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Cyano-stabilized triphenylphosphonium ylids

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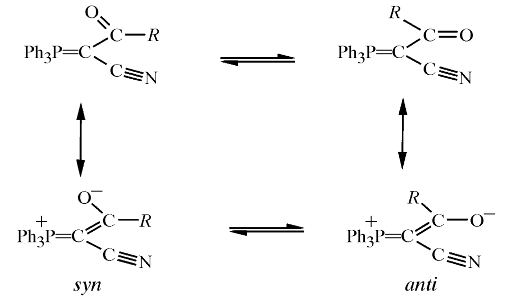
Crystalline cyano-stabilized triphenylphosphonium ylids with keto or ester groups give rise to an extended electronic delocalization. In methyl 2-cyano-2-(trimethylphosphonio)-ethenoate, $\mathrm{Ph_3P{=}C(CN)CO_2CH_3}$ or $\mathrm{C_{22}H_{18}NO_2P}$, (I), and 1-cyano-1-(trimethylphosphonio)prop-1-en-2-olate, $\mathrm{Ph_3P{=}C(CN)CO{-}CH_3}$ or $\mathrm{C_{22}H_{18}NOP}$, (II), the carbonyl groups are oriented toward the cationoid P atom. Bond lengths and angles, torsion angles and P$\cdots$O contact distances are consistent with a dominant coplanar conformation where the molecular structures are the result of a balance between intra- and intermolecular interactions. The main interactions presented by cyano-ester (I) and cyano-keto (II) are intramolecular interactions between the carbonyl O and the P atoms. In addition, both compounds show other less important intramolecular interactions between the carbonyl O and phenyl H atoms, which could contribute to form a preferred conformation in the crystal structure.

Comment

Electronic delocalization involving acyl keto and ester groups stabilizes phosphonium ylids and is maximized by their taking up planar conformations with favorable interactions between anionoid O atoms and cationoid phosphorus (Castañeda *et al.*, 2001; Castañeda, Recabarren *et al.*, 2003; Castañeda, Terraza *et al.*, 2003). However, in crystalline diethyl ester derivatives, interference involving the trigonal ester groups leads to a conformation where the acyl O atoms are *anti* to phosphorus, and the acyl groups are twisted out of the ylidic plane (Castañeda *et al.*, 2005, 2007). The linear cyano group is strongly electron withdrawing and should facilitate electronic delocalization in a planar ylidic unit (see scheme).

We therefore expected that the cyano group would favor cyano-keto or -ester compounds taking up conformations that allow extensive electronic delocalization and interactions between phosphorus and an acyl O atom. The conformations should be similar in the solid and in solution, and we discuss here the geometries of the following ylids in the crystal structure. Complete details of the geometries in solution will be given elsewhere. Crystalline methyl 2-cyano-2-(trimethylphosphonio)ethenoate, (I), and 1-cyano-1-(trimethylphosphonio)prop-1-en-2-olate, (II), have the molecular structures and selected geometric parameters shown in Figs. 1 and 2, and Tables 1 and 3, respectively. In both ylids, the configurations about the P atom are approximately tetrahedral, with phenyl groups forming a propeller-like arrangement. For (I) and (II), the bond angles C31—P1—C11, C21—P1—C11 and C31—P1—C21 are 107.42 (12), 107.44 (12) and 106.35 (12)°, and 108.17 (9), 105.79 (10) and 106.81 (9)°, respectively. The sums of the angles about the ylidic C1 atom for (I) and (II) are 359.9 and 360° respectively, consistent with sp^2-hybridization in an almost trigonal–planar geometry. It is well known that stabilized ylids have a longer P═C bond as a result of the electronic delocalization caused



(I) *R*=OMe
(II) *R*=Me

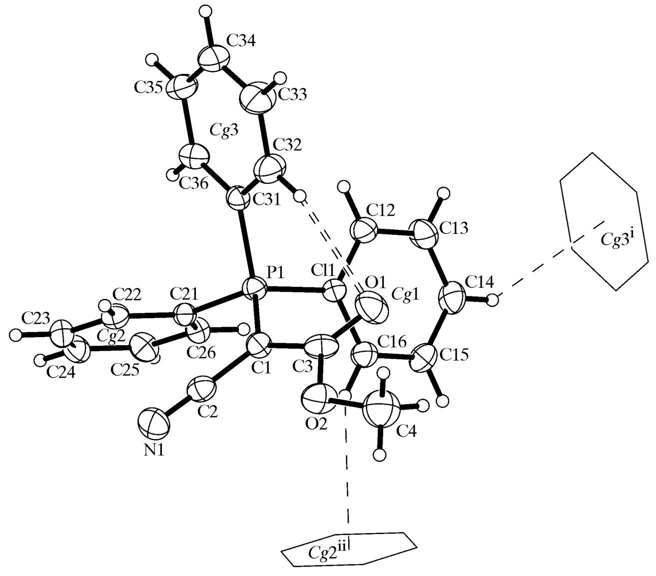


Figure 1
The molecular structure of (I), showing the numbering scheme used. The intramolecular hydrogen bond is shown as a double-dashed line and the intermolecular C—H$\cdots\pi$ contacts as single-dashed lines. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes are as given in Table 2.

