ORGANIC COMPOUNDS

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O—H···π(arene) Intermolecular Hydrogen Bonding in the Structure of 1,1,2-Triphenylethanol

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Abstract

The 1,1,2-triphenylethanol molecule, $Ph_2(PhCH_2)COH$ (I), forms centrosymmetric dimers in the solid state. The shortest O···O separation, 5.837 (3) Å, is too long for any O—H···O hydrogen-bond formation. Instead, there are O—H···π(arene) interactions between the hydroxyl group of one molecule and a phenyl group of a centrosymmetrically related molecule. The O···C and H···C distances between the hydroxyl group and the closest phenyl-ring C atom are 3.525 (4) and 2.73 (4) Å, respectively. These intermolecular contacts are the only driving force towards dimer formation in the solid state.

Comment

Hydrogen bonds often provide the strongest intermolecular forces between molecules in organic molecular crystals and hence often dictate the preferred packing arrangement. The general principles underlying hydrogen-bond formation are reasonably well understood and the structures of hydrogen-bonded crystals can often be rationalized in preferred combinations of hydrogen-bond donors and acceptors (Etter, 1990; Etter, McDonald & Bernstein, 1990; Etter & Reutzel, 1991). In general, the strongest hydrogen-bond donors pair off with the strongest hydrogen-bond acceptors. Similar pairing processes are repeated until all the hydrogen-bond donors and acceptors have been utilized. However, when a system contains excess donors or acceptors, at least two hydrogen-bonding strategies are available to accommodate the mismatch (Hanton, Hunter & Purvis, 1992): (i) change in hybridization or (ii) the formation of hydrogen bonds involving the π system of an aromatic group as the acceptor. Several examples of the formation of intermolecular X—H···π(arene) bonds for X = O or N have been observed where there is a deficiency of sterically accessible acceptor sites of the conventional type (Atwood, Hamada, Robinson, Orr & Vincent, 1991; Hanton, Hunter & Purvis, 1992; Rzepa, Webb, Slawin & Williams, 1991).

Herein we report the formation of intermolecular O—H···π(arene) bonds in a system, Ph_2RCOH [R = CH_2Ph, (I)], having no deficiency of hydrogen-bond acceptors and whose closest analogues, (II) (R = ferrocenyl, Fc) (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*) and (III) (R = Ph) (Ferguson, Gallagher, Glidewell, Low, & Scrimgeour, 1992), both exhibit O—H···O hydrogen bonds, albeit of a markedly different pattern.

The 1,1,2-triphenylethanol molecule (I) forms centrosymmetric dimeric aggregates in the solid state (Fig. 1). The O—C distance is 1.445 (3) Å, the C_{sp^3}—C_{sp^3} bond is 1.536 (4) Å and the range and mean of the three C_{sp^3}—

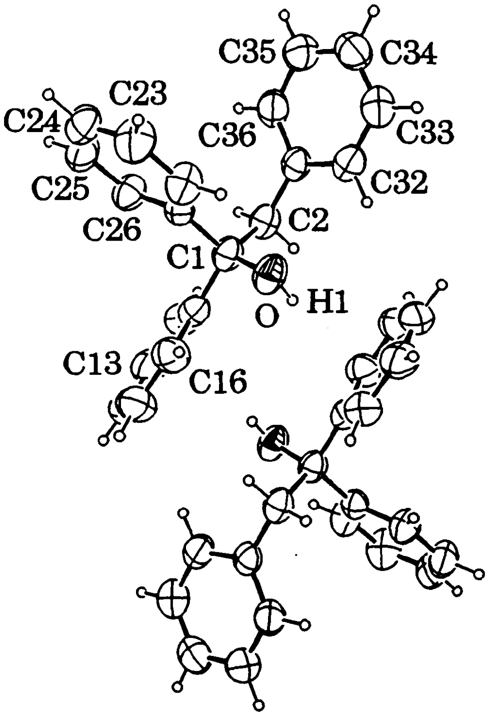

Fig. 1. An *ORTEP* (Johnson, 1976) view of the 1,1,2-triphenylethanol molecule, (I), with labeling scheme, drawn as the hydrogen-bonded dimer with the non-H atoms depicted with their thermal ellipsoids drawn at the 50% probability level. For clarity, the H atoms are drawn as small spheres of arbitrary size.

