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Triphenylmethanol–triphenylphosphine oxide (1/1)

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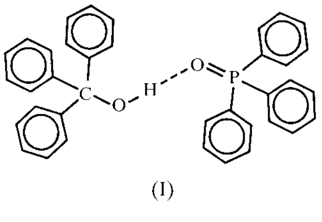
In the crystalline 1:1 molecular complex of triphenylmethanol (TPMeOH) and triphenylphosphine oxide (TPPO), $C_{19}H_{16}O\cdot C_{18}H_{15}OP$, molecular dimers are formed which are linked by O—H···O=P hydrogen bonds. The dimers are aligned by sixfold phenyl embraces to form columns. The structure is disordered with half a dimer per asymmetric crystal unit, *i.e.* with only one molecular site which is half-occupied by both TPMeOH and TPPO.

Comment

In recent years, there has been considerable interest in multiple phenyl interactions of $-X\text{Ph}_3$ groups and $X\text{Ph}_4^+$ cations (Dance & Scudder, 1996). The most characteristic of these interactions is the 'sixfold phenyl embrace' (6PE) that involves six concerted edge-to-face phenyl–phenyl interactions. Typically, 6PEs are formed between chemically equivalent groups, such as $M\text{PPh}_3$ (M is a transition metal atom) or PPh_4^+, and frequently, the groups are even equivalent crystallographically. 6PEs can also be formed between unequal $X\text{Ph}_3$ groups; an example has been described in some detail for $-\text{SiPh}_3\cdots\text{Ph}_3\text{P}=$ (Steiner *et al.*, 1997). 6PEs frequently aggregate in molecular columns which form hexagonal or quasi-hexagonal supramolecular arrays (Scudder & Dance, 1998; Steiner, 1998). Relative frequencies of 6PE formation in crystals have been determined for $-X\text{Ph}_3$ groups with all tetrahedral central atoms X (Steiner, 2000).



(I)

The typical 6PE found in crystal structures has not been made on purpose, but appeared unintentionally. To see if it can also be controlled in an experiment, it was planned to make a particular kind of 6PE in a new crystal structure. Because there is little literature on 6PEs between unequal $X\text{Ph}_3$ groups, the aim was to create a 6PE of the kind $X\text{Ph}_3\cdots\text{Ph}_3Y$, with $X \neq Y$. A promising system would be a molecular complex of triphenylmethanol (TPMeOH) and triphenylphosphine oxide (TPPO). The idea is that in a complex of these compounds, there would be dimer formation by O—H···O=P hydrogen bonding, (I). Such a dimer carries unequal $X\text{Ph}_3$ groups at its ends, and can readily aggregate in columns linked by 6PEs, $-\text{CPh}_3\cdots\text{Ph}_3\text{P}=$. With this aim in mind, complex (I) was prepared from methanolic solution.

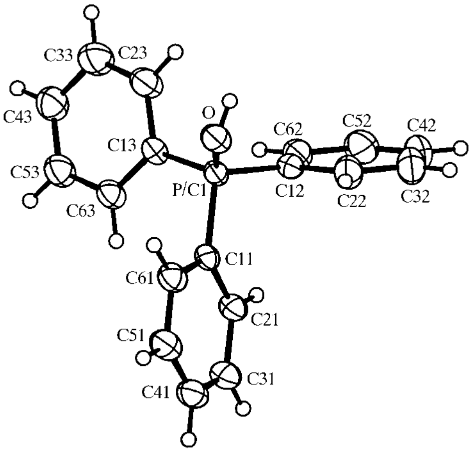


Figure 1
The molecular structure of (I) showing 30% probability displacement ellipsoids.

In the crystal structure of (I) (space group $P2_1/c$), only one triphenyl molecule per asymmetric unit is found, as shown in Fig. 1. The refined molecule represents neither pure TPMeOH nor TPPO, but rather an overlay of the two. The central atom cannot be refined well as C or P, but refines nicely with site occupation $\frac{1}{2}$C + $\frac{1}{2}$P. The average X—C(Ph) bond length is 1.690 (4) Å, which is close to the average of P—C(Ph) in TPPO (1.803 Å, average over three modifications; Brock *et al.*, 1985; Spek, 1987) and C—C(Ph) in TPMeOH (1.514 Å; Ferguson *et al.*, 1992). The H(O) atom shown in Fig. 1 has been found in difference Fourier calculations, is in proper covalent geometry [O—H = 0.82 (6) Å, X—O—H = 104 (4)°, staggered conformation with C11—X—O—H = 167 (5)°], and has a refined occupancy of 0.49 (7) and a displacement parameter of U_{eq} = 0.05 (3) Å^2. All this indicates that the molecular site in crystalline (I) is equally populated by TPMeOH and TPPO

