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3-(Triphenylphosphoranylidene)-pentane-2,4-dione and diethyl 2-(triphenylphosphoranylidene)-malonate

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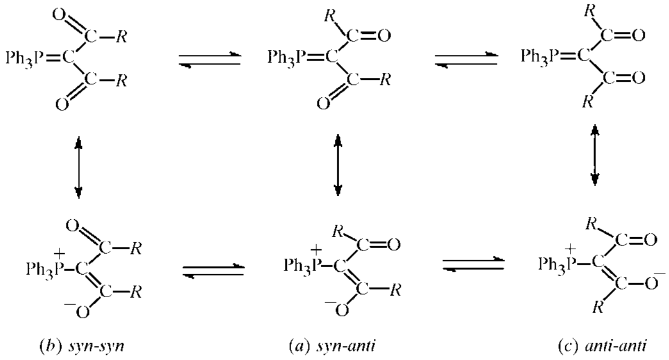
The title ylides, 3-(triphenylphosphoranylidene)pentane-2,4-dione, $C_{23}H_{21}O_2P$, (I), and diethyl 2-(triphenylphosphoranylidene)malonate, $C_{25}H_{25}O_4P$, (II), differ in the conformations adopted by their extended ylide moieties. In (I), one carbonyl O atom is *syn* and the other is *anti* with respect to the P atom, the ylide group is nearly planar, with a maximum P—C—(C═O) angle of 18.2 (2)°, and the P—C, C—C and C═O bond lengths are consistent with electronic delocalization involving the O atoms. In (II), both carbonyl O atoms are *anti* and the ester groups are twisted out of the plane of the near trigonal ylide C atom, reducing delocalization, the largest P—C—(C═O) angle being 30.2 (2)°.

Comment

For acyl(alkoxycarbonyl)phosphoranes (keto esters), the conformations are similar in solution and in the solid state, with the keto and alkoxy O atoms oriented towards the phosphorus and the acyl groups in the ylide plane, thus allowing extended ylide resonance (Abell & Massy-Westropp, 1982; Abell *et al.*, 1988, 1989). Classical structures of stabilized ylides are accordingly written with a double bond between the ylide C atom and the stabilized group (Bachrach & Nitsche, 1994). We have shown elsewhere (Castañeda, Terraza *et al.*, 2003) that acyl(alkoxycarbonyl)phosphoranes, $Ph_3P{=}C(COR')CO_2R$, can adopt a near planar preferred conformation that allows extensive electronic delocalization and favorable interactions between the cationoid P atom and the keto and alkoxy O atoms, both in the solid state and in solution. The preferred conformations result from both attractive and repulsive intramolecular interactions in solution, and possible intermolecular interactions in the solid state. Diacylphosphorane conformations should be similar to those of the keto esters.

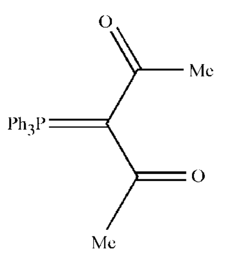


(*b*) *syn-syn* (*a*) *syn-anti* (*c*) *anti-anti*

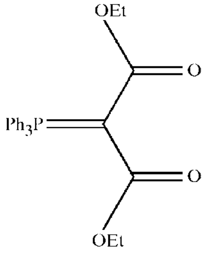
(I) R=Me
(II) R=OEt

The scheme above depicts a diacyl ylide that can adopt various conformations depending on the orientations of the carbonyl groups relative to the P atom. The methyl signal in the ^{1}H NMR spectrum in $CHCl_3$ is a sharp singlet over a wide temperature range. In ylide solutions, these groups are therefore equivalent or are equilibrating rapidly on the NMR timescale, although equilibration is slow in monoacyl ylides (Wilson & Tebby, 1972). These differences are consistent with energy barriers for equilibration from *ab initio* computations (Castañeda, Recabarren *et al.*, 2003; Bachrach, 1992). Conformer (*b*), with both carbonyl O atoms *syn* with respect to the P atom, has favorable interactions between anionoid O atoms and cationoid P atoms, and this structure is supported by chemical evidence (Cooke & Goswami, 1973). However, in a near planar ylide moiety, there will be methyl–methyl repulsions. The *anti–anti* coplanar conformation, (*c*), should be electrostatically disfavored because of dipole repulsions between the carbonyl groups and possible steric repulsions between methyl and phenyl groups.

