Compound (2)

Crystal data

$C_{24}H_{22}N_3OPS$	Mo $K\alpha$ radiation
$M_r = 431.48$	$\lambda = 0.7107$ Å
Triclinic	Cell parameters from 250
$P\bar{1}$	reflections
$a = 8.666$ (2) Å	$\theta = 1.97$–$25.04°$
$b = 10.985$ (3) Å	$\mu = 0.247$ mm^{-1}
$c = 12.373$ (3) Å	$T = 150$ (1) K
$\alpha = 79.291$ (12)°	Block
$\beta = 75.62$ (2)°	$0.30 \times 0.28 \times 0.26$ mm
$\gamma = 70.693$ (14)°	Yellow
$V = 1069.8$ (4) Å^3	
$Z = 2$	
$D_x = 1.339$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius diffractometer with FAST area detector	2507 reflections with $I > 2\sigma(I)$
MADNES scans (Pflugrath & Messerschmidt, 1989)	$R_{int} = 0.073$
	$\theta_{max} = 25.04°$
Absorption correction: none	$h = -9 \rightarrow 9$
4077 measured reflections	$k = -12 \rightarrow 11$
2788 independent reflections	$l = -14 \rightarrow 13$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.065$	$\Delta\rho_{max} = 0.778$ e Å^{-3}
$wR(F^2) = 0.164$	$\Delta\rho_{min} = -0.474$ e Å^{-3}
$S = 1.084$	Extinction correction: none
2788 reflections	Scattering factors from
273 parameters	*International Tables for*
H atoms riding	*Crystallography* (Vol. C)

$w = 1/[\sigma^2(F_o^2) + (0.1220P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Table 1. *Selected geometric parameters (Å, °)*

	(1)	(2)
N6—C6	1.360 (2)	1.348 (3)
P6—N6	1.592 (2)	1.588 (2)
P6—C11	1.799 (2)	1.808 (3)
P6—C21	1.811 (2)	1.803 (3)
P6—C31	1.798 (2)	1.796 (3)
P6—N6—C6	125.77 (14)	127.7 (2)
N6—P6—C11	117.81 (9)	118.22 (13)
N6—P6—C21	113.53 (9)	112.87 (13)
N6—P6—C31	105.57 (9)	105.75 (12)
C11—P6—C21	107.00 (9)	105.58 (12)
C11—P6—C31	106.53 (9)	107.03 (13)
C21—P6—C31	105.50 (9)	106.76 (13)
N1—C2—O2—C2A	−12.4 (3)	−
N1—C2—S2—C2A	−	−3.2 (3)
C6—N6—P6—C11	46.9 (2)	45.7 (3)

Molecule (1) crystallized in the monoclinic system; space groups *I2/a* or *Ia* were indicated by the systematic absences, and *I2/a* was assumed and confirmed by the analysis. Molecule (2) crystallized in the triclinic system; space group *P*1̄ was assumed and confirmed by the analysis. In both structures, H atoms were treated as riding atoms, with C—H 0.93–0.98 Å and N—H 0.86 Å. Examination of the structures with *PLATON* (Spek, 1998) showed that there were no solvent-accessible voids in the crystal lattices

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1053). Services for accessing these data are described at the back of the journal.

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'Guest-Free' Dianin's Compound

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Abstract

The existence of empty hour-glass-shaped cavities is confirmed for the crystal of the title compound, 4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman [systematic name:

4-(2,2,4-trimethylchroman-4-yl)phenol, $C_{18}H_{20}O_2$]. The structure of the cavities is essentially invariant when guest molecules are intercalated. The effects of the cage structure on ^{13}C NMR chemical shifts of the methyl C atoms are elucidated.

Comment

Dianin's compound, (1), has been reported to intercalate a wide variety of compounds in the hour-glass-shaped cavity formed by six molecules. This cavity has been considered to be invariant, whether guest molecules are intercalated or not (MacNicol *et al.*, 1978; MacNicol, 1984). The free energies of the inclusion process of *n*-alkane molecules (Imashiro, 1993), and the minimum energy positions and energy barriers of *o*- and *p*-xylene guest molecules (Zaborowski & Vega, 1993), were calculated on the assumption of the skeletal invariance of the hour-glass-shaped cage. In order to confirm the existence of empty cavities in the 'guest-free' or unsolvated crystal of (1), and the essential invariance of the cage structure independent of inclusion, we determined the crystal and molecular structure of guest-free (1). We also discuss how ^{13}C NMR chemical-shift changes due to inclusion relate to the cage structure (Ripmeester, 1983; Davies & Knott, 1988).