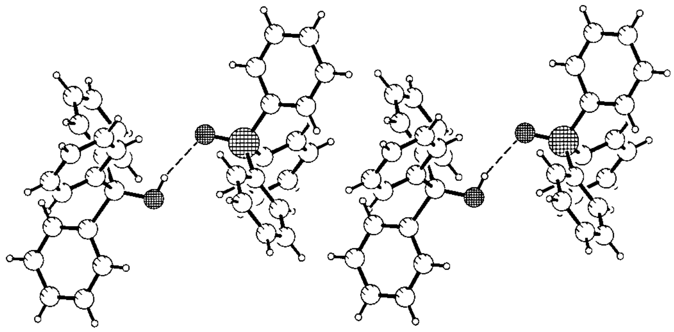


Figure 2
The molecular column in (I), organized by O—H···O hydrogen bonds and sixfold phenyl embraces.

molecules. The phenyl rings form a propeller, with dihedral angles between the phenyl least-squares planes and the O—X—C1n planes of 28.4 (2), 44.1 (2) and 48.8 (2)° for rings 1, 2 and 3, respectively.

In the crystal lattice, the O atoms form intermolecular contacts across a centre of symmetry with an O···O distance of 2.824 (5) Å. The H atom is in almost ideal hydrogen-bonding geometry, with an H···O distance of 2.04 (6) Å [O—H = 0.82 (6) Å] and an O—H···O angle of 161 (6)°. Because there can be no such interaction between two molecules of the same kind, be it TPPO or TPMeOH [for the latter case, there would be an H···H contact of 1.3 (1) Å], this means that in each molecular pair in the lattice, one molecule is TPMeOH and one is TPPO. The two molecules are linked by the expected C—O—H···O═P hydrogen bond.

The TPMeOH–TPPO dimers are arranged in columns as shown in Fig. 2 (only one of the two possible orientations per dimer is shown). The dimers are linked by 6PEs of close to ideal geometry, with an $X\cdots X$ distance between the central atoms of 6.751 (3) Å and an O—X···O angle of 177.6 (1)°. In the ideal 6PE, this angle (‘collinearity’; Dance & Scudder, 1995) would be 180°. It should be noted that, similar to the hydrogen bond, the 6PE is also formed across a symmetry centre. Between neighbouring columns, there are lateral phenyl–phenyl interactions which need not be shown here.

The disorder within the columns deserves a closer look. The molecules TPMeOH and TPPO have dissimilar polar groups, but their triphenyl moieties are almost identical in size and shape. In consequence, the outer surface of dimer (I) is close to centrosymmetric and it is not really surprising that (I) can crystallize on a centre of symmetry. In the molecular columns formed, the dimers are incorporated in two different ways, $Ph_3C—OH\cdots O═PPh_3$ and $Ph_3P═O\cdots HO—CPh_3$. It would be of interest to know whether the dimer orientation is completely random or if there are locally ordered sequences; unfortunately, this cannot be answered from data of the present kind. In any case, there are three kinds of 6PEs in the disordered columns, depending on the mutual orientation of neighbouring dimers: $–CPh_3\cdots Ph_3P═$, $–CPh_3\cdots Ph_3C–$ and $═PPh_3\cdots Ph_3P═$. The mere fact of disorder indicates that formation of a 6PE involving, say, a $═PPh_3$ group is not very specific for discriminating a $–CPh_3$ from a $═PPh_3$ group. In the complex of triphenylsilylacetylene with TPPO, peculiarly, there are 3.5 symmetry-independent dimers, forming two ordered and two disordered columns (Steiner *et al.*, 1997). In the related complex 4-(triphenylmethyl)phenol–TPPO (Jetti *et al.*, 1999), molecular columns assembled by O—H···O hydrogen bonds and 6PEs are formed too, but no disorder is observed. This important difference compared to (I) is most probably due to the lack of pseudo-centrosymmetry of that adduct.

Experimental

Crystals were obtained by slow evaporation of a 1:1 methanolic solution of triphenylmethanol (Aldrich) and triphenylphosphine oxide (Lancaster).

Crystal data

$C_{19}H_{16}O\cdot C_{18}H_{15}OP$
M_r = 538.59
Monoclinic, $P2_1/c$
a = 8.483 (2) Å
b = 15.994 (3) Å
c = 10.988 (2) Å
β = 104.50 (3)°
V = 1443.3 (5) Å^3
Z = 2

D_x = 1.239 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 15.0–16.9°
μ = 0.127 mm^{-1}
T = 293 K
Plate, colourless
0.50 × 0.30 × 0.05 mm

Data collection

Rigaku AFC-5 diffractometer
ω scans
7018 measured reflections
3306 independent reflections
2195 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.033
$\theta_{\rm max}$ = 27.52°

$h = -2 \rightarrow 10$
$k = -20 \rightarrow 20$
$l = -14 \rightarrow 13$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.160
S = 1.190
3306 reflections
201 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 0.8066P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.20 e Å^{-3}

H atoms bonded to carbon were treated in the default riding model with isotropic displacement parameters allowed to vary. The hydroxyl H atom was located in difference Fourier calculations, and refined isotropically with a free occupation factor, leading to realistic values [occupied = 0.49 (7) and $U_{\rm eq}$ = 0.05 (3) Å^2].

Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1126). Services for accessing these data are described at the back of the journal.

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