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Benzoylmethyltriphenylphosphonium hydrogen maleate: supramolecular layer formation due to C—H···O interactions

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The molecule of the title salt, $C_{26}H_{22}OP^{+}.C_4H_3O_4^{-}$, consists of a benzoylmethyltriphenylphosphonium cation (HBPPY) and a hydrogen maleate anion. Owing to a strong O—H···O intraionic hydrogen bond, each hydrogen maleate ion forms a ring, described by the graph-set notation $S_1^1(7)$. Several C—H···O interactions are present between the cations and anions and contribute to the stabilization of the crystal structure.

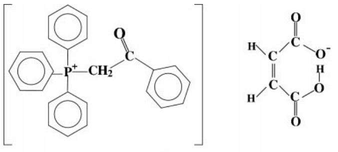
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.041
wR factor = 0.106
Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Resonance-stabilized ketophosphorus ylides containing basic carbon and oxygen sites undergo C-protonation readily with mineral acids (Antipin & Struchkov, 1984; Baby Mariyatra *et al.*, 2002*a*). The proton affinity values of benzoylmethylenetriphenylphosphorane (BPPY) have been determined using PM3 calculations and reveal that C-protonation is energetically more favourable than O-protonation by only 13 kJ mol^{-1} (Laavanya, 2002). By varying the anionic component of this salt we have attempted to obtain the O-protonated form of the benzoylmethyltriphenylphosphonium cation. Mineral acids and some hydrated metal salts are known to C-protonate the ylide, BPPY, forming the corresponding phosphonium salts and the phosphonium metalates respectively (Baby Mariyatra *et al.*, 2002*a*,*b*, 2003; Albanese *et al.*, 1989). To investigate the influence of some dicarboxylic acids on the mode of protonation, the reaction of maleic acid with BPPY has been performed. The formation of benzoylmethyltriphenylphosphonium hydrogen maleate, (I), was confirmed by single-crystal X-ray diffraction.



(I)

The solid-state structure of the title salt, (I) (Fig. 1), comprises of benzoylmethyltriphenylphosphonium cations and hydrogen maleate anions. The presence of COOH and COO^{-} groups in the hydrogen maleate ion is indicated by a pair of C—O bond lengths (C27—O2 and C27—O3) which differ by 0.078 (2) Å and by the corresponding bond lengths at C30 with a difference of 0.055 (2) Å (Table 1). The stability of the hydrogen maleate ion is ascribed to the presence of a strong O2—H1···O5 hydrogen bond (Table 2). The location of two H atoms, H8*A* and H8*B*, and the angle H8*A*—C8—H8*B* of 106.4 (16)° confirms C8 as the site of protonation. The P1—C8, C7—O1 and C8—C7 distances of 1.8020 (16),

