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O-Phenyl (triphenylphosphoniomethyl)phosphonate phenol solvate: supramolecular structure generated by O—H···O, C—H···O and C—H···π(arene) hydrogen bonds

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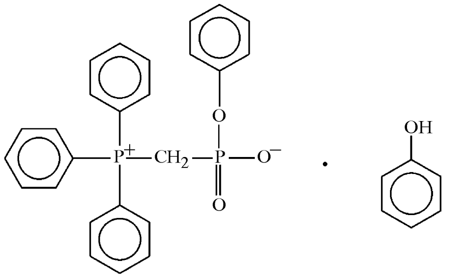
The title compound, $C_{25}H_{22}O_3P_2\cdot C_6H_6O$, has a zwitterionic betaine-like structure and crystallizes as a phenol solvate. The two molecular components are held together by an almost linear intermolecular O—H···O hydrogen bond. The structure also contains three weak C—H···O and two C—H···π(arene) interactions.

Comment

Betaine (*N*,*N*,*N*-trimethylglycine) acts as an important biochemical donor of the methyl group for tetrahydrofolic acid (N^5,N^{10}-methylenetetrahydrofolate synthesis) and homocysteinic acid (methionine synthesis) (Stryer, 1995). The phosphonic analogue of betaine – trimethylammoniummethanophosphonic acid – was first synthesized over five decades ago (Medved & Kabachnik, 1951; Kabachnik & Medved, 1953; Myers & Jibril, 1957); more than a decade ago, its biological activity became recognized (Abdel-Ghany *et al.*, 1993). However, to our knowledge, no example of a betaine analogue containing two P atoms (phosphoniummethylenephosphonic acid or its ester) has been described in the literature. We present here the synthesis and crystal and molecular structures of the first phosphoniophosphonic analogue of betaine, namely *O*-phenyl (triphenylphosphoniomethyl)phosphonate as a phenol solvate, (I).

The first example of phosphoniummethylenephosphonic acid was synthesized in the form of the *O*-phenyl ester by controlled hydrolysis of [(diphenoxyphosphinyl)methylidene]triphenylphosphorane, (II), and obtained in the crystalline form as the phenol solvate, (I). Its structure was tentatively assigned by MS, NMR and elemental analysis; however, an unequivocal confirmation was obtained from crystallographic analysis.



(I)

The molecular structure of (I), with the atom-numbering scheme, is shown in Fig. 1. The phosphonate molecule exists as a zwitterion. The positive charge is located on atom P1, while the negative charge is attributed formally to atom O2. Taking into account the P2—O2 and P2—O3 bond lengths (Table 1), partial delocalization of the charge between the two O atoms within the O2$\cdots$P2$\cdots$O3 fragment can be proposed. The P2—O3 bond is slightly shorter than the P2—O2 bond; however, both distances are longer than the P═O linkage within $(C,N)(O)_2$—P═O systems [1.457 (9) Å; Allen *et al.*, 1987] and close to the mean value of 1.483 (8) Å for $(C—O)_2P(\cdots O)_2^-$ systems, indicating bond delocalization (Allen *et al.*, 1987).

In the molecule of (I), two P atoms are joined through a Csp^3 atom. The P1—C1 and P2—C1 distances differ from each other significantly (Table 1). The coordination around P1 is nearly tetrahedral, with angles ranging from 106.98 (7) to 114.31 (7)°, whereas within the phosphonate group, the geometry around atom P2 indicates a considerable distortion of the tetrahedron, especially in the O2—P2—O3 and O1—P2—C1 bond angles (Table 1). The P^+—C(phenyl) bond lengths are very close to the mean distance of 1.793 (10) Å

