

The 2:1 adducts of (benzoylmethylene)triphenylphosphorane with fumaric and terephthalic acids

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Co-crystals of the ylide (benzoylmethylene)triphenylphosphorane (BPPY) with either fumaric acid, *viz.* (benzoylmethylene)triphenylphosphorane–fumaric acid (2/1), C₂₆H₂₁OP·0.5C₄H₄O₄, or terephthalic acid, *viz.* (benzoylmethylene)triphenylphosphorane–terephthalic acid (2/1), C₂₆H₂₁OP·0.5C₈H₆O₄, have a stoichiometric ratio of 2:1 between the ylide and the corresponding dicarboxylic acid. In both adducts, the acid component lies across a centre of inversion. In neither case is the ylide protonated by the organic acid; instead the H atoms of the non-ionized dicarboxylic acid molecules participate in the formation of strong O–H···O hydrogen bonds with the benzoyl O atom of the ylide species. These structures are the first reported examples of co-crystals containing non-protonated BPPY.

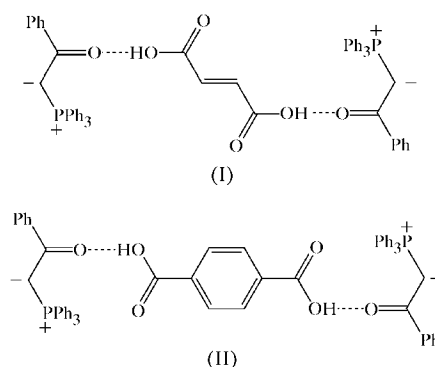
Comment

Resonance-stabilized phosphorus ylides are a class of compounds that have attracted considerable interest in the field of synthetic organometallic chemistry. Their popularity arises from their high stability, their reactivity towards a diverse range of metal salts and their ability to be tailored chemically to allow a variety of coordination modes to be accessed (Falvello *et al.*, 1996, 1997, 1998; Kalyanasundari *et al.*, 1995, 2004; Vicente *et al.*, 1988).

The manner of protonation of the resonance-stabilized ylide (benzoylmethylene)triphenylphosphorane (BPPY) has been the focus of our most recent studies. A search of the Cambridge Structural Database (Version 5.25; Allen, 2002) for the BPPY moiety yielded six cases of protonated BPPY (only structures in which BPPY featured as a discrete molecular entity, *i.e.* uncomplexed, were considered). All six structures exhibited C-protonation (Antipin & Struchkov, 1984; Baby Mariyatra *et al.*, 2002*a,b*, 2003; Albanese *et al.*, 1989); no examples of O-protonated BPPY were found. These results are surprising, as PM3 calculations of the proton affinities for

the ylide C and the benzoyl O atoms give values that differ by only 13 kJ mol⁻¹ (Laavanya, 2002), implying that although C-protonation is energetically more favourable both O- and C-protonation of BPPY are feasible.

In our previous work, we have observed that the C-protonated cation of BPPY is produced by the action of picric and maleic acids (Baby Mariyatra *et al.*, 2004*a,b*). In order to investigate the influence of organic dicarboxylic acids on the mode of protonation of BPPY, the reactions of this ylide with fumaric and terephthalic acid, yielding compounds (I) and (II), respectively, have been undertaken. The first-step p*K_a* value in aqueous solution is 3.03 for fumaric acid and 3.51 for terephthalic acid, and the second-step values are 4.44 and 4.82, respectively (Lide, 1994). These figures suggest that both of these acids are sufficiently strong to protonate BPPY (p*K_a* of 6.0; Speziale & Ratts, 1963).



Figs. 1 and 2 display the molecular structures of (I) and (II), respectively. In both cases, the dicarboxylic acid molecule resides on a site of inversion symmetry, and consequently each of the asymmetric units of (I) and (II) comprises a single BPPY molecule and half an acid molecule.

Tables 1 and 3 list selected geometries for (I) and (II), respectively. The inequality of the O2–C27 and O3–C27 bond lengths in (I), and the O2–C30 and O3–C30 bond lengths in (II), is indicative of the dicarboxylic acid molecules in both co-crystals existing in the un-ionized form.