The crystal structures of two ylides are discussed here, *viz.* 3-(triphenylphosphoranylidene)pentane-2,4-dione, (I), and diethyl 2-(triphenylphosphoranylidene)malonate, (II), stabilized by diketo and diester groups, respectively (Figs. 1 and 2).



(I)



(II)

The structural results are consistent with previous NMR, chemical and computational evidence (Castañeda, Terraza *et al.*, 2003) regarding differences in the solid state and in solution. Selected bond lengths and angles are presented in Tables 1 and 3, with hydrogen-bond and short-contact geometry in Tables 2 and 4.

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The two ylides share a number of common features, in particular a slightly distorted tetrahedral arrangement around the P atom, as observed for stabilized keto–ester phosphorus ylides (Castañeda, Terraza *et al.*, 2001). The P—C bonds [P1—C1 = 1.7521 (18) and 1.748 (3) Å for (I) and (II), respectively] are longer than typical double bonds, because of the ylidic resonance, and intermediate between commonly accepted values for single and double bonds (P—C = 1.80–1.83 Å and P═C = 1.66 Å; Howells *et al.*, 1973). In both ylides, ylide atom C1 is clearly sp^2-hybridized, the sum of the bond angles being essentially 360° [359.9 (5) and 359.6 (5)°, respectively].

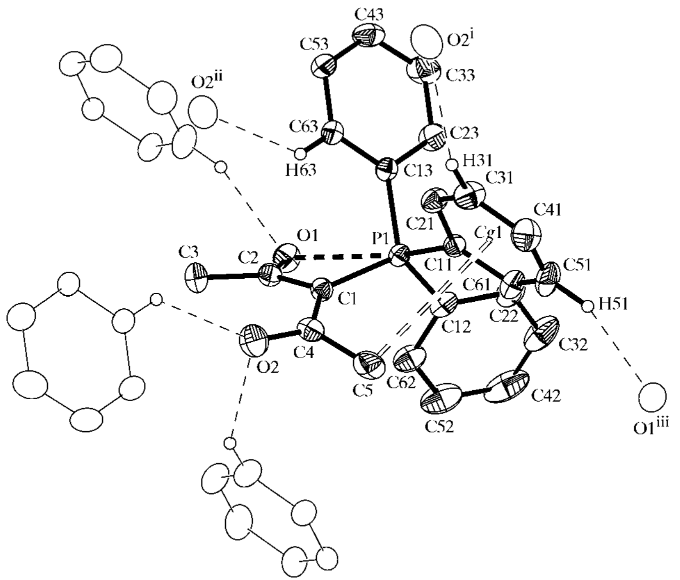

Figure 1
The molecular structure of (I), showing the atomic numbering scheme, and intermolecular (single broken lines) and intramolecular (double broken lines) contacts. H atoms, except phenyl H atoms involved in hydrogen bonds, have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. For symmetry codes, refer to Table 2.

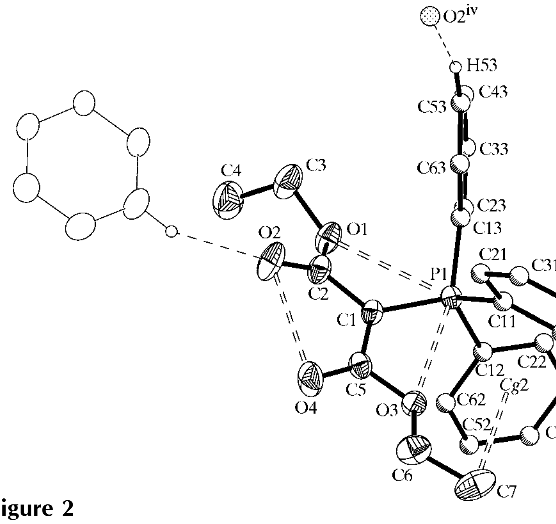

Figure 2
The molecular structure of (II), showing the atomic numbering scheme, and intermolecular (single broken lines) and intramolecular (double broken lines) contacts. H atoms, except phenyl H atoms involved in hydrogen bonds, have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. For symmetry codes, refer to Table 4.

A distinctive feature that differentiates the two structures is the disposition of the C═O groups; in (I), one carbonyl O atom is *syn* and the other is *anti* with respect to the P atom, while in (II), both O atoms are positioned *anti*. Though neither of the two extended ylide groups is planar, the carbonyl groups in (I) deviate less from the plane defined by the nearly trigonal ylide C atom than those in (II), the maximum absolute value for the P—C_{ylide}—C═O torsion angles being 18.2 (2)° for (I) and 30.2 (2)° for (II). This structural disposition favors an extensive electronic delocalization in the nearly planar ylide system in (I) and the interaction of one carbonyl O atom with the cationoid P atom, and minimizes intramolecular interference involving methyl groups.