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C_{sp^2} bond lengths are 1.507 (4)-1.535 (3) and 1.521 (4) Å, respectively. The C_{ar}—C_{ar} bond lengths are in the range 1.364 (6)-1.391 (4) with the mean 1.377 (4) Å. The bond angles in (I) are unexceptional. The shortest O···O separation, 5.837 (4) Å, is too long for any O—H···O hydrogen bonding to arise in (I). Examination of the three-dimensional packing shows that O—H···π(arene) interactions exist between the hydroxyl group of one molecule and a phenyl group of a centrosymmetrically related molecule (Fig. 2). The O···C(13) and H···C(13) distances between the hydroxyl group and the closest phenyl-ring C atom are 3.525 (4) and 2.73 (4) Å, respectively.

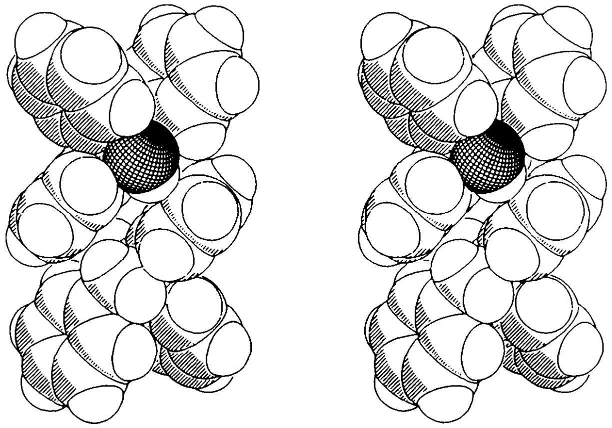

Fig. 2. A stereoview of the dimeric aggregate of (I) showing the hydroxyl moiety of one molecule engaged in O—H···π(arene) hydrogen bonding with a phenyl ring of a centrosymmetrically related molecule; all atoms are drawn as their van der Waals spheres.

In contrast to 1,1,2-triphenylethanol (I), the analogue (II), $FcPh_2COH$, which also forms centrosymmetric dimers (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*), has an O—H···O—H hydrogen-bond motif, graph set $R_2^2(4)$ (Etter, 1990; Etter, McDonald & Bernstein, 1990; Etter & Reutzel, 1991), with an O···O distance of 2.876 (2) Å. (III), Ph_3COH (Ferguson, Gallagher, Glidewell, Low, & Scrimgeour, 1992), crystallizes as distorted tetrahedral tetramers with crystallographic $3m$ (C_{3v}) symmetry [O···O distances 2.88 (1) and 2.90 (1) Å], in which the H atoms are disordered over the four-O-atom framework. In each of the closely related compounds (I)-(III), the ratio of conventional hydrogen-bond acceptor to donor sites is constant, yet three entirely different hydrogen-bond patterns are observed.

Previously, we have also examined the structures of the 1,2,3-triphenyl-2-propanol (IV) and tribenzylmethanol (V) molecules (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*), where no intermolecular O—H···O hydrogen bonding is present. This arises presumably because of the steric bulk of the molecules and their packing, which prevents the close approach of the O atoms of adjacent molecules. Thus, molecule (I) represents an intermediate case in the series Ph_3COH (III), $Ph_2(PhCH_2)COH$ (I), $Ph(PhCH_2)_2COH$ (IV), and $(PhCH_2)_3COH$ (V), where the tendency to form O—H···O hydrogen bonds is balanced by steric effects (no hydrogen bonding) resulting in the observed O—H···π(arene) hydrogen bonding. In the present example (I), the O—H···π(arene) interaction, using a single O—H bond per molecule, is the only driving force towards dimer formation in the solid state.