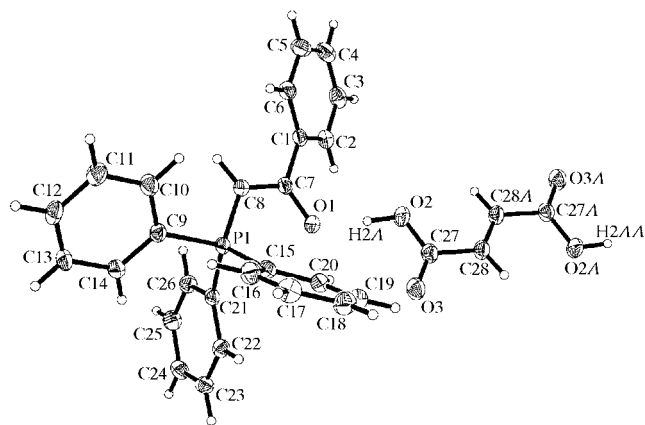


Figure 1

The molecular structure of the co-crystal, (I), of BPPY with fumaric acid. Displacement ellipsoids are drawn at the 50% probability level. The symmetry-generated atoms C28A, C27A, O2A, O3A and H2AA have been included for completeness [symmetry code: (A) 1 - x, 1 - y, 1 - z].

The O1—C7 bond lengths are longer than the value of 1.210 Å expected for ketones, and the C7—C8 distances are greater than the expected C=C distance (1.331 Å; Wilson, 1992). These facts are strongly suggestive of resonance delocalization within the ylide molecules. The torsion angles surrounding atom C8 in both structures signify that the environment about this carbanion is distorted trigonal planar. These bond lengths and angles provide conclusive evidence of the presence of unprotonated BPPY in the structures of (I) and (II). Corroborating evidence for the absence of the phosphonium cation has been provided by the ¹H NMR spectra of (I) and (II).

In both cases, the P1—C8 and O1—C7 bonds are slightly elongated with respect to the equivalent bonds in the parent ylide, where the P—C bond lengths are 1.716 (5) and 1.725 (4) Å, and the O—C bond lengths are 1.265 (7) and 1.247 (7) Å (two ylide molecules in the asymmetric unit; Kalyanasundari & Panchanatheswaran, 1994). The presence of an exceptionally strong hydrogen bond between the O atoms of the benzoyl groups and an acid H atom of the relevant acid molecule in (I) and (II) (Tables 2 and 4) may account for this disparity.

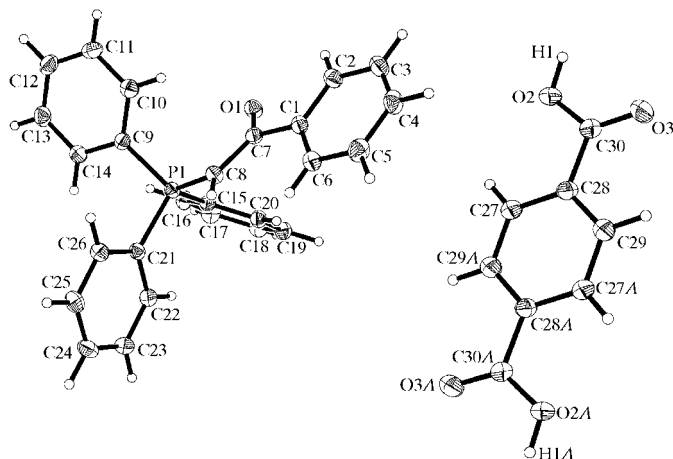


Figure 2
The molecular structure of the co-crystal, (II), of BPPY with terephthalic acid. Displacement ellipsoids are drawn at the 50% probability level. The symmetry-generated atoms C28A, C27A, C29A, C30A, O2A, O3A and H1A have been included for completeness [symmetry code: (A) $1 - x, 1 - y, 1 - z$].

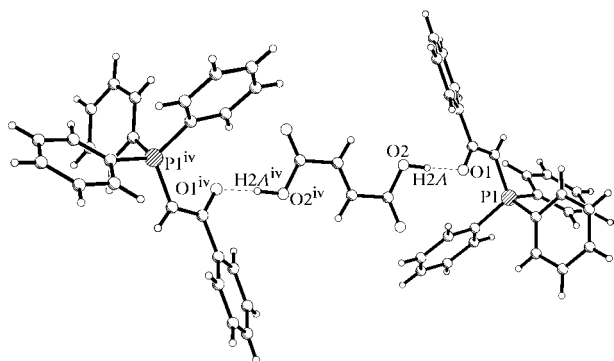


Figure 3
The unit formed by the O2—H2A...O1 hydrogen bond in (I) and its symmetry equivalent at $(1 - x, 1 - y, 1 - z)$ (*viz.* symmetry code iv).

The non-bonded P1...O1 distances [2.991 (1) Å in (I) and 2.907 (1) Å in (II)] are considerably shorter than the sum of the van der Waals radii of phosphorus and oxygen (3.3 Å; Dunitz, 1979), indicating the presence of strong intramolecular interactions between the charged P⁺ and O⁻ centres of the ylide molecules; these interactions explain the observed *cis* orientation about the partial C=C double bond in (I) and (II).

