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Triphenyl(benzoylmethyl)phosphonium nitrate: a three-dimensional hydrogen-bonded network

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.039
wR factor = 0.114
Data-to-parameter ratio = 17.9

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

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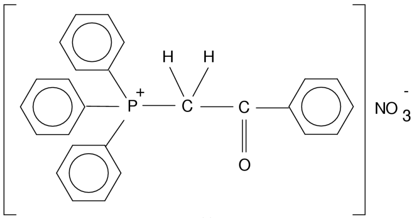
The title phosphonium salt, $C_{26}H_{22}OP^+\cdot NO_3^-$, is formed by the hydrolytic cleavage of the acetyl group with concomitant protonation of the ylidic carbon of α-acetyl-α-benzoylmethylenetriphenylphosphorane. The structure is stabilized by significant intermolecular C—H$\cdots$O interactions, involving both the methylene H atoms. The O atoms of the nitrate ion and the benzoyl group, acting as acceptors, contribute to the network of hydrogen bonds.

Comment

Protonation of both $(C_6H_5)_3PC(COPh)(COMe)$ (ABPPY) and $(C_6H_5)_3PCHCOPh$ (BPPY) to give the O-protonated and C-protonated salts, respectively, were reported previously (Antipin *et al.*, 1978, 1979; Antipin & Struchkov, 1984). A search in the October 2001 version of the Cambridge Structural Database (Allen & Kennard, 1993) indicated that, out of 180 structures containing the triphenyl(benzoylmethyl)phosphonium moiety, only two structures with O-protonated triphenyl(acetylbenzoylmethyl)phosphonium groups (Antipin *et al.*, 1978, 1979) and one with a C-protonated (benzoylmethyl)triphenylphosphonium group (Antipin & Struchkov, 1984) have been reported. In an attempt to prepare C-protonated salts of ABPPY, the above ylide was reacted with nitric acid. The ^{1}H NMR spectrum of the crystalline product in $CDCl_3$ ($\delta = 6.07$, $J = 12.3$, 2H; $\delta = 8.23$–7.21, 20H) revealed the presence of the P—CH$_2$ group and the absence of the acetyl group.



(I)

Fig. 1 shows that the title compound, (I), is a phosphonium salt, derived from $(C_6H_5)_3PCHCOPh$ (BPPY). The P1—C1 distance of 1.8016 (11) Å is significantly longer than the average analogous distance in BPPY [1.716 (5) Å] (two molecules in the asymmetric unit). The C1—C2 and C2—O1 bonds are elongated and shortened, respectively, with respect to the corresponding average distances [1.403 (8) and 1.256 (7) Å, respectively] in BPPY (Kalyanasundari *et al.*, 1994). The near *cis* orientation of the P and O centres is confirmed by the P1—C1—C2—O1 torsion angle of 19.8 (1)°. No direct interaction is found between the P$^+$ and O$^-$ centres of the phosphonium and nitrate ions, respectively.

The centrosymmetric crystal structure is stabilized by several C—H$\cdots$O hydrogen-bonding interactions, with H$\cdots$O