There are numerous other examples of O—H···π(arene) interactions. Intramolecular O—H···π(phenyl) hydrogen bonding occurs in the structure of (6,6′-di-*tert*-butyl-4,4′-dimethyl)-2,2′-isopropylidenediphenol (Hardy & MacNicol, 1976), where the two hydroxyl H···C_{ar} distances are 2.13 (3) and 2.19 (3) Å (C_{ar} is the closest phenyl C atom to the H atom). Intermolecular O—H···π(phenyl) hydrogen bonding between H_2O and the aromatic rings of BPh_4^- has been reported in the structure of tributylammonium tetraphenylborate monohydrate (Aubry, Protas, Moreno-Gonzalez & Marraud, 1977), where the water H···C_{ar} distances are 2.55 (3) and 2.49 (3) Å. It is noteworthy that most previous examples of intermolecular *X*—H···π(arene) hydrogen bonding (*X* = O or N) are accompanied by other forms of intermolecular interactions, such as conventional O—H···O hydrogen bonding, as in $HO(SiPh_2)_7OH$ (Ovchinnikov, Shklover, Struchkov, Dement'ev, Frunze & Antipova, 1987), or π···π facial interactions, as in (9-anthryl)$CHC(CF_3)OH$ (Rzepa, Webb, Slawin & Williams, 1991), or both (Hanton, Hunter & Purvis, 1992). However, *X*—H···π(arene) interactions (*X* = O or C) appear to be the sole form of intermolecular interaction in three calix[4]arene guest-host complexes, where H_2O (Atwood, Hamada, Robinson, Orr & Vincent, 1991) or CH_2Cl_2 (Atwood, Bott, Jones & Raston, 1992; Böhmer, Ferguson, Gallagher, Lough, McKervey, Madigan, Moran, Phillips & Williams, 1993) each use both *X*—H bonds to bind to two different arene rings.

Toda, Tanaka, Nagamatsu & Mak (1985) have commented previously on the lack of hydrogen bonding in *trans*-9,10-diphenyl-9,10-dihydroanthracen-9,10-diol. A re-examination of the three-dimensional packing of this structure shows that there are O—H···π(arene) interactions exactly analogous to those in (I), with a hydroxyl H···C_{arene} intermolecular distance 2.80 Å.

Experimental

Crystal data

$C_{20}H_{18}O$
M_r = 274.36
Monoclinic
$P2_1/c$
a = 16.2124 (13) Å
b = 5.9458 (6) Å
c = 17.2602 (17) Å
β = 115.965 (7)°

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12.0-17.0°
μ = 0.07 mm^{-1}
T = 293 K
Block

V = 1495.9 (2) Å^3
Z = 4
D_x = 1.22 Mg m^{-3}
0.35 × 0.20 × 0.15 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2710 measured reflections
2624 independent reflections
1298 observed reflections [$I_{\rm net} > 3.0\sigma(I_{\rm net})$]
$R_{\rm int}$ = 0.011
$\theta_{\rm max}$ = 25.0°
$h = -19 \rightarrow 17$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity variation: <1%

