References

FRENZ, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package.* Version 3.0. Enraf–Nonius, Delft, The Netherlands.

JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KILLEAN, R. C. G. & LAWRENCE, J. L. (1969). *Acta Cryst.* B25, 1750–1752.

LUSS, H. R. GARTI, N. & TEXTER, J. (1992). To be published.

LUSS, H. R. & TEXTER, J. (1991). *Acta Cryst.* C47, 1491–1493.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

SAKAMOTO, K., TANAKA, M., HANZAWA, T. & KASAI, J. (1972). US Patent 3 700 454.

TONG, L. K. J. (1977). *The Theory of the Photographic Process,* edited by T. H. JAMES, pp. 339–353. New York: Macmillan.

The Structure of Triphenylmethanol, Ph₃COH

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Abstract. $C_{19}H_{16}O$, $M_r = 260.3$, trigonal, $R\overline{3}$, $a = 19.307$ (3), $c = 26.735$ (4) Å, $V = 8631$ (2) Å^3, $Z = 24$, $D_x = 1.20$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.7$ cm^{-1}, $F(000) = 3312$, $T = 294$ K, $R = 0.083$, $wR = 0.068$ for 1022 observed reflections. The structure contains hydrogen-bonded pyramidal tetramers (which have approximate 32 symmetry) with one molecule lying on a crystallographic threefold axis and another in a general position. The analysis was complicated by disorder in the crystal lattice where 71% of the tetramers occupy one orientation and 29% another; these moieties have their phenyl rings in the same volume elements in the lattice. The O⋯O separations in the hydrogen-bond systems are 2.884 (10) and 2.896 (11) Å in the major tetramer and 2.80 (3) and 2.90 (3) Å in the minor tetramer.

Introduction. We have been interested for some time in the structures of the series Ph₃MOH (*M* = C, Si, Ge, Sn, Pb). Although full structural data are available (*see below*) for the Si, Ge, Sn and Pb derivatives, no structural data are available for the Ph₃COH

compound [a recent search of the Cambridge Structural Database (October 1991, 90 295 entries) for the unsolvated triphenylmethanol molecule yielded no hits]. In a brief footnote to a paper on the structures of methanol and dimethyl sulfoxide hydrogen-bonded clathrates of triphenylmethanol, Weber, Skobridis & Goldberg (1989) mention that a crystal structure analysis of the unsolvated triphenylmethanol led to a structural model which would not refine satisfactorily. This was attributed to poor crystal quality, possibly resulting from twinning or the inclusion of small non-stoichiometric amounts of solvent; no structural data or details were given apart from the statement that the compound 'self-associates by forming H-bonded tetramers which pack rather loosely in the crystalline state'. We have obtained well formed unsolvated crystals of triphenylmethanol by slow evaporation of a saturated benzene solution and report the crystal structure.

Experimental. A crystal measuring 0.45 × 0.30 × 0.30 mm was mounted on a glass fibre with its long

axis roughly parallel to the φ axis of the goniometer. Cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation, from a least-squares refinement of the setting angles of 25 reflections in the range $19 < 2\theta < 30°$. Intensities of reflections with indices h -21 to 21, k 0 to 24, l 0 to 25 and with $2 < 2\theta < 54°$ measured; ω–2θ scans; ω-scan width $(0.8 + 0.35\tan\theta)°$. Data collection was terminated midway through the 40–54° 2θ shell when it became obvious that no 'observable' data were being collected. Intensities of three reflections were measured at 2 h intervals; these standards remained constant within experimental error throughout data collection. In all, 3916 reflections were measured, of which 2467 were unique (R_{int} 0.016 on I) and only the 1022 which had $I > 2.5\sigma(I)$ were labelled observed and used in structure solution and refinement. The conditions governing reflection (hkl only present if $-h + k + l = 3n$) and Laue symmetry $\bar{3}$ allow the space group to be $R3$ or $R\bar{3}$. $R\bar{3}$ was indicated by analysis of E statistics and confirmed by the refinement. Data were corrected for Lorentz and polarization effects. The structure was solved with some difficulty. Our initial attempts by direct methods ($SHELXS86$; Sheldrick, 1986) yielded directly what looked to be a very good solution, with one molecule on a threefold axis and another in a general position to produce a hydrogen-bonded pyramidal tetramer. Although all the metrical details appeared reasonable ('normal' bond lengths and no untoward intermolecular contacts), the structure would not refine below an R value of 0.20. Careful inspection of difference maps with the graphics programs of $NRCVAX$ (Gabe, Le Page, Charland, Lee & White, 1989) led us to conclude that the structure contained two intertwined tetramers (which we subsequently showed by refinement to be in a 71/29 ratio in the crystal lattice). The tetramer clearly revealed by $SHELXS86$ was the major component; what made it difficult to interpret the structure initially was the fact that each phenyl-ring site (four independent ones in the asymmetric unit) of the minor tetramer lay in the same volume element as a phenyl ring of the major tetramer, with many atoms in common sites.