Both structures have several intra- and intermolecular non-bonding interactions, which, despite being weak, have profound effects on both the molecular and the packing conformations. The intramolecular interactions and contacts are mainly of the C—H···π type, involving methyl H atoms and phenyl groups. In (I), methyl atom C5 interacts with a phenyl ring, with a H5*B*···*Cg*1 distance of 2.79 Å and a C5···*Cg*1 distance of 3.541 (3) Å (Fig. 1; *Cg*1 is the centroid of the C11/C21/C31/C41/C51/C61 ring). In (II), the C···π(arene) contacts involve methyl atom C7, with a C7···*Cg*2 distance of 3.984 (6) Å (Fig. 2; *Cg*2 is the centroid of the C12/C22/C32/C42/C52/C62 ring). The first of these interactions has an important effect on the molecular geometry, through the reduction of the C11—P1—C13 angle to 103.31 (8)°, sensibly smaller than expected for a strictly tetrahedral P atom, and with the concomitant opening of the C1—P1—C12 angle [114.62 (9)°; Fig. 1].

There are also several short P···O contacts of different types, as a result of conformational differences in the two structures; in (I), such contacts involve carbonyl atom O1, which is *syn* to phosphorus and thus favored for this type of interaction [P1···O1 = 2.767 (2) Å]. The corresponding O atoms (O2 and O4) in (II) are oriented away from phosphorus and are therefore prohibited from this kind of contact but have a short O2···O4 intramolecular distance of 2.816 (3) Å. The *syn*-oriented alkoxy atoms O1 and O3 (relative to phosphorus) are oriented near phosphorus [P···O = 3.028 (3) and 2.775 (3) Å, respectively]. Intermolecular interactions are mainly C—H···O hydrogen bonds involving phenyl donors and carbonyl acceptors (Tables 2 and 4). However, the most important effects are those that allow (or forbid) electronic delocalization.

In (I), the distortions from planarity of the extended ylide group (as induced by non-bonding interactions) are not extremely severe; the P—C—C═O torsion angles (Table 1) suggest some degree of coplanarity and, concomitantly, ylide resonance involving both acyl moieties. This interpretation correlates with the IR carbonyl stretching frequencies in KBr (1600 and 1557 cm^{-1}), which are similar to those in $CHCl_3$ (1601 and 1540 cm^{-1}). In (II), however, they appear to favor the out-of-plane geometry of the ylide and carbonyl moieties, and the consequent decrease in ylide resonance. The out-of-plane torsion angles (Table 3) are consistent with the IR carbonyl stretching frequencies (1711 and 1632 cm^{-1}), indicating that in the solid state only one carbonyl group is sufficiently close to coplanarity with respect to the ylide moiety to participate significantly in electronic delocalization.

It is often assumed that in the search for a balance between opposing ylide resonance and non-bonding interactions it is the former that dominates conformations of stabilized phosphorus ylides, and structures are usually written with a formal double bond between the ylide and acyl C atoms. This structural assumption appears to be valid for (I) both in the crystal and in solution, and for the keto esters, but it is not valid for (II). To this extent, (II) behaves differently from the other ylides stabilized by keto and ester groups as a result of interactions in the solid state of carbonyl atoms O2 and O4 with H atoms of neighboring ylides. The presence (or absence) of such interactions is therefore a major factor controlling conformation both in the crystalline state and in solution.

Experimental

Compound (I) was prepared by reaction of 1-(triphenylphosphoranylidene)propan-2-one with acetic anhydride (Chopard *et al.*, 1965) (yield 80%, m.p. 437–438 K from ethyl acetate/cyclohexane, 1:1). Compound (II) was prepared by Horner & Oediger (1958) from triphenylphosphine dichloride and diethyl malonate in a basic medium (56% yield), but we report here a simpler synthesis by transylidation. A solution of ethyl chloroformate (39 mmol) in dry benzene (10 ml) was added slowly to (carboethoxymethylene)-triphenylphosphorane (60 mmol) in dry benzene (100 ml) under a dry atmosphere at room temperature. After 1 h, (carboethoxymethyl)triphenylphosphonium chloride separated from the stirred solution as a white solid. The filtered solvent was evaporated to give an oil which was crystallized from ethyl acetate (yield 85%, m.p. 379–380 K).