Refinement

Refinement on F
R = 0.037
wR = 0.042
S = 1.29
1298 reflections
212 parameters
Hydroxyl H-atom Us refined; other H atoms riding with C—H = 0.95 Å
$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.13 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.12 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 4183 (1048)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O	0.67037 (14)	0.3001 (3)	0.12619 (13)	0.0608 (14)
C1	0.66992 (16)	0.5358 (4)	0.14641 (15)	0.0483 (17)
C2	0.70384 (17)	0.6729 (5)	0.09057 (16)	0.0535 (19)
C11	0.57241 (16)	0.5979 (5)	0.13212 (14)	0.0506 (17)
C12	0.52978 (18)	0.7991 (5)	0.09722 (17)	0.0636 (20)
C13	0.44436 (20)	0.8521 (6)	0.09298 (19)	0.0722 (21)
C14	0.40069 (19)	0.7039 (7)	0.12323 (19)	0.0765 (24)
C15	0.44130 (21)	0.5032 (7)	0.15695 (20)	0.078 (3)
C16	0.52603 (19)	0.4504 (5)	0.16107 (17)	0.0652 (20)
C21	0.73458 (15)	0.5650 (4)	0.24141 (14)	0.0443 (15)
C22	0.79275 (18)	0.3960 (5)	0.28993 (17)	0.0620 (20)
C23	0.84947 (20)	0.4298 (6)	0.37653 (18)	0.0729 (22)
C24	0.84935 (19)	0.6291 (6)	0.41570 (17)	0.0679 (22)
C25	0.79259 (19)	0.7982 (5)	0.36762 (17)	0.0653 (19)
C26	0.73620 (17)	0.7672 (5)	0.28158 (16)	0.0549 (18)
C31	0.80080 (17)	0.6208 (5)	0.10606 (14)	0.0486 (17)
C32	0.82443 (19)	0.4257 (5)	0.07687 (15)	0.0594 (19)
C33	0.91373 (21)	0.3813 (6)	0.09284 (18)	0.0657 (21)
C34	0.98136 (19)	0.5322 (6)	0.13772 (18)	0.0687 (23)
C35	0.95996 (20)	0.7272 (6)	0.16704 (18)	0.0714 (23)
C36	0.87057 (20)	0.7708 (5)	0.15130 (17)	0.0610 (20)

Table 2. *Selected geometric parameters* (Å, °)

O—C1	1.445 (3)	C21—C26	1.382 (4)
C1—C2	1.536 (4)	C22—C23	1.385 (4)
C1—C11	1.535 (3)	C23—C24	1.365 (5)
C1—C21	1.521 (3)	C24—C25	1.370 (4)
C2—C31	1.507 (4)	C25—C26	1.373 (4)
C11—C12	1.381 (4)	C31—C32	1.384 (4)
C11—C16	1.383 (4)	C31—C36	1.383 (4)
C12—C13	1.391 (4)	C32—C33	1.376 (4)
C13—C14	1.369 (5)	C33—C34	1.365 (5)
C14—C15	1.364 (6)	C34—C35	1.369 (5)
C15—C16	1.380 (4)	C35—C36	1.377 (4)
C21—C22	1.382 (4)	O—H1	0.87 (4)
O—C1—C2	108.8 (2)	C1—O—H1	99 (3)
O—C1—C11	107.9 (2)	C1—O—C12$^{\rm i}$	107.4 (2)
O—C1—C21	107.3 (2)	C1—O—C13$^{\rm i}$	116.9 (2)
C2—C1—C11	113.5 (2)	C1—O—C14$^{\rm i}$	103.9 (2)
C2—C1—C21	110.4 (2)	O—H1—C12$^{\rm i}$	164 (3)
C11—C1—C21	108.7 (2)	O—H1—C12$^{\rm i}$	152 (3)
C1—C2—C31	114.3 (2)	O—H1—C12$^{\rm i}$	145 (3)

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

The title compound was prepared by reaction of phenyllithium with deoxybenzoin. ^{13}C NMR ($CDCl_3$): 47.3 (*t*, CH_2), 77.3 (*s*, COH), 125.6 (*d*), 126.2 (*d*), 126.3 (*d*), 127.4 (*d*), 127.5 (*d*), 130.3 (*d*), 135.2 (*s*), 146.0 (*s*). Crystals of (I) were grown from hexane (m.p. 363-364 K).