A strong hydrogen bond exists between the O2—H2A donor group of the fumaric acid molecule and atom O1 of the ylide molecule (see Table 2). This bond and its symmetry equivalent at $(1 - x, 1 - y, 1 - z)$ link the fumaric acid and ylide molecules, as shown in Fig. 3.

The secondary interactions for (I) include several C—H... π contacts (Table 2). Cg1, Cg2 and Cg3 are the centroids of the rings defined by atoms C21—C26, C15—C20 and C1—C6. Two π — π interactions complete the complex network of secondary interactions present in the crystal packing of (I) (Fig. 4). Both interactions are 3.99 Å in length, and the β angles are 28 and 23° for the Cg3...Cg2^{iv} and Cg2...Cg3^v interactions, respectively [symmetry codes: (iv) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (v) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$].

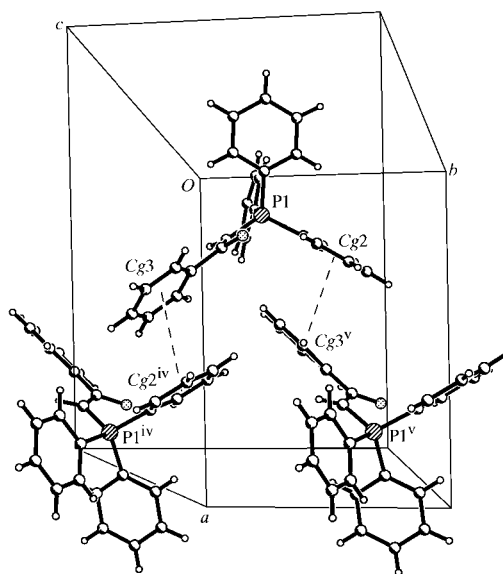


Figure 4
The π — π interactions present in the crystal structure of (I) [symmetry codes: (iv) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (v) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$].

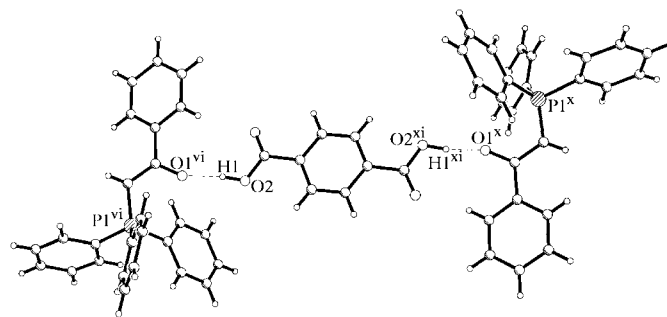


Figure 5
The unit formed by the O2—H1...O1^{vi} hydrogen bond and its symmetry equivalent O2^{xi}—H1^{xi}...O1^x [symmetry codes: (vi) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (x) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (xi) $1 - x, -y, -z$].

Table 4 provides details of all the secondary interactions observed in the crystal structure of (II). The strong O2—H1^{vi}··O1^{vi} hydrogen bond and its symmetry equivalent O2^{xi}—H1^{xi}··O1^x generate a unit comprising a single terephthalic acid molecule and two BPPY molecules (symmetry codes as in Fig. 5). The similarity of this unit to that observed in (I) (Fig. 3) is immediately apparent.

The structure of (II) is further stabilized by several C—H··· π interactions (Table 4).

In conclusion, the co-crystals (I) and (II) of BPPY with fumaric acid and terephthalic acid, respectively, are the first reported examples in which BPPY remains unprotonated. We attribute this phenomenon to the preferential formation of a strong O—H···O hydrogen bond between the benzoyl O atom of the ylide molecule and the acid H atom of the relevant un-ionized dicarboxylic acid group. These short strong hydrogen bonds result in the formation of units with a 2:1 stoichiometric ratio of BPPY to dicarboxylic acid.

Experimental

Crystals of (I) were prepared by stirring BPPY and fumaric acid together in a 1:2 molar ratio in 95% ethanol. Colourless diffraction-quality crystals were obtained on allowing the solution to stand for a week (m.p. 423–425 K). Crystals of (II) were prepared by refluxing BPPY in 95% ethanol with terephthalic acid in a 1:2 molar ratio for 20 h. On cooling the solution to room temperature, colourless crystals of diffraction quality were obtained (m.p. 498–500 K).

Compound (I)

Crystal data

C₂₆H₂₁OP·0.5C₄H₄O₄
M_r = 438.43
 Monoclinic, *P*2₁/*c*
a = 13.0883 (6) Å
b = 9.7883 (5) Å
c = 17.9970 (9) Å
 β = 102.500 (2)°
V = 2250.98 (19) Å³
Z = 4

D_x = 1.294 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 984 reflections
 θ = 2.4–27.5°
 μ = 0.15 mm⁻¹
T = 120 (2) K
 Block, colourless
 0.39 × 0.27 × 0.22 mm

Data collection

Bruker SMART CCD 6K area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1998)
T_{min} = 0.756, *T_{max}* = 0.968
 17 181 measured reflections

5164 independent reflections
 4281 reflections with *I* > 2 σ (*I*)
R_{int} = 0.033
 θ_{\max} = 27.5°
h = -16 → 16
k = -11 → 12
l = -23 → 23

Table 1

Selected geometric parameters (Å, °) for (I).