Once a plausible model had been assembled, the structure was refined by block-diagonal least-squares methods (on F), with all phenyl rings constrained to be regular hexagons (C—C 1.395, C—H 0.95 Å). The relative occupancies of the two components were determined during isotropic refinement and fixed at 0.71 (2) and 0.29 (2) before the final refinement. Because of the paucity of observed data, in the final refinement cycles only the non-H atoms of the major isomer were allowed anisotropic motion. H-atom thermal parameters were assigned values 1.1 times

the mean U_{iso} value of the atom to which they were bonded. The hydroxyl H atoms could not be unequivocally located (presumably because of the internal disorder). The final refinement cycles included 253 variable parameters, $R = 0.083$, $wR = 0.068$, goodness of fit 0.89, unit weights. Max. shift/e.s.d. 0.024; density range in final difference map from -0.19 to $+0.19$ e Å^{-3}. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculations were performed on a PC386/33 computer system ($SHELXS86$; Sheldrick, 1986) and on a Silicon Graphics 4D-35TG computer using the $NRCVAX$ suite of programs (Gabe *et al.*, 1989). Atomic coordinates and selected molecular dimensions are given in Tables 1 and 2 respectively.* Fig. 1 is a view of the major tetramer and Fig. 2 is a stereoview showing the two components of the disordered system prepared using $ORTEPII$ (Johnson, 1976).

Discussion. The structural motif is a hydrogen-bonded pyramidal tetramer which is disordered (71/29) about two interpenetrating sites. Both component systems have similar geometry and have threefold crystallographic symmetry, with one Ph_3COH molecule lying with its C—O bond along a crystallographic threefold axis and one molecule in a general position. A view of the major tetramer with our numbering scheme is in Fig. 1; Fig. 2 shows how the major and minor components are intertwined with their phenyl rings almost overlapping. Inspection of the drawing of the tetramer in Fig. 1 shows that it has approximate 32 symmetry but this is not a crystallographic requirement. To have a tetramer with a crystallographic symmetry higher than threefold would require the Laue symmetry of the diffraction pattern to be $\bar{3}m$; it was obvious from a listing of the reflection data in $(\sin\theta)/\lambda$ order that this is not so and averaging the data assuming $\bar{3}m$ symmetry yielded numerous very bad individual 'agreements' and an R_{int} of 0.300 on I (compare with 0.016 on I for $\bar{3}$ symmetry).

The O···O separations in the major tetramer [O(1)···O(2) 2.884 (10), O(2)···O(2^i) 2.896 (12) Å] are entirely consistent with these being hydrogen-bonded distances. The minor-tetramer component has similar geometry with hydrogen-bonded distances O(3)···O(4) 2.80 (3), O(4)···O(4^i) 2.90 (3) Å. The hydroxyl H atoms have to be disordered because of