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by the stabilizing groups (Bachrach & Nitsche, 1994; Howells *et al.* 1973). In cyano-ester ylid (I) and cyano-keto ylid (II), the P1—C1 bond lengths are 1.730 (3) and 1.744 (2) Å, respectively. These values are between those reported for a P—C single bond (1.80–1.83 Å; Howells *et al.*, 1973) and P═C double bond (1.63–1.73 Å; Howells *et al.*, 1973) and they are considerably longer than the P═C bond in methylenetriphenylphosphorane, $Ph_3P{=}CH_2$ [1.661 (8) Å; Bart, 1969], where there is no opportunity for conjugation with other groups. Electronic delocalization toward the carbonyl groups shortens the C1—C3 and lengthens the C═O carbonyl bonds. In comparison with the normal value of 1.21 Å, the keto carbonyl bond is longer [1.239 (3) Å] than the ester carbonyl bond [1.212 (4) Å], as was reported by Castañeda *et al.* (2001, 2005) for keto-esters, diesters and diketo ylides. However, delocalization of the P═C bond toward the cyano group is small. Comparison of C≡N bond lengths for (I) [1.145 (4) Å] and (II) [1.150 (3) Å] with a normal value of 1.140 Å (Smith & March, 2001) could indicate that the CN group is mainly acting by inductive instead of resonance effects. Coplanarity between the ylidic, carbonyl and cyano units is established by their torsion angles (Tables 1 and 3). Ylids (I) and (II) present nearly coplanar systems with the carbonyl O atoms oriented *syn* to the P atoms, showing O1···P1 contact distances of 3.022 (2) and 2.928 (2) Å, respectively. These attractive intramolecular interactions between the acyl O atoms and the cationoid P atoms lead to *syn*-preferred conformations where the alkoxy or alkyl groups adopt an *anti* conformation to avoid repulsive steric interactions with the phenyl groups. There is no evidence of a CH interaction involving alkoxy and phenyl groups (Castañeda, Terraza *et al.*, 2003). The structures of (I) and (II) have as a second intramolecular interaction C—H···O hydrogen bonds between phenyl donors and carbonyl acceptors (Tables 2 and 4). These types of non-classical interactions, despite being weak, could make a significant contribution to stabilizing conformations in the solid state. Several intermolecular interactions with phenyl groups acting as donors and acceptors are shown in Figs. 1 and 2. These interactions could affect favorably the observed molecular geometry and the packing conformations. The carbonyl IR stretching frequencies in KBr for (I) (1650 cm^{-1}) and (II) (1584 cm^{-1}) correlate with the crystallographic results, indicating an extensive electronic delocalization for the carbonyl groups.

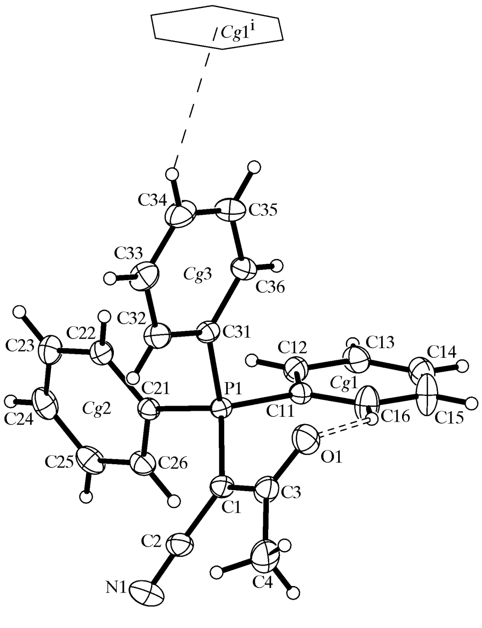

Figure 2
The molecular structure of (II), showing the numbering scheme used. The intramolecular hydrogen bond is shown as a double-dashed line and the intermolecular C—H···π contact as a single-dashed line. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes are as given in Table 4.

Experimental

(Cyanomethylene)triphenylphosphorane was prepared according to a literature method (Trippet & Walker, 1959). Ylids (I) and (II) have been reported previously (Horner & Oediger, 1958; Kobayashi *et al.*, 2000). In this work, both (I) and (II) were synthesized by reaction of (cyanomethylene)triphenylphosphorane with methyl chloroformate or acetyl chloride under transylidation conditions. A general synthetic procedure was as follows: a solution of alkyl chloroformate (9.1 mmol) or acetyl chloride (9.1 mmol) in dry benzene (5 ml) was added slowly to (cyanomethylene)triphenylphosphorane (18.2 mmol) dissolved in dry benzene (50 ml) under an inert atmosphere. The stirred solution was maintained at room temperature for 6 h to allow a white solid to separate. After filtration of (cyanomethyl)-triphenylphosphonium chloride, the solvent was evaporated under reduced pressure to give the products, which were crystallized from ethanol. For (I): yield 75%, m.p. 485–486 K; ^{1}H NMR ($CDCl_3$): δ 3.64 (*s*, 3H), 7.5–7.8 (*m*, 15H); IR (KBr): 2179 (–CN), 1650 (CO) cm^{-1}. For (II): yield 65%, m.p. 478 K; ^{1}H NMR ($CDCl_3$): δ 2.38 (*s*, 3H), 7.5–7.7 (*m*, 15H); IR (KBr): 2172 (–CN), 1584 (CO) cm^{-1}.

