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Phenacyltriphenylphosphonium picrate: intra-and interionic C—H···O interactions

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Key indicators

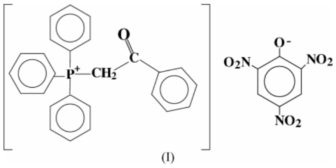
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.108
Data-to-parameter ratio = 13.3

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

The crystal structure of the title compound, (benzoylmethyl)-triphenylphosphonium 2,4,6-trinitrophenolate, $C_{26}H_{22}OP^{+}\cdot C_6H_2N_3O_7^{-}$, consists of phosphonium cations and picrate anions stabilized by intra- and interionic C—H···O interactions, leading to an extended hydrogen-bonded network structure.

Comment

Phosphonium salts containing anions with electronegative atoms readily form ionic liquids (m.p. < 373 K; Welton, 1999). The reaction of different acids with ylides offers a flexible method for the preparation of phosphonium salts that are not easily accessible by other means (Baby Mariyatra *et al.*, 2002). The ylides $Ph_3P{=}CHCOPh$ (BPPY) and $Ph_3PCH(COPh)$-(COMe) (ABPPY) are susceptible to protonation at the carbon and oxygen sites, leading to the formation of the corresponding phosphonium salts (Antipin *et al.*, 1978, 1979; Antipin & Struchkov, 1984). It is also possible that ylides could undergo C—C cleavage reaction with acids. Such a reaction has been observed in the case of ABPPY with 1 *M* HNO_3 (Baby Mariyatra *et al.*, 2002). The ylide BPPY forms 1:2 molecular complexes with fumaric and terephthalic acids which involve no protonation (Baby Mariyatra, 2003). Picric acid, which possesses no carboxylic acid group, is known to act as an acceptor and form charge transfer complexes with electron donors such as aromatic hydrocarbons (Ferguson, 1969). The reaction of BPPY with picric acid has been carried out to determine whether a molecular complex or a phosphonium salt is produced.



(I)

The solid-state structure of the title salt, (I), can be considered as an ion pair consisting of a triphenylphenacyl-phosphonium cation and picrate anion (Fig. 1 and Table 1). The P1—C8 distance of 1.816 (2) Å is elongated compared to that in the parent ylide BPPY [1.716 (5) and 1.724 (4) Å for two molecules in the asymmetric unit; Kalyanasundari *et al.*, 1994]. The C7—C8 and C7—O1 distances [1.524 (2) and 1.217 (2) Å, respectively] confirm that the site of protonation is at the ylidic atom C8. The torsion angle O1—C7—C8—P1 of 21.99 (19)° indicates the close proximity of the P and O centres.

In the crystal structure, the phosphonium and picrate ions are present in alternating layers along the *a* axis and the

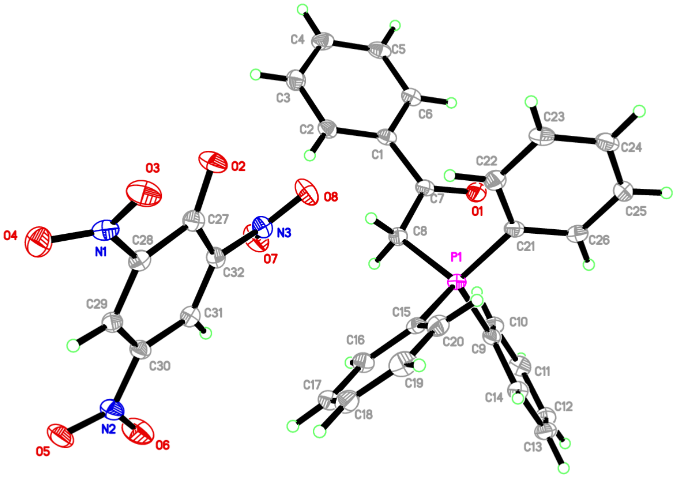


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

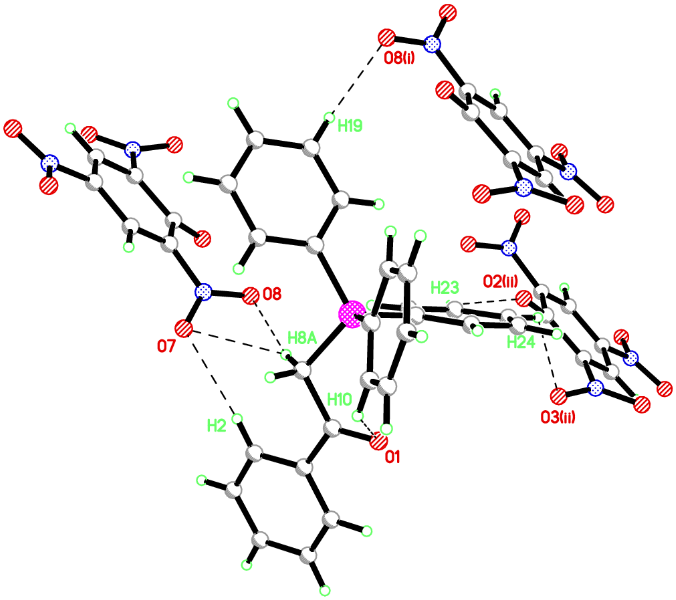


Figure 2
View showing the inter- and intraionic hydrogen bonding. [Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $-x, -y, 1 - z$.]