(1)
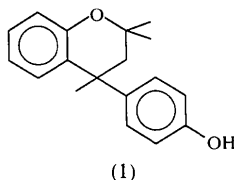
A comparison of the cage structures of (1) in clathrates with ethanol, $CHCl_3$ (Flippen *et al.*, 1970) and CCl_4 (Abriel *et al.*, 1990; Ping *et al.*, 1990) with that of guest-free (1) shows no remarkable differences: the differences in the positions of the non-H atoms of (1) in these inclusion compounds, compared with those of guest-free (1), are 0.03, 0.08 and 0.06 Å for the ethanol, $CHCl_3$ and CCl_4 clathrates, respectively. Fourier synthesis showed no electron cloud due to enclathration in the cavities of our guest-free sample of (1), confirming the existence of a significant volume of empty space in the guest-free crystal of (1). The molecular structure of guest-free (1) is also very similar to that found in the ethanol, $CHCl_3$ and CCl_4 clathrates: the differences in the bond lengths, bond angles and torsion angles, for the non-H atoms of (1) in these clathrates, compared with those of guest-free (1) (as listed selectively in Table 1), are only 0.008 Å, and 0.4 and 0.7°, respectively. One can thus conclude that the structure of the cavities of guest-free (1) is essentially invariant and independent of intercalation. Some small but characteristic changes in the cage structure of (1) due to inclusion should, however, be noted. The distance of the O20 atom (2.761 Å)

from the C_3 axis, which coincides with the long axis of the cavity, is smaller than those in the inclusion compounds (> 2.81 Å), resulting in a rather short O—H···O hydrogen bond (2.798 Å) for guest-free (1), compared to > 2.83 Å for the clathrates.
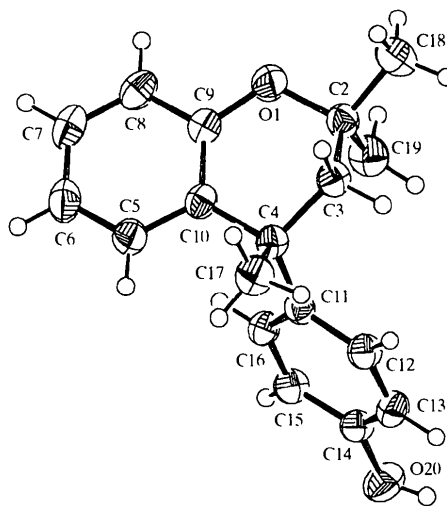
Fig. 1. View of the title molecule (*ORTEP*II; Johnson, 1976), with displacement ellipsoids plotted at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

In the hour-glass-shaped cavity of (1), the C18 methyl C atom protrudes into the upper or lower half of the cavity, and the C19 methyl C atom is directed into the neck of the cavity, while the C17 methyl C atom does not explicitly participate in the cavity. The ^{13}C NMR chemical shift of C18 is, therefore, expected to be sensitive to the existence of guest molecules, and that of C19 should be susceptible to interactions between guest molecules and the neck of the cage (Ripmeester, 1983; Barker *et al.*, 1984; Lee *et al.*, 1988). Accordingly, ^{13}C CP-MAS–NMR spectra (CP-MAS = cross-polarization magic-angle spinning) were measured at room temperature, as described elsewhere (Imashiro, 1993). The ^{13}C chemical shifts of these three methyl C atoms were measured both for guest-free (1), and for the clathrates with pentane, hexane, heptane and octane, *i.e.* (2)–(5), respectively. The chemical shift of C18 (25.10 p.p.m.) for guest-free (1) moves significantly downfield due to inclusion [27.22, 27.40, 27.04 and 27.15 p.p.m. for (2)–(5), respectively], whereas that of C17 (34.62 p.p.m.) for guest-free (1) is apparently invariant in the clathrates [34.26, 34.61, 34.45 and 34.76 p.p.m. for (2)–(5), respectively]. The chemical shifts of C19 are observed at 30.74, 30.57, 30.57, 30.06 and 30.10 p.p.m. for (1)–(5), respectively, showing a notable change between (3) and (4). On the basis of *MM2* molecular mechanics calculations (Imashiro, 1993), the conformations of the intercalated pentane and hexane molecules are almost all-*anti*, but those of the

intercalated heptane and octane molecules are not. Steric interactions between the guest molecule and the neck of the cavity may become significant in the latter clathrates, resulting in the notable change in the chemical shifts of C19.
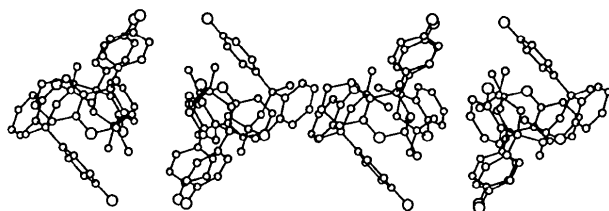