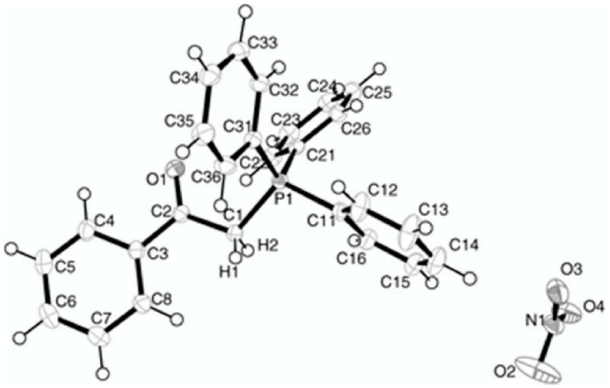


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

distances in the range 2.2–2.6 Å (Table 2). In particular, atom H1 of the Csp^3 atom of the CH_2 group is involved in an intermolecular weak hydrogen-bond interaction (Jeffrey, 1997) with the O atom of a neighbouring benzoyl group. This leads to chain formation linking the phosphonium cations along the *a* axis (Fig. 2). Nitrate ions exhibit C—H···O intermolecular interactions with five neighbouring phosphonium cations, including the chelate formation of H2 with O2 and O4 (Fig. 3). The H2···O2 and H2···O4 distances differ by only 0.11 Å. The resulting configuration is best regarded as a three-centre symmetrical hydrogen-bonded chelate (Desiraju, 1989) and observed in molecules containing fewer functional H atoms and several acceptors. The O2···H2···O4 bite angle is 54.6° and the sum of the angles around H2, 359.8°, indicates the configuration around it to be planar, as observed for many molecules with such hydrogen bonds (Jeffrey & Mitra, 1984). Least-squares-plane calculations (Spek, 1997) also support the planarity around H2, the deviations of atoms from the plane being −0.003, −0.001, −0.01 and 0.014 Å for O2, O4, C1 and H2, respectively.

We attribute the facility with which the H atoms of the CH_2 group participate in C—H···O bonding to the acidity of the CH_2 group that results from the presence of the adjacent phosphonium and the benzoyl groups. PM3 calculations of the proton affinity values of the ylides BPPY and ABPPY (Laavanya, 2002) reveal that there are two and three possible sites for protonation, respectively. The proton affinity values for the different sites of the ylide are within 13 kJ mol^{-1}, showing that all the sites are favourable for protonation. The present results reveal the possibility of cleavage of the acetyl group attached to the ylidic carbon and the preponderance of C-protonation of $(C_6H_5)_3PCH(COPh)$, both in solution and in the crystalline state.

Experimental

Crystals of (I) were obtained by the reaction of 1 *M* nitric acid with a methanolic solution of α-acetyl-α-benzoylmethylene triphenylphosphorane (ABPPY). The above ylide was prepared from the reaction of benzoylmethylenetriphenylphosphorane with acetic anhydride (Chopard *et al.*, 1965).

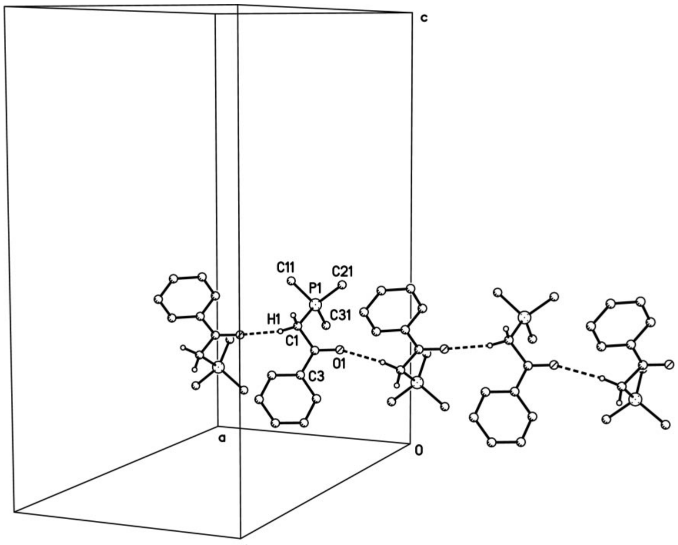


Figure 2
View of the chains of cations along the *a* axis, due to the C1—H1···O1 non-bonded interaction.

Crystal data

$C_{26}H_{22}OP^+ \cdot NO_3^-$
$M_r = 443.42$
Orthorhombic, *Pbca*
$a = 10.7617$ (5) Å
$b = 19.1957$ (7) Å
$c = 21.4568$ (9) Å
$V = 4432.5$ (3) Å^3
$Z = 8$
$D_x = 1.329$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 940 reflections
$\theta = 10.2$–22.5°
$\mu = 0.16$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.36 × 0.30 × 0.26 mm

