···H interaction: consistent with this, the intramolecular O···N distance in (2), 2.605 (7) Å, is very much shorter than the intermolecular O···N distance in the isomeric (4-pyridyl)diphenylmethanol, 2.861 (6) Å. Also supporting the deduction of an attractive intramolecular hydrogen bond is the only modest deviation from planarity of the fragment H1—O1—C1—C11—N12: the torsional angles H1—O1—C1—C11 and O1—C1—C11—N12 are −13 and 26.4 (6)°, respectively.

Within these trimers of (4), the unique O···O distance is 2.864 (7) Å, but with the hydroxyl H atoms disordered. The O1—C1 bond is almost coplanar with the O_3 plane, while the C1—C21 bond (that joining one of the phenyl groups to the rest of the molecule) projects almost at right angles to the O_3 plane: the torsional angles C2—C1—O1—O1^{i}, C11—C1—O1—O1^{i} and C21—C1—O1—O1^{i} (where O1^{i} is in the molecule at $1-y, x-y, z$) are 33.8 (3), 157.4 (4) and −86.2 (3)°, respectively.

Hydrogen-bonding motifs

The hydrogen-bond motif in (2) has graph set $S(5)$ (Etter, 1990; Etter, MacDonald & Bernstein, 1990) rather than the graph-set $R_2^2(10)$, which would be expected for a cyclic dimer. The motif observed in (2) may be contrasted both with that in 4,4-dimethyl-(5-diphenylhydroxymethyl)-4,5-dihydroisoxazole, $(C_5H_8NO)CPh_2OH$ (Armesto, Barnes, Horspool & Langa, 1990), which forms dimers, with graph set $R_2^2(12)$, by the formation of intermolecular O—H···N hydrogen bonds rather than monomers containing intramolecular $S(5)$ O—H···O hydrogen bonds, and with that in (4-pyridyl)diphenylmethanol (Glidewell & Ferguson, 1994), an isomer of (2), which forms chains generated by intermolecular O—H···N hydrogen bonding, with graph set $C(7)$. In (3), where the hydrogen bonding is of the O—H···π(arene) type, there is neither O—H···O hydrogen bonding nor any participation of the C≡C triple bond in the hydrogen bonding (Fig. 6); by contrast, the dimeric aggregates in 2-ethynyl-2-adamantanol are formed solely by O—H···π(C≡C) interactions (Lin, Okaya, Chiou & Le Noble, 1982).

In the cyclic trimer of (4), the unique O···O distance is 2.864 (7) Å and the graph set for the hydrogen-bonding motif is $R_3^3(6)$, while in the cyclic hexamer of (6), where the hydrogen-bonding motif has graph set $R_6^6(12)$, the oxygen arrangement can be alternatively described as a slightly puckered plane or as a very flattened chair. At room temperature the O···O distance is 2.702 (4) Å with the O atoms displaced from the mean oxygen plane by ±0.155 (3) Å. At 173 K, the O···O distance is 2.683 (4) Å, and the oxygen displacement is ±0.141 (3) Å. Within the asymmetric unit chosen here for (7), and defined in Fig. 12, the O···O distance is 2.878 (3) Å, and the other O···O distance within the chain is 2.826 (3) Å; the hydrogen-bonding motif has graph set $C(4)$.

The closest O···O distances in (4) and (7), and those in Ph_3COH, all exceed 2.80 Å, and thus represent only 'weak' hydrogen bonds (Novak, 1974; Emsley, 1980), as typically found in alcohols. On the other hand, the O···O distances in (6) represent 'intermediate' strength hydrogen bonds in the classifications of Emsley and of Novak, and are comparable with those found in phenol (Gillier-Pandraud, 1967). The O···O distances in (7) are both significantly longer than the O···O distances of 2.672 (5) Å reported (Lariucci, de Almeida Santos & Lechat, 1986) for the hydrogen-bonded 1:1 adduct of (7) with triphenylphosphine; this must also be regarded as an 'intermediate' strength bond.

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