Fig. 2. Stereoview (PLUTO; Motherwell & Clegg, 1978) of the empty hour-glass-shaped cavity of guest-free Dianin's compound, (1), along the c axis. H atoms are omitted for clarity.

Experimental

Single crystals of guest-free (1) were obtained by recrystallization of (1) from dodecane, in a similar manner to that described elsewhere (Imashiro, 1993).

Crystal data

$C_{18}H_{20}O_2$	Cu $K\alpha$ radiation
$M_r = 268.355$	$\lambda = 1.54050$ Å
Trigonal	Cell parameters from 25
$R\bar{3}$	reflections
$a = 26.965\,(6)$ Å	$\theta = 18.13–20.34°$
$c = 10.933\,(2)$ Å	$\mu = 0.585$ mm^{-1}
$V = 6884\,(3)$ Å^3	$T = 293\,(2)$ K
$Z = 18$	Block
$D_x = 1.1651$ Mg m^{-3}	$0.42 \times 0.33 \times 0.23$ mm
$D_m = 1.160\,(3)$ Mg m^{-3}	Colorless
D_m measured by flotation	

Data collection

Rigaku AFC-5R diffractometer	$R_{int} = 0.028$
ω–2θ scans	$\theta_{max} = 62.49°$
Absorption correction: none	$h = 0 \rightarrow 31$
2689 measured reflections	$k = -26 \rightarrow 26$
2455 independent reflections	$l = 0 \rightarrow 12$
2025 reflections with	3 standard reflections
$F > 4\sigma(F)$	every 100 reflections
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.005$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$\Delta\rho_{max} = 0.169$ e Å^{-3}
$wR(F^2) = 0.101$	$\Delta\rho_{min} = -0.133$ e Å^{-3}
$S = 1.038$	Extinction correction:
2454 reflections	SHELXL
186 parameters	Extinction coefficient:
H-atom parameters not	0.00050 (4)
refined	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2$	International Tables for
$+ 5.3523P]$	Crystallography (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (Å, °)

O1—C9	1.368 (2)	C3—C4	1.538 (2)
O1—C2	1.459 (2)	C4—C10	1.524 (2)
C2—C18	1.511 (2)	C4—C11	1.540 (2)
C2—C19	1.513 (2)	C4—C17	1.545 (2)
C2—C3	1.519 (2)	C9—C10	1.393 (2)
C9—O1—C2	118.28 (12)	C10—C4—C3	107.31 (12)
O1—C2—C18	104.50 (14)	C10—C4—C11	112.10 (12)
O1—C2—C19	107.84 (13)	C3—C4—C11	111.92 (12)
C18—C2—C19	110.59 (15)	C10—C4—C17	109.61 (13)
O1—C2—C3	108.47 (12)	C3—C4—C17	106.82 (12)
C18—C2—C3	109.80 (13)	C11—C4—C17	108.94 (13)
C19—C2—C3	115.08 (14)	O1—C9—C10	124.42 (14)
C2—C3—C4	116.08 (12)	C9—C10—C4	121.62 (14)
C9—O1—C2—C18	-157.1 (1)	C2—O1—C9—C10	14.3 (2)
C9—O1—C2—C19	85.3 (2)	O1—C9—C10—C4	-1.4 (2)
C9—O1—C2—C3	-40.0 (2)	C3—C4—C10—C9	15.9 (2)
O1—C2—C3—C4	57.3 (2)	C11—C4—C10—C9	-107.3 (2)
C18—C2—C3—C4	171.0 (1)	C17—C4—C10—C9	131.6 (2)
C19—C2—C3—C4	-63.5 (2)	C10—C4—C11—C12	179.1 (1)
C2—C3—C4—C10	-44.4 (2)	C3—C4—C11—C12	58.5 (2)
C2—C3—C4—C11	79.0 (2)	C17—C4—C11—C12	-59.4 (2)
C2—C3—C4—C17	-161.9 (1)		

The structure was solved by direct methods (MULTAN78; Main et al., 1978). The H atoms were introduced at calculated positions, and included as riding atoms in the structure-factor calculations. The H atoms were fixed with displacement parameters of $1.2U_{eq}$ that of the parent atom.