The space group for (I) was determined unambiguously from the systematic absences ($h0l$ absent if $h + l = 2n + 1$, $0k0$ absent if $k = 2n + 1$) as $P2_1/n$. The H atoms attached to the C atoms were clearly visible in difference maps; they were positioned geometrically (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations (the hydroxyl H atom was clearly visible in a difference map and refined isotropically). Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX*, *ORTEPII* (Johnson, 1976) and *PLUTON* (Spek, 1991). Software used to prepare material for publication: *NRCVAX TABLES*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and contact distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71476 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1055]

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Self Inclusion in a Calix[5]arene Structure; Structure of the Cone Conformer of a Pentahydroxy-*p*-*tert*-butylcalix[5]arene

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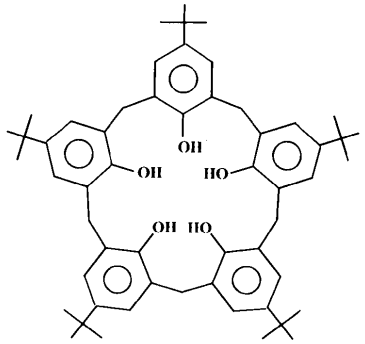
Abstract

The pentahydroxy-*p*-*tert*-butylcalix[5]arene, 5,11,17,23,29-penta-*tert*-butylhexacyclo[25.3.1.$1^{3,7}$.$1^{9,13}$.$1^{15,19}$.$1^{21,25}$]pentatriaconta-1(31),3,5,7(35),9,11,13(34),15,17,19(33),21,23,25(32),27,29-pentadecaene-31,32,33,34,35-pentaol-*n*-hexane (1/0.3), $C_{55}H_{70}O_5.0.3C_6H_{14}$ (I), adopts an open distorted chalice-shaped conformation in the solid state, primarily through O—H···O intramolecular hydrogen bonding involving all of the aromatic hydroxyl groups. The five phenolic O···O separations are in the range 2.735 (7)–2.880 (8) Å [mean 2.793 (8) Å], with all hydroxyl H atoms disordered equally over two sites. The aromatic rings are tilted back from the calixarene cavity producing a pentagonal-shaped cavity in which the *tert*-butyl group of a neighboring calix[5]arene related by a *c*-glide is enclathrated. This self-inclusion process extends through the lattice as a one-dimensional molecular 'zipper'.

Comment

The structural chemistry of calixarenes continues to be of immense interest primarily because of their recognized practical use as organic guest-host systems (Gutsche, 1989; Vicens & Böhmer, 1991). This is of fundamental importance in the quest for a better understanding of natural molecular-recognition processes.

We are currently studying the molecular structures of calix[4]arenes and calix[6]arenes, and their metal complexes. Several of these have been shown to enclathrate small organic molecules within the molecular cavity, *e.g.* dichloromethane (Böhmer *et al.*, 1993), ethanol (Ferguson, Gallagher & Pappalardo, 1993) and acetonitrile (McKervey, Seward, Ferguson & Ruhl, 1986). Until recently, there have been few structural studies reported for calix[5]arenes, mainly because of difficulties with synthesis and purification. Herein we report the structure of (I).0.3(*n*-hexane).



(I)

Our X-ray analysis of (I) shows that it adopts a distorted chalice conformation in the solid state (Figs. 1 and 2); the *tert*-butyl group on ring *C* is disordered over two orientations. The major conformation-determining feature in this molecule is the presence of O—H···O intramolecular hydrogen bonding involving all five aromatic hydroxyl groups; the O···O separations are in the range 2.735 (7)–2.880 (8) Å [mean 2.793 (8) Å]. Difference maps show that all five hydroxyl H atoms are disordered equally over two orientations; a similar situation was observed with the hydroxyl H atoms in pentahydroxycalix[5]arene acetone solvate, (II) (Coruzzi, Andreetti, Bocchi, Pochini & Ungaro, 1982).

The conformation of (I) is defined by the angles which the aromatic rings make with the plane of the five methylene C atoms which link them, *viz.* 149.7 (3) (*A*), 136.0 (3)

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