Ylid (I)

Crystal data

$C_{22}H_{18}NO_2P$
$M_r = 359.34$
Monoclinic, $P2_1/c$
$a = 9.9601$ (14) Å
$b = 9.0436$ (13) Å
$c = 20.708$ (3) Å
$\beta = 94.659$ (3)°
$V = 1859.1$ (5) Å^3

$Z = 4$
$D_x = 1.284$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.16$ mm^{-1}
$T = 297$ (2) K
Plate, colorless
0.30 × 0.24 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
14118 measured reflections

3659 independent reflections
2645 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\rm max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.150$
$S = 1.07$
3659 reflections
236 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.3502P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.36$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

P1—C1	1.730 (3)	C2—C1	1.407 (4)
O2—C3	1.350 (4)	C1—C3	1.427 (4)
O2—C4	1.432 (4)	O1—C3	1.212 (4)
C2—N1	1.145 (4)		
C3—O2—C4	117.0 (3)	C3—C1—P1	118.8 (2)
N1—C2—C1	179.2 (3)	O1—C3—O2	122.5 (3)
C2—C1—C3	120.8 (3)	O1—C3—C1	126.0 (3)
C2—C1—P1	120.3 (2)	O2—C3—C1	111.5 (3)
C4—O2—C3—O1	−4.1 (5)	P1—C1—C3—O1	4.4 (5)
C4—O2—C3—C1	175.0 (3)	C2—C1—C3—O2	7.5 (4)
C2—C1—C3—O1	−173.5 (3)		

Table 2
Non-bonding interactions and short contacts (Å, °) in (I).

*Cg*2 and *Cg*3 are the centroids of rings C21–C26 and C31–C36, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C32—H32···O1	0.93	2.51	3.294 (4)	142
C14—H14···*Cg*3^{i}	0.93	2.93	3.738 (3)	146
C16—H16···*Cg*2^{ii}	0.93	2.99	3.835 (3)	153
P1···O1	–	–	3.022 (2)	–

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

Ylid (II)

Crystal data

$C_{22}H_{18}NOP$
$M_r = 343.34$
Monoclinic, $P2_1/c$
$a = 10.1144$ (11) Å
$b = 8.9938$ (10) Å
$c = 19.968$ (2) Å
$\beta = 91.744$ (2)°
$V = 1815.6$ (3) Å^3
$Z = 4$
$D_x = 1.256$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 0.16$ mm^{-1}
$T = 298$ (2) K
Plate, colorless
0.42 × 0.32 × 0.14 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
13496 measured reflections
3569 independent reflections
2789 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\rm max} = 26.0$°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.143$
$S = 1.03$
3569 reflections
227 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0819P)^2 + 0.1374P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.009$
$\Delta\rho_{\rm max} = 0.45$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}

H atoms were placed at idealized positions [C—H = 0.93 (aromatic) and 0.96 Å (methyl)] and allowed to ride on the corresponding host, with $U_{\rm iso}$(H) values of $xU_{\rm eq}$(C) [x = 1.2 (aromatic) and 1.5 (methyl)].

For both ylids, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2001); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2001); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

Table 3
Selected geometric parameters (Å, °) for (II).

P1—C1	1.744 (2)	C1—C2	1.410 (3)
O1—C3	1.239 (3)	C1—C3	1.419 (3)
N1—C2	1.150 (3)	C3—C4	1.514 (3)
C2—C1—C3	121.8 (2)	O1—C3—C1	121.6 (2)
C2—C1—P1	120.27 (17)	O1—C3—C4	119.4 (2)
C3—C1—P1	117.95 (17)	C1—C3—C4	119.0 (2)
N1—C2—C1	178.4 (3)		
C2—C1—C3—O1	177.0 (2)	C2—C1—C3—C4	−3.3 (4)
P1—C1—C3—O1	−3.3 (3)		

Table 4
Non-bonding interactions and short contacts (Å, °) in (II).

*Cg*1 is the centroid of ring C11–C16.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16···O1	0.93	2.34	3.130 (3)	142
C34—H34···*Cg*1^{i}	0.93	2.91	3.703 (3)	144
P1···O1	–	–	2.928 (2)	–

Symmetry code: (i) $x, y+1, z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3045). Services for accessing these data are described at the back of the journal.

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