Data collection: Rigaku/AFC Diffractometer Control Software (Rigaku Corporation, 1985). Cell refinement: Rigaku/AFC Diffractometer Control Software. Data reduction: Rigaku/AFC Diffractometer Control Software. Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: PLUTO (Motherwell & Clegg, 1978) and ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

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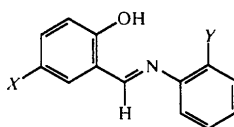
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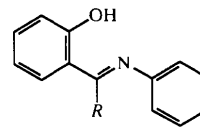
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Methyl- and Phenyl-Substituted Salicylideneanilines

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Abstract

The angles between the phenol and anil ring systems attached to the imine functions of 2-hydroxyacetophenone anil [IUPAC name: 2-(1-phenyliminoethyl)-phenol; $C_{14}H_{13}NO$] and 2-hydroxybenzophenone anil {IUPAC name: 2-[phenyl(phenylimino)methyl]phenol; $C_{19}H_{15}NO$} are 101.6(1) and 103.2(1)°, respectively. These are larger than in the corresponding salicylideneanilines derived from aldehydes because of steric repulsions arising from the substitution of H by Me or Ph. Bond lengths and angles are, however, broadly similar in the aldehyde- and ketone-derived systems.

Comment

Although there are several reports of crystal structures of salicylaldehyde anils, including the parent member of the series, (1) (Destro *et al.*, 1978), none is available for derivatives of the corresponding ketones. Here we rectify this omission in the literature and report the crystal structures of two anil derivatives of acetophenone and benzophenone, (2) and (3), respectively.
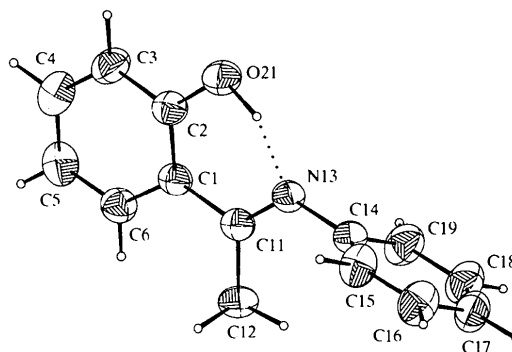
(1) X=Y=H
(4) X=Cl, Y=H
(5) X=H, Y=Cl

(2) R=Me
(3) R=Ph

While the crystal structure of the parent salicylideneaniline, (1), is severely disordered, precluding detailed comparison with (2) and (3), data for the chloro derivatives (4) (Bregman, Leiserowitz & Schmidt, 1964) and (5) (Bregman, Leiserowitz & Osaki, 1964) are adequate for this purpose. All of the compounds (1)–(5) have an *E* (or *anti*) configuration at the C=N moiety in order to accommodate hydrogen bonding with the *ortho*-hydroxy function (Figs. 1 and 2). The overall conformation of this family of compounds appears to be governed by steric factors in the neighbourhood of the imine function. Thus compound (4), in which $Y = H$, is planar to within 1°, whereas in (5) ($Y = Cl$), the angle between the two phenyl rings is 51.5°, and in

Fig. 1. A view of (2) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces. Hydrogen-bonding parameters are O21···N13 2.554 (3) and H21···N13 1.63 (3) Å.

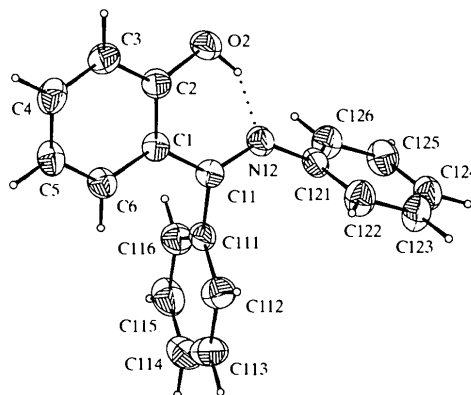Fig. 2. A view of (3) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces. Hydrogen-bonding parameters are O2···N12 2.550 (2) and H2···N12 1.70 (2) Å.