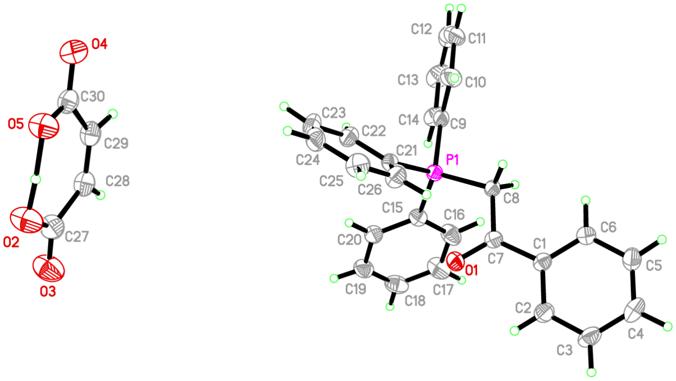


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

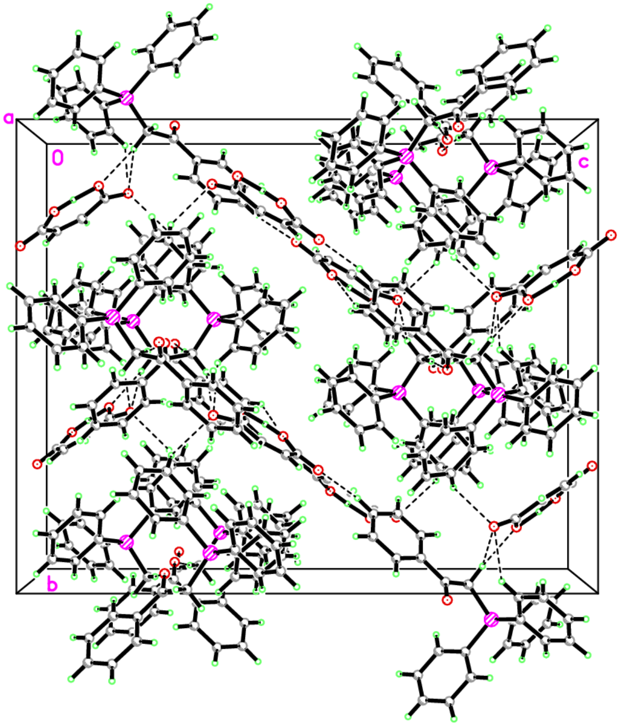


Figure 2
The crystal structure of (I), projected along the *a* axis.

1.2198 (19) and 1.516 (2) Å, respectively, are comparable with those of the previously reported phosphonium salts (Baby Mariyatra *et al.*, 2002*a*,*b*, 2003). The O1—C7—C8—P1 torsion angle of −11.78 (19)° shows the near-coplanarity of the P and O centres.

In the crystal structure, the phosphonium cations are interlinked through C—H···O interactions between one of the methylene H atoms and the benzoyl O atom of the neighbouring phosphonium cation at $(x - \frac{1}{2}, y, \frac{1}{2} - z)$. The HBPPY cations and the hydrogen maleate anions are connected through C—H···O interactions, forming close-packed zigzag layers in the *bc* plane (Table 2 and Fig. 2). Both the methylene H8*A* and H8*B* atoms are involved in the interionic C—H···O interactions (Fig. 3). Atom H8*B* forms a bifurcated hydrogen bond with O4 and O5 of the hydrogenmaleate ion at $(1 - x, -y, 1 - z)$. A C—H···π interaction of 2.79 (2) Å between H25 and $Cg1(-x, 1 - y, -z)$ also contributes to the intermolecular interactions, *Cg*1 being the centroid of the aromatic ring of the benzoyl group (C1–C6).

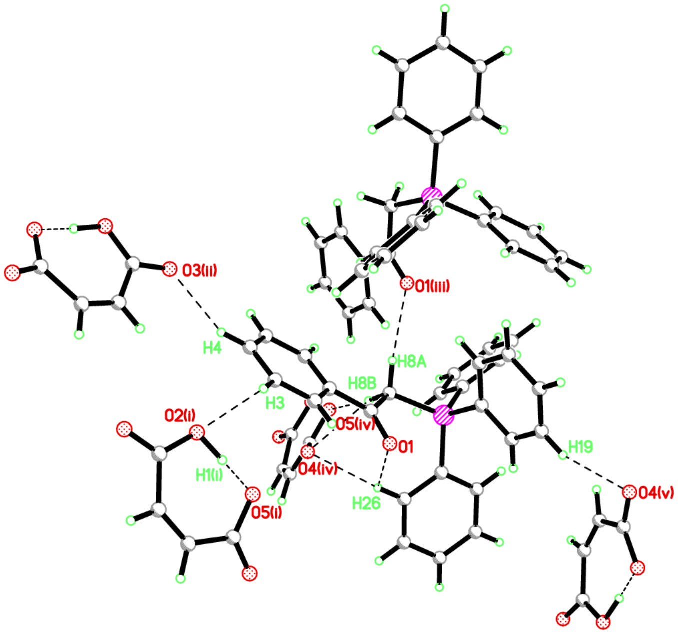


Figure 3
Diagram showing the intermolecular interactions in the structure of (I). [Symmetry codes: (i) $\frac{3}{2} - x, -y, \frac{1}{2} + z$; (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (iv) $1 - x, -y, 1 - z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.]