Table 1. *Atomic parameters x, y, z and B_{eq} (Å^2)*

	x	y	z	B_{eq}*
O(1)	0	0	0.3204 (4)	7.0 (5)
C(1)	0	0	0.3746 (6)	5.1 (7)
O(2)	−0.0975 (4)	−0.0297 (5)	0.2325 (3)	6.7 (5)
C(2)	−0.1757 (6)	−0.0525 (6)	0.2139 (3)	5.0 (7)
O(3)	0	0	0.1908 (12)	7.5 (9)
C(3)	0	0	0.1368 (15)	4.9 (10)
O(4)	−0.0723 (12)	−0.0962 (13)	0.2750 (8)	8.7 (5)
C(4)	−0.1315 (15)	−0.1788 (15)	0.2906 (9)	5.3 (6)
C(11)	−0.0597 (4)	−0.0836 (3)	0.3921 (3)	4.8 (7)
C(12)	−0.1313 (4)	−0.1276 (4)	0.3659 (2)	6.5 (8)
C(13)	−0.1887 (3)	−0.2032 (4)	0.3829 (3)	7.8 (8)
C(14)	−0.1745 (4)	−0.2347 (3)	0.4261 (3)	8.1 (9)
C(15)	−0.1029 (5)	−0.1907 (5)	0.4523 (2)	7.5 (9)
C(16)	−0.0456 (4)	−0.1152 (4)	0.4353 (3)	7.7 (9)
C(21)	−0.2336 (4)	−0.1369 (4)	0.2304 (3)	5.4 (7)
C(22)	−0.2070 (4)	−0.1919 (5)	0.2336 (3)	6.8 (9)
C(23)	−0.2602 (6)	−0.2710 (5)	0.2469 (3)	9.5 (12)
C(24)	−0.3400 (5)	−0.2951 (4)	0.2570 (3)	10.7 (13)
C(25)	−0.3666 (4)	−0.2401 (5)	0.2538 (3)	9.7 (11)
C(26)	−0.3135 (5)	−0.1610 (5)	0.2404 (3)	7.8 (10)
C(31)	−0.1994 (4)	0.0062 (4)	0.2332 (3)	5.3 (7)
C(32)	−0.2361 (5)	0.0377 (5)	0.2033 (2)	7.1 (9)
C(33)	−0.2575 (5)	0.0910 (5)	0.2236 (3)	8.3 (10)
C(34)	−0.2421 (5)	0.1127 (5)	0.2739 (3)	9.2 (11)
C(35)	−0.2054 (6)	0.0812 (5)	0.3038 (2)	11.2 (14)
C(36)	−0.1840 (5)	0.0279 (5)	0.2835 (3)	8.3 (10)
C(41)	−0.1701 (4)	−0.0469 (4)	0.1571 (2)	5.1 (7)
C(42)	−0.2336 (4)	−0.1022 (4)	0.1278 (3)	7.0 (8)
C(43)	−0.2310 (5)	−0.0932 (6)	0.0760 (3)	19.2 (20)
C(44)	−0.1650 (6)	−0.0291 (6)	0.0534 (2)	11.8 (14)
C(45)	−0.1015 (5)	0.0262 (5)	0.0827 (3)	7.1 (8)
C(46)	−0.1040 (4)	0.0173 (4)	0.1346 (3)	7.3 (8)
C(51)	−0.0764 (8)	−0.0149 (11)	0.1234 (7)	7.4 (7)
C(52)	−0.1446 (11)	−0.0745 (11)	0.1472 (5)	7.1 (7)
C(53)	−0.2181 (9)	−0.1103 (8)	0.1224 (5)	5.5 (6)
C(54)	−0.2232 (8)	−0.0866 (9)	0.0739 (5)	3.0 (4)
C(55)	−0.1550 (10)	−0.0270 (10)	0.0502 (5)	6.4 (7)
C(56)	−0.0815 (8)	0.0088 (9)	0.0750 (7)	8.8 (9)
C(61)	−0.2146 (9)	−0.1967 (12)	0.2718 (7)	5.4 (6)
C(62)	−0.2283 (12)	−0.1325 (9)	0.2760 (7)	10.8 (11)
C(63)	−0.3033 (15)	−0.1427 (12)	0.2644 (8)	8.8 (9)
C(64)	−0.3646 (10)	−0.2171 (15)	0.2486 (8)	13.4 (14)
C(65)	−0.3510 (10)	−0.2814 (10)	0.2443 (7)	7.2 (7)
C(66)	−0.2760 (11)	−0.2711 (10)	0.2560 (6)	6.0 (7)
C(71)	−0.1054 (12)	−0.2359 (12)	0.2699 (9)	6.7 (7)
C(72)	−0.0935 (14)	−0.2313 (13)	0.2183 (9)	12.8 (13)
C(73)	−0.0767 (15)	−0.2855 (17)	0.1943 (6)	13.7 (14)
C(74)	−0.0719 (14)	−0.3442 (14)	0.2219 (10)	11.3 (11)
C(75)	−0.0838 (13)	−0.3488 (12)	0.2736 (10)	10.8 (11)
C(76)	−0.1006 (12)	−0.2947 (14)	0.2975 (6)	7.8 (8)
C(81)	−0.1297 (12)	−0.1783 (12)	0.3498 (5)	5.5 (6)
C(82)	−0.0589 (9)	−0.1273 (10)	0.3750 (6)	7.1 (8)
C(83)	−0.0558 (9)	−0.1299 (10)	0.4270 (6)	5.2 (6)
C(84)	−0.1236 (12)	−0.1836 (12)	0.4539 (5)	7.7 (8)
C(85)	−0.1944 (10)	−0.2346 (11)	0.4288 (7)	8.3 (8)
C(86)	−0.1974 (9)	−0.2319 (11)	0.3767 (7)	9.3 (9)

*B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Table 2. *Selected interatomic distances (Å) and angles (°)*