Data collection

Bruker SMART-6000 CCD diffractometer
ω scans
Absorption correction: none
63180 measured reflections
6766 independent reflections
5801 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 30.5°$
$h = -15 \rightarrow 15$
$k = -27 \rightarrow 27$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.114$
$S = 1.03$
6766 reflections
377 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 1.9368P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.43$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—C31	1.7909 (11)	C1—C2	1.5132 (14)
P1—C21	1.7929 (11)	C2—C3	1.4863 (15)
P1—C11	1.7939 (11)	N1—O2	1.2348 (15)
P1—C1	1.8016 (11)	N1—O3	1.2469 (14)
O1—C2	1.2237 (13)	N1—O4	1.2487 (15)
C31—P1—C21	114.55 (5)	O1—C2—C3	121.63 (10)
C31—P1—C11	109.24 (5)	O1—C2—C1	119.63 (10)
C21—P1—C11	105.51 (5)	O2—N1—O3	119.57 (12)
C31—P1—C1	108.14 (5)	O2—N1—O4	119.10 (11)
C2—C1—P1	112.77 (7)	O3—N1—O4	121.32 (11)
P1—C1—C2—O1	19.75 (13)	O1—C2—C3—C8	173.52 (11)
P1—C1—C2—C3	−160.44 (8)		

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{C1-H1\cdots O1^{i}}$	0.969 (17)	2.457 (17)	3.4061 (14)	166.1 (13)
$\mathrm{C1-H2\cdots O2^{ii}}$	0.921 (18)	2.279 (18)	3.1856 (16)	168.2 (15)
$\mathrm{C1-H2\cdots O4^{ii}}$	0.921 (18)	2.386 (18)	3.1230 (15)	137.0 (14)
$\mathrm{C16-H16\cdots O2^{ii}}$	0.947 (18)	2.504 (18)	3.2621 (16)	137.0 (14)
$\mathrm{C24-H24\cdots O2^{iii}}$	0.935 (17)	2.571 (16)	3.3777 (16)	144.7 (13)
$\mathrm{C14-H14\cdots O3}$	0.94 (2)	2.34 (2)	3.1614 (16)	145.1 (16)
$\mathrm{C35-H35\cdots O3^{iv}}$	0.951 (17)	2.509 (17)	3.1834 (16)	128.0 (13)
$\mathrm{C33-H33\cdots O4^{v}}$	0.957 (17)	2.459 (17)	3.1377 (16)	127.8 (13)

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

All H atoms were located in a difference Fourier maps and their positional and isotropic displacement parameters were refined. The C—H bond lengths are in the range 0.921 (18)–0.988 (19) Å.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*97 (Spek, 1997); software used to prepare material for publication: *PARST* (Nardelli, 1983).

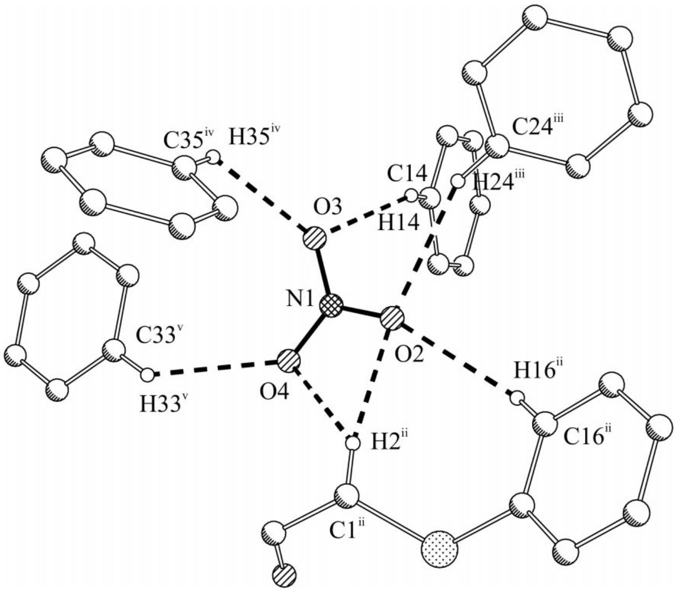

Figure 3
Diagram showing the hydrogen-bond interactions involving the nitrate anion.

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