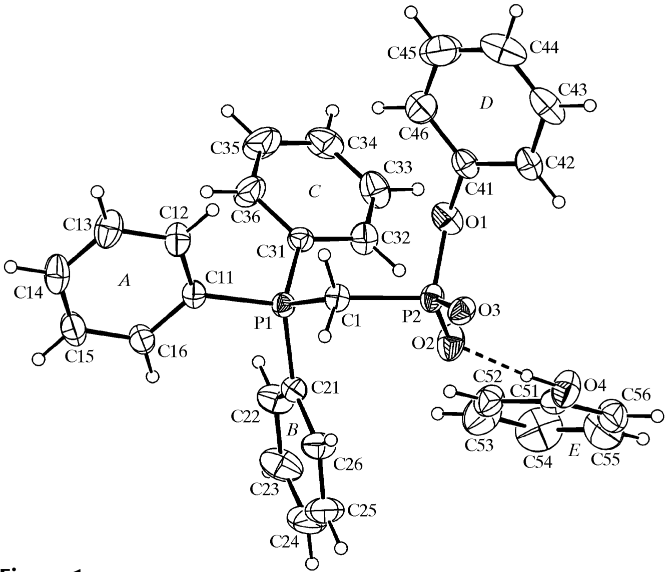


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

found for 118 $Ph_3P^+{-}Csp^3H_2$ fragments (3 × 118 = 354 values) in the Cambridge Structural Database (Version 5.27; Allen, 2002); the minimum and maximum distances are 1.752 (3) and 1.854 (3) Å, respectively.

All benzene rings, including the phenol ring, are planar; a maximum deviation of −0.010 (2) Å was observed for atom C12 from the least-squares plane of ring *A*. (The labelling scheme, *A*–*E*, applied for phenyl rings, is introduced in Fig. 1.) The C—C bond lengths and angles within these rings are typical for aromatic systems [1.384 (13) Å; Allen *et al.*, 1987], hence no detailed discussion is needed. The dihedral angles between the mean planes of the rings are summarized in Table 3. This spatial arrangement enables the formation of C—H···O and C—H···π(arene) interactions; however, aromatic π–π stacking interactions are absent in the structure.

Two molecular components are linked within the selected asymmetric unit by an almost linear O4—H4···O2 intermolecular hydrogen bond (Fig. 1 and Table 2).

There are also three short intermolecular C—H···O contacts (Table 2), which on the basis of observed H···O and C···O distances can be regarded as weak hydrogen-bonding interactions (Taylor & Kennard, 1982). Atoms C1 and C12 act as hydrogen-bond donors to atom O3^{i} [symmetry code: (i) $-x + 1, -y + 1, -z + 2$], forming a centrosymmetric dimer. The former of these hydrogen bonds generates a graph-set motif of $R_2^2(8)$, while the second generates an $R_2^2(14)$ ring (Bernstein *et al.*, 1995) (Fig. 2). Such a dimer is additionally stabilized by C1—H1*A*···π(ring *D*) hydrogen bonds.

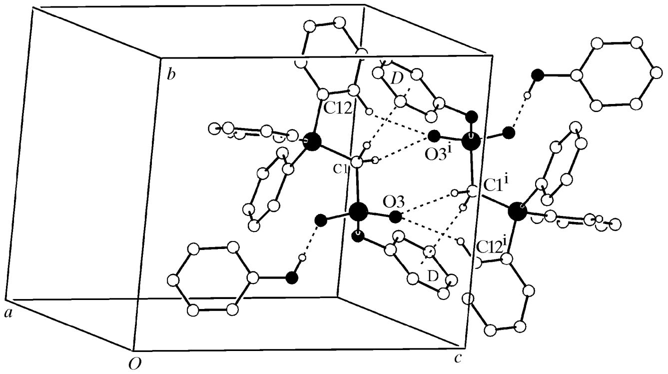


Figure 2
Part of the crystal structure of (I), showing the formation of a centrosymmetric dimer. For the sake of clarity, C-bound H atoms that are not involved in the motif shown have been omitted. [Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.]