O(1)—C(1)	1.448 (19)	O(1)—C(1)—C(11)	107.9 (6)
C(1)—C(11)	1.514 (7)	C(11)—C(1)—C(11^i)	111.0 (7)
O(2)—C(2)	1.434 (11)	O(2)—C(2)—C(21)	109.1 (8)
C(2)—C(21)	1.510 (12)	O(2)—C(2)—C(31)	108.6 (7)
C(2)—C(31)	1.509 (14)	O(2)—C(2)—C(41)	107.3 (7)
C(2)—C(41)	1.522 (10)	C(21)—C(2)—C(31)	111.8 (7)
		C(21)—C(2)—C(41)	110.8 (7)
		C(31)—C(2)—C(41)	109.1 (8)
O(3)—C(3)	1.44 (5)	O(3)—C(3)—C(51)	105 (2)
C(3)—C(51)	1.40 (2)	C(51)—C(3)—C(51^i)	114 (2)
O(4)—C(4)	1.49 (3)	O(4)—C(4)—C(61)	108 (2)
C(4)—C(61)	1.54 (3)	O(4)—C(4)—C(71)	108 (2)
C(4)—C(71)	1.53 (4)	O(4)—C(4)—C(81)	106 (2)
C(4)—C(81)	1.58 (3)	C(61)—C(4)—C(71)	114 (2)
		C(61)—C(4)—C(81)	110 (2)
		C(71)—C(4)—C(81)	111 (2)
O(1)···O(2)	2.884 (10)		
O(2)···O(2^i)	2.896 (12)		
O(3)···O(4)	2.80 (3)		
O(4)···O(4^i)	2.90 (3)		

The phenyl rings were constrained to be regular hexagons with C—C 1.395, C—H 0.95 Å.
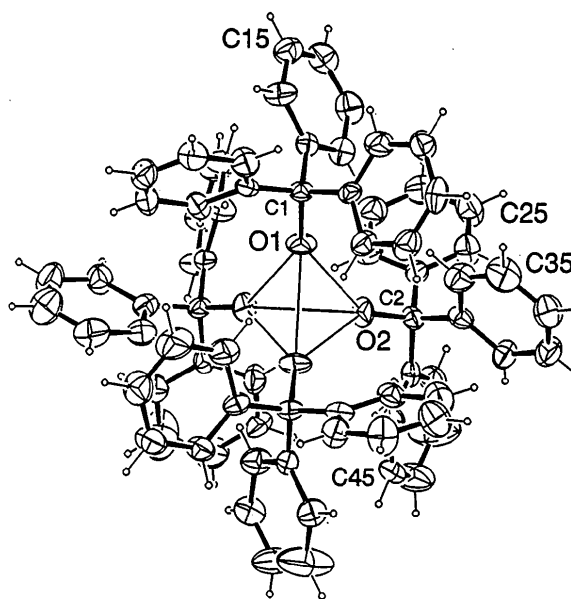
Symmetry code: (i) $-y, x - y, z$.

Fig. 1. A view of the major tetramer in the Ph$_3$COH structure with an indication of the numbering scheme used. Thermal ellipsoids are at the 50% level except for the H atoms (small spheres of arbitrary size). The crystallographic threefold axis lies along the O(1)—C(1) bond.

the crystallographically imposed threefold symmetry and no clear indication of any of the H atoms involved in the H bonding was seen.

In the major tetramer, the phenyl rings in the Ph$_3$COH molecules adopt regular propeller-like conformations. In the molecule with threefold symmetry, the dihedral angle between the plane through atoms O(1)—C(1)—C(11) and C(1)—C(11)···C(16), is 36.7 (10)°; corresponding dihedral angles in the molecule in the general position are 33.7 (9), 43.8 (8) and 38.8 (8)°. The analogous angles in the minor tetramer are respectively 36 (3)° and 37 (2), 53 (2) and 29 (2)°.

Because of the disorder and the relatively low percentage of observed data (24.1%), the accuracy of the structure (as expressed in terms of the e.s.d.'s of