P1—C8	1.739 (1)	O1—C7	1.280 (2)
P1—C21	1.803 (1)	O2—C27	1.311 (2)
P1—C9	1.805 (1)	O3—C27	1.214 (2)
P1—C15	1.807 (1)	C7—C8	1.386 (2)
C8—P1—C21	114.40 (7)	C7—C8—P1	121.1 (1)
C8—P1—C9	105.92 (6)	C7—C8—H8	124 (1)
C8—P1—C15	114.83 (6)	P1—C8—H8	115 (1)
O1—C7—C8	122.0 (1)		

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.038
wR(*F*²) = 0.104
S = 1.02
 5164 reflections
 381 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.8208P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.41 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{Å}^{-3}$

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the rings defined by atoms C21–C26, C15–C20 and C1–C6, respectively.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2—H2A···O1	0.99 (3)	1.52 (3)	2.509 (2)	176 (3)
C14—H14··· <i>Cg</i> 1	0.92 (2)	3.00	3.72	136
C12—H12··· <i>Cg</i> 1 ⁱ	0.98 (2)	2.61	3.50	152
C13—H13··· <i>Cg</i> 2 ⁱⁱ	0.98 (2)	2.96	3.69	133
C24—H24··· <i>Cg</i> 3 ⁱⁱⁱ	0.96 (2)	2.98	3.87	155

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

Compound (II)

Crystal data

C₂₆H₂₁OP·0.5C₈H₆O₄
M_r = 463.46
 Monoclinic, *P*2₁/*n*
a = 10.0900 (6) Å
b = 17.9737 (9) Å
c = 13.1613 (7) Å
 β = 92.048 (2)°
V = 2385.3 (2) Å³
Z = 4

D_x = 1.291 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 948 reflections
 θ = 2.8–27.3°
 μ = 0.15 mm⁻¹
T = 120 (2) K
 Block, colourless
 0.30 × 0.25 × 0.12 mm

Data collection

Bruker SMART CCD 6K area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1998)
T_{min} = 0.940, *T_{max}* = 0.983
 18 211 measured reflections

5463 independent reflections
 4288 reflections with *I* > 2 σ (*I*)
R_{int} = 0.039
 θ_{\max} = 27.5°
h = -13 → 10
k = -23 → 21
l = -17 → 16

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.041
wR(*F*²) = 0.111
S = 1.03
 5463 reflections
 403 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 1.0579P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{Å}^{-3}$

Table 3

Selected geometric parameters (Å, °) for (II).

P1—C8	1.729 (2)	C7—O1	1.277 (2)
P1—C9	1.806 (2)	C7—C8	1.388 (2)
P1—C15	1.810 (2)	C30—O3	1.205 (2)
P1—C21	1.810 (2)	C30—O2	1.319 (2)
C8—P1—C9	114.72 (8)	C7—C8—P1	118.4 (1)
C8—P1—C15	112.28 (7)	C7—C8—H8	124 (1)
C8—P1—C21	106.63 (7)	P1—C8—H8	118 (1)
O1—C7—C8	121.1 (1)		

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

C_g1, C_g2 and C_g3 are the centroids of the rings defined by atoms C9–C14, C21–C26 and C1–C6, respectively.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O2–H1...O1 ^{vi}	0.92 (3)	1.64 (3)	2.526 (2)	161 (3)
C3–H3...Cg1 ^{vi}	0.96 (2)	2.84	3.59	135
C19–H19...Cg2 ^{vii}	0.99 (2)	3.00	3.79	137
C13–H13...Cg2 ^{viii}	0.93 (2)	2.73	3.59	156
C18–H18...Cg3 ^{ix}	0.94 (2)	2.71	3.53	146

Symmetry codes: (vi) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $-x, -y, 1 - z$; (viii) $-x, -y, 2 - z$; (ix) $x - 1, y, z$.

All H atoms were located in difference Fourier maps, and their positional and *U*_{iso} parameters were refined. The refined C–H distances for (I) are in the range 0.920 (17)–0.995 (19) Å; for (II), the range is 0.92 (2)–0.99 (2) Å. The secondary interaction analysis was performed using a combination of *MERCURY* (Bruno *et al.*, 2002) and *PLATON* (Spek, 2003).

For both compounds, data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1343). Services for accessing these data are described at the back of the journal.

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