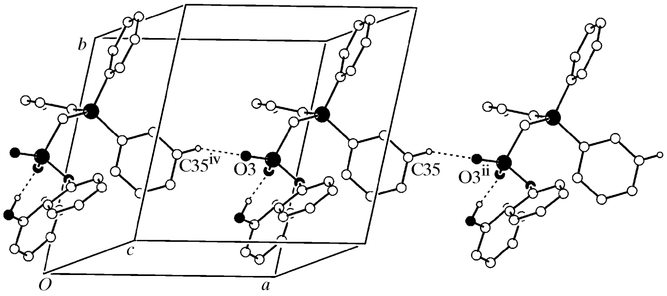


Figure 3
Part of the crystal structure of (I), showing the formation of an infinite C—H···O chain running parallel to the [100] direction. For the sake of clarity, C-bound H atoms that are not involved in the motif shown have been omitted. [Symmetry codes: (ii) $x + 1, y, z$; (iv) $x - 1, y, z$.]

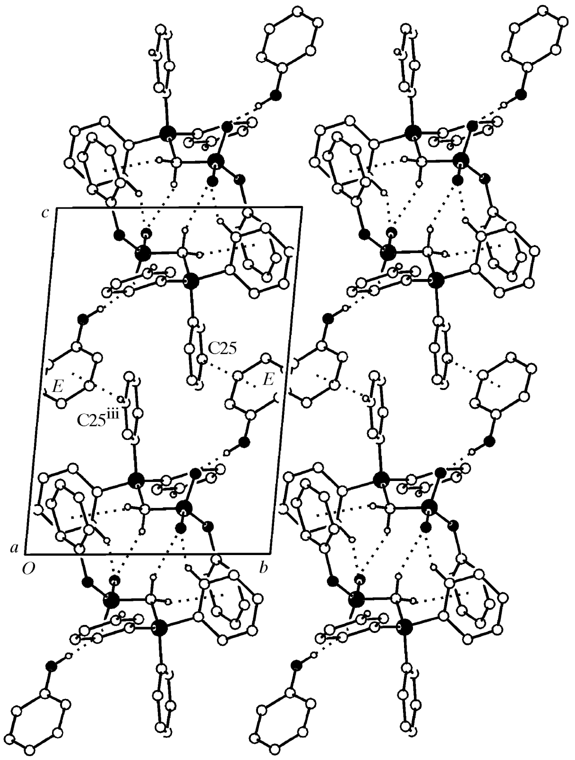


Figure 4
Part of the crystal structure of (I), showing (010) sheets generated by C—H···π interactions between chains of dimers. For the sake of clarity, C-bound H atoms that are not involved in the motif shown have been omitted. [Symmetry code: (iii) $-x + 1, -y + 1, -z + 1$.]

Fig. 3 shows another hydrogen-bonded motif that plays an important role in the supramolecular structure of (I). Atom C35, *via* atom H35, acts as a hydrogen-bond donor towards atom O3^{ii} [symmetry code: (ii) $x + 1, y, z$], thereby producing an infinite *C*(8) chain running parallel to the [100] direction.

In summary, the combination of all three weak C—H···O interactions produces infinite chains of centrosymmetric dimers along the *a* axis. The aforementioned chains are linked into (010) sheets by C25—H25···π^{iii} interactions [ring *E*; symmetry code: (iii) $-x + 1, -y + 1, -z + 1$; Fig. 4]. Every sheet passes through the unit cell in the domain $-0.07 < y < 1.07$. There are no direction-specific interactions between adjacent sheets.

Experimental

The title compound, (I), was synthesized from [(diphenoxyphosphinyl)methylidene]triphenylphosphorane, (II), which was prepared exactly as described in our previous paper (Chęcińska *et al.*, 2003). For (II): ^{31}P NMR (CD_3CN): δ 20.98 (*d*, $Ph_3P{=}$), 28.03 [*d*, $(PhO)_2P(O)$–, $^2J_{PP}$ = 46.4 Hz]. The ylide (II) (1.08 g, 1 mmol) was dissolved in 20 ml of acetonitrile containing 2% water. The solution was kept for 48 h at 323 K in a closed flask and evaporated. The