Experimental

The title compound, (I), was prepared by warming BPPY (0.40 g, 1.05 mmol) and maleic acid (0.12 g, 1.03 mmol) in methanol. Diffraction-quality crystals were obtained by slow evaporation of the solvent.

Crystal data

$C_{26}H_{22}OP^+\cdot C_4H_3O_4^-$
$M_r = 496.47$
Orthorhombic, *Pbca*
$a = 10.5582$ (5) Å
$b = 19.5961$ (8) Å
$c = 24.0030$ (11) Å
$V = 4966.2$ (4) Å^3
$Z = 8$
$D_x = 1.328$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 973 reflections
$\theta = 2.2$–27.0°
$\mu = 0.15$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.34 × 0.29 × 0.17 mm

Data collection

Bruker SMART 6K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998*a*)
$T_{min} = 0.820$, $T_{max} = 0.975$
36772 measured reflections
5704 independent reflections
4255 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 11$
$k = -25 \rightarrow 23$
$l = -31 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.106$
$S = 1.01$
5704 reflections
425 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 2.7423P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Acta Cryst. (2004). E**60**, o162–o164 Mahimaidoss Baby Mariyatra *et al.* • $C_{26}H_{22}OP^+\cdot C_4H_3O_4^-$ **o163**

Table 1
Selected geometric parameters (Å, °).

P1—C8	1.8020 (16)	C27—O2	1.299 (2)
C7—O1	1.2198 (19)	C30—O4	1.233 (2)
C7—C8	1.516 (2)	C30—O5	1.288 (2)
C27—O3	1.221 (2)		
C7—C8—P1	112.26 (11)	O4—C30—O5	122.85 (17)
O3—C27—O2	121.51 (19)	O4—C30—C29	118.13 (17)
O3—C27—C28	119.36 (17)	O5—C30—C29	119.02 (16)
O2—C27—C28	119.13 (17)		
O1—C7—C8—P1	−11.78 (19)	C27—C28—C29—C30	2.7 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O2^{i}	0.94 (2)	2.44 (2)	3.243 (2)	143.0 (16)
C4—H4···O3^{ii}	0.98 (2)	2.36 (2)	3.277 (2)	156.8 (16)
C8—H8*A*···O1^{iii}	0.984 (19)	2.397 (19)	3.371 (2)	170.3 (15)
C8—H8*B*···O4^{iv}	1.00 (2)	2.42 (2)	3.184 (2)	132.9 (16)
C8—H8*B*···O5^{iv}	1.00 (2)	2.28 (2)	3.270 (2)	171.0 (17)
C26—H26···O4^{iv}	0.98 (2)	2.494 (19)	3.267 (2)	135.4 (15)
C19—H19···O4^{v}	0.93 (2)	2.49 (2)	3.210 (2)	134.8 (19)
C26—H26···O1	0.98 (2)	2.47 (2)	3.042 (2)	117.1 (14)
O2—H1···O5	1.07 (3)	1.35 (3)	2.4197 (19)	176 (3)

Symmetry codes: (i) $\frac{3}{2} - x, -y, \frac{1}{2} + z$; (ii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (iv) $1 - x, -y, 1 - z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

All H atoms were located in difference Fourier maps, and their positional and $U_{\rm iso}$ parameters were refined. The C—H bond lengths are in the range 0.92 (2)–1.00 (2) Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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o164 Mahimaidoss Baby Mariyatra *et al.* • $C_{26}H_{22}OP^{+}\cdot C_4H_3O_4^{-}$ *Acta Cryst.* (2004). E**60**, o162–o164