the molecular dimensions) is not high, but serves to establish the structure unequivocally. The mean Csp^3—O and Csp^3—Csp^2 bond lengths (1.44 and 1.51 Å, respectively, see Table 2) are in accord with values (1.440 and 1.506 Å, respectively) reported by Allen, Kennard, Watson, Brammer & Orpen (1987). Distances between tetramers of the same sort correspond to normal van der Waals distances. Analysis
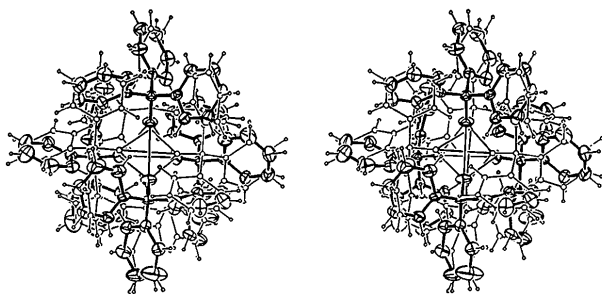
Fig. 2. A stereoview showing the intertwining of the major and minor tetramers in Ph_3COH. The view is such that the orientation of the major isomer is the same as in Fig. 1. For clarity, the atoms of the minor tetramer are shown as spheres of arbitrary size.

of the structural coordinates with *PLATON* (Spek, 1991) shows that there are no voids in the lattice which could have contained solvent.

This analysis completes the series for the group 14 Ph_3MOH molecules (M = C, Si, Ge, Sn, Pb). Ph_3SiOH (Puff, Braun & Reuter, 1991) is isomorphous with Ph_3GeOH (Puff *et al.*, 1991; Ferguson, Gallagher, Murphy, Spalding, Glidewell & Holden, 1992) and the structures consist of hydrogen-bonded tetramers with the O atoms in a flattened tetrahedral arrangement. Both Ph_3SnOH and Ph_3PbOH have structures consisting of zigzag chains of planar Ph_3M (M = Sn, Pb) groups joined by OH groups giving trigonal bipyramidal geometry at M (Glidewell & Liles, 1978). The molecular volumes (U/Z) for

Ph_3MOH show an increase from M = C to Pb with C 360, Si 381, Ge 385, Sn 389 and Pb 394 $Å^3$. The unique nature of the pyramidal hydrogen-bonded tetramer in Ph_3COH probably accounts for its relatively low molecular volume compared with the other molecules of the series.

References

ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L. & ORPEN, A. G. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
FERGUSON, G., GALLAGHER, J. F., MURPHY, D., SPALDING, T. R., GLIDEWELL, C. & HOLDEN, H. D. (1992). *Acta Cryst.* C48, 1228–1231.
GABE, E. J., LE PAGE, Y., CHARLAND, J. P., LEE, F. L. & WHITE, P. S. (1989). *J. Appl. Cryst.* 22, 384–389.
GLIDEWELL, C. & LILES, D. C. (1978). *Acta Cryst.* B34, 129–134.
JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
PUFF, H., BRAUN, K. & REUTER, H. (1991). *J. Organomet. Chem.* 409, 119–129.
SHELDRICK, G. M. (1986). *SHELXS86.* Program for the solution of crystal structures. Univ. of Göttingen, Germany.
SPEK, A. L. (1991). *PLATON. Program to Analyze Structural Data.* Univ. of Utrecht, The Netherlands.
WEBER, E., SKOBRIDIS, K. & GOLDBERG, I. (1989). *J. Chem. Soc. Chem. Commun.* pp. 1195–1197.

trans-5-(n-Heptyl)-4-(1-iodovinyl)-2-oxazolidinone and syn-[4-Cyclohexyl-2-iodo-3-(N-tosylamino)-1-buten-4-yl] Acetate

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Abstract. *trans*-5-(*n*-Heptyl)-4-(1-iodovinyl)-2-oxazolidinone, (6), $C_{12}H_{20}INO_2$, M_r = 337.2, monoclinic, $P2_1/a$, a = 13.820 (2), b = 6.205 (1), c = 17.550 (3) Å, β = 106.06 (1)°, V = 1446.2 (4) $Å^3$, Z = 4, D_x = 1.55 g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 21.8 cm^{-1}, $F(000)$ = 672, room temperature, R = 0.037 for 2679 observed reflections. *syn*-[4-Cyclohexyl-2-iodo-3-(*N*-tosylamino)-1-buten-4-yl]

acetate, (7), $C_{19}H_{26}INO_4S$, M_r = 491.4, monoclinic, $P2_1/a$, a = 12.233 (3), b = 13.733 (3), c = 14.169 (6) Å, β = 112.75 (3)°, V = 2213.1 $Å^3$, Z = 4, D_x = 1.49 g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 15.5 cm^{-1}, $F(000)$ = 992, room temperature, R = 0.047 for 1311 observed reflections. The tentative assignments of the relative stereochemistries of compounds (6) and (7) were confirmed by the structure determinations. Molecules of (6) form hydrogen-bonded chains [N(—H)$\cdots$O 2.975 (4) Å] while in (7) pairs of molecules form hydrogen-bonded centro-

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