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residue was crystallized from ethyl acetate, yielding 0.61 g (58%) of phenol-solvated betaine (I) in the form of colorless crystals (m.p. 476–479 K). ^{31}P NMR ($CDCl_3$): δ −1.64 [*d*, (PhO)P(O)O$^-$], 212.36 (*d*, Ph_3P^+, $^2J_{PP}$ = 10.1 Hz). ^{1}H NMR ($CDCl_3$): δ 3.565 (*dd*, 2H, P—CH_2—P, $^2J_{HP}$ = 15.7 and 17.1 Hz), 6.7–7.2 (*m*, 10H, PhO H atoms), 7.45–7.8 (*m*, 15H, Ph_3P H atoms), 9.44 (*br s*, 1H, OH). MS FAB (Cs^+, negative ions): *m*/*z* 431 (16%), 355 (100%), 278 (8%), 261 (28%). Elemental analysis found: C 70.49, H 5.25, P 11.58%; calculated for $C_{31}H_{28}O_4P_2$: 70.72, H 5.36, P 11.77%.

Crystal data

$C_{25}H_{22}O_3P_2 \cdot C_6H_6O$
M_r = 526.47
Triclinic, $P\overline{1}$
a = 9.793 (2) Å
b = 10.170 (2) Å
c = 14.374 (2) Å
α = 82.78 (2)°
β = 80.07 (2)°
γ = 78.35 (2)°
V = 1374.9 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 293 (2) K
0.5 × 0.2 × 0.1 mm

Data collection

Rigaku AFC-5*S* diffractometer
6644 measured reflections
6293 independent reflections
4137 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
3 standard reflections
every 150 reflections
intensity decay: 1.6%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.082
S = 1.02
6293 reflections
338 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—C1	1.7855 (14)	P2—O2	1.4815 (11)
P1—C21	1.7923 (14)	P2—O1	1.6189 (12)
P1—C11	1.7991 (15)	P2—C1	1.8202 (15)
P1—C31	1.8009 (15)	O1—C41	1.3809 (18)
P2—O3	1.4695 (10)	O4—C51	1.3523 (19)
C1—P1—C21	110.26 (7)	O3—P2—O1	111.10 (6)
C1—P1—C11	106.98 (7)	O2—P2—O1	105.09 (7)
C21—P1—C11	109.54 (7)	O3—P2—C1	107.50 (7)
C1—P1—C31	114.31 (7)	O2—P2—C1	107.85 (7)
C21—P1—C31	107.97 (7)	O1—P2—C1	101.60 (7)
C11—P1—C31	107.68 (7)	C41—O1—P2	124.97 (9)
O3—P2—O2	121.84 (7)	P1—C1—P2	120.06 (8)

Table 2
Hydrogen-bond geometry (Å, °).

CgD and *CgE* are the centroids of rings *D* and *E*, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O2	0.89 (2)	1.72 (2)	2.601 (2)	175 (2)
C1—H1*B*···O3^{i}	0.97	2.30	3.142 (2)	145
C12—H12···O3^{i}	0.93	2.57	3.269 (2)	133
C35—H35···O3^{ii}	0.93	2.36	3.200 (3)	150
C1—H1*A*···*CgD*^{i}	0.93	2.79	3.727 (2)	161
C25—H25···*CgE*^{iii}	0.93	2.90	3.667 (2)	141

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+1$.

Table 3
The dihedral angles between the mean planes for the phenyl rings (°).

Symbols *A*–*E* refer to the phenyl rings as defined in Fig. 1.

Ring/ring	Dihedral angle
A/*B*	78.1 (1)
A/*C*	77.4 (1)
A/*D*	36.1 (1)
A/*E*	44.1 (1)
B/*C*	72.8 (1)
B/*D*	43.8 (1)
B/*E*	68.5 (1)
C/*D*	83.1 (1)
C/*E*	58.6 (1)
D/*E*	52.8 (1)

Atom H4, involved in the O4—H4···O2 hydrogen bond, was located in a difference map and refined isotropically. All C-bound H atoms of methylene and phenyl groups were positioned geometrically (C—H = 0.97 and 0.93 Å, respectively) and constrained to ride on their parent atoms [U_{iso}(H) = 1.2U_{eq}(C)].

Data collection: *MSC*/*AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC*/*AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3145). Services for accessing these data are described at the back of the journal.

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