network displays a number of intra- and interionic C—H⋯O interactions (Table 2 and Fig. 3). The intraionic C—H⋯O interaction of the phosphonium cation involves benzoyl atom O1 and phenyl atom H10. The methylene atom H8*A* is engaged in a bifurcated hydrogen bond with atoms O7 and O8 of a nitro group (Fig. 2). Other interionic interactions are also listed in Table 2. The *Cg*1—*Cg*5 distance is 3.5573 (10) Å and the stacking angle, β, which represents the extent of non-eclipsing of the rings, is 21.75°. *Cg*1 and *Cg*5 are the centroids of the aromatic rings of the phenacyl moiety and the picrate anion, respectively. Also contributing to the crystal structure are C—H⋯π interactions at 2.792 (18) Å between H6 and *Cg*2 (the centroid of phenyl group C9–C14; symmetry code: $x - 1, y, z$) and at 2.537 (17) Å between H16 and *Cg*1 (C1–C6; symmetry code: $x + 1, y, z$). We attribute the relatively low melting point of (I) to the weak interionic interactions.

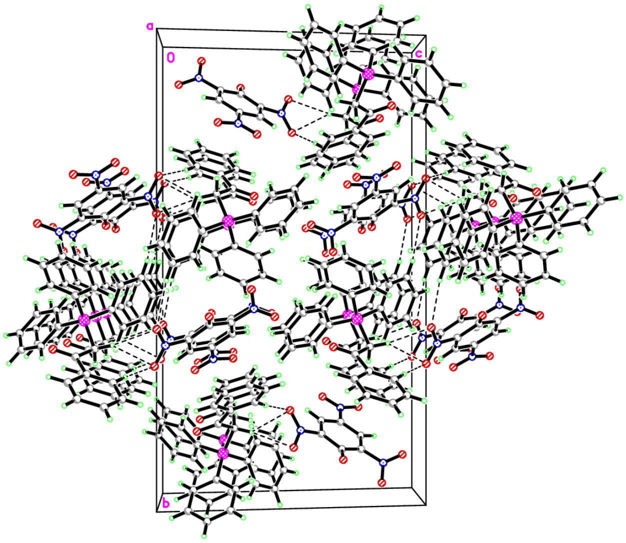


Figure 3
Packing diagram of (I), showing alternating layers along the *a* axis.

Experimental

A solution of picric acid (0.12 g, 0.52 mmol) in methanol was added dropwise to a solution of benzoylmethylenetriphenylphosphorane, BPPY (0.20 g, 0.52 mmol), in methanol under ice-cold conditions. The mixture was stirred overnight. Diffraction quality crystals of (I) were obtained by the slow evaporation of the solvent. The presence of the unconjugated keto group in the phosphonium cation is revealed by $\nu_{C=O}$ at 1680 cm^{-1} in the IR spectrum. The ^{1}H NMR spectrum in CDCl$_3$ indicates that the C-protonated form of the phosphonium ion is retained in solution. The doublet at 5.99 p.p.m. ($^2J_{P-H}$ = 12.32) is attributable to the protons of the P—CH$_2$ group. The singlet at 8.71 p.p.m. corresponds to the protons of the picrate anion.

Crystal data

$C_{26}H_{22}OP^+\cdot C_6H_2N_3O_7^-$
$M_r = 609.51$
Monoclinic, $P2_1/n$
$a = 7.5305$ (10) Å
$b = 25.241$ (3) Å
$c = 14.490$ (2) Å
$\beta = 98.639$ (3)°
$V = 2722.9$ (6) Å^3
$Z = 4$
$D_x = 1.487$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 882 reflections
$\theta = 2.9$–27.4°
$\mu = 0.16$ mm^{-1}
$T = 120$ (2) K
Block, yellow
0.23 × 0.15 × 0.13 mm

Data collection

Bruker SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.874$, $T_{max} = 0.979$
19 386 measured reflections
6244 independent reflections
5138 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -32 \rightarrow 25$
$l = -14 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.108$
$S = 1.01$
6244 reflections
469 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 1.0479P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

P1—C8	1.8157 (16)	C32—N3	1.447 (2)
C1—C7	1.491 (2)	O3—N1	1.2304 (18)
C7—O1	1.2172 (19)	O4—N1	1.2311 (19)
C7—C8	1.524 (2)	O5—N2	1.2317 (18)
C27—O2	1.2318 (19)	O6—N2	1.2372 (18)
C28—N1	1.457 (2)	O7—N3	1.2360 (18)
C30—N2	1.437 (2)	O8—N3	1.2331 (18)
C7—C8—P1	112.93 (11)		
O1—C7—C8—P1	21.99 (19)	C1—C7—C8—P1	−158.18 (11)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19—H19···O8^{i}	0.96 (2)	2.55 (2)	3.510 (2)	170.7 (17)
C23—H23···O2^{ii}	0.91 (2)	2.59 (2)	3.240 (2)	128.6 (16)
C24—H24···O3^{ii}	0.94 (2)	2.59 (2)	3.223 (2)	124.7 (15)
C2—H2···O7	0.92 (2)	2.51 (2)	3.428 (2)	173.9 (16)
C8—H8*A*···O7	0.97 (2)	2.52 (2)	3.222 (2)	129.0 (14)
C8—H8*A*···O8	0.97 (2)	2.45 (2)	3.401 (2)	166.5 (16)
C10—H10···O1	0.94 (2)	2.38 (2)	3.057 (2)	128.8 (15)

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

All the H atoms were located in difference Fourier maps and their positional parameters were refined with $U_{\rm iso} = 1.2U_{\rm eq}$(parent atom). The C—H bond lengths are in the range 0.92 (2)–0.99 (2) Å.

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

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