Compound (I)

Crystal data

$C_{23}H_{21}O_2P$
$M_r = 360.37$
Monoclinic, $P2_1/c$
$a = 14.9365\ (18)$ Å
$b = 9.6588\ (13)$ Å
$c = 13.7975\ (16)$ Å
$\beta = 107.907\ (9)^\circ$
$V = 1894.1\ (4)$ Å^3
$Z = 4$
$D_x = 1.264$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–12.5°
$\mu = 0.16$ mm^{-1}
$T = 295\ (2)$ K
Rectangular prism, colorless
0.40 × 0.24 × 0.20 mm

Data collection

Siemens *R*3*m* diffractometer
$\omega/2\theta$ scans
3480 measured reflections
3325 independent reflections
2782 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\rm max} = 25.0^\circ$
$h = -17 \rightarrow 16$
$k = -11 \rightarrow 0$
$l = 0 \rightarrow 16$
2 standard reflections every 98 reflections intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.106$
$S = 1.05$
3325 reflections
237 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.5296P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.004$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}

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

P1—C1	1.7521 (18)	O2—C4	1.228 (2)
P1—C11	1.8109 (18)	C1—C2	1.444 (3)
P1—C12	1.8159 (18)	C1—C4	1.449 (3)
P1—C13	1.8182 (18)	C2—C3	1.507 (3)
O1—C2	1.243 (2)		
C1—P1—C11	110.03 (8)	C12—P1—C13	111.14 (8)
C1—P1—C12	114.62 (9)	C2—C1—P1	110.80 (13)
C1—P1—C13	109.22 (8)	C4—C1—P1	125.20 (14)
C11—P1—C12	107.92 (9)	C2—C1—C4	123.94 (17)
C11—P1—C13	103.31 (8)		
P1—C1—C2—O1	18.2 (2)	P1—C1—C4—O2	164.61 (16)

Table 2
Hydrogen-bond and short-contact geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C31—H31···O2$^{\rm i}$	0.93	2.59	3.422 (3)	149
C63—H63···O2$^{\rm ii}$	0.93	2.47	3.183 (2)	134
C51—H51···O1$^{\rm iii}$	0.93	2.52	3.376 (3)	153

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

Compound (II)

Crystal data

$C_{25}H_{25}O_4P$
$M_r = 420.42$
Monoclinic, $P2_1/c$
$a = 12.572\ (14)$ Å
$b = 9.022\ (12)$ Å
$c = 19.52\ (2)$ Å
$\beta = 90.12\ (2)^\circ$
$V = 2214\ (4)$ Å^3
$Z = 4$
$D_x = 1.261$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.5$–12.5°
$\mu = 0.15$ mm^{-1}
$T = 295\ (2)$ K
Rectangular prism, colorless
0.35 × 0.20 × 0.15 mm

Data collection

Siemens *R*3*m* diffractometer
$\omega/2\theta$ scans
4069 measured reflections
3880 independent reflections
3138 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\rm max} = 25.1^\circ$
$h = 0 \rightarrow 14$
$k = -10 \rightarrow 0$
$l = -23 \rightarrow 23$
2 standard reflections every 98 reflections intensity decay: 1.8%

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

P1—C1	1.748 (3)	O3—C5	1.372 (3)
P1—C11	1.828 (3)	O3—C6	1.438 (3)
P1—C12	1.819 (4)	O4—C5	1.214 (3)
P1—C13	1.814 (3)	C1—C2	1.453 (3)
O1—C2	1.363 (3)	C1—C5	1.440 (4)
O1—C3	1.482 (4)	C3—C4	1.466 (5)
O2—C2	1.214 (4)		
C1—P1—C11	108.60 (15)	C2—O1—C3	117.4 (2)
C1—P1—C12	115.14 (16)	C5—O3—C6	116.4 (2)
C1—P1—C13	111.66 (11)	P1—C1—C2	122.95 (19)
C11—P1—C12	108.71 (12)	P1—C1—C5	117.87 (17)
C11—P1—C13	106.69 (11)	C2—C1—C5	118.8 (2)
C12—P1—C13	105.68 (13)		
P1—C1—C2—O2	−149.8 (2)	P1—C1—C5—O4	170.8 (2)

Table 4

Hydrogen-bond and short-contact geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C53—H53···O2^{iv}	0.93	2.36	3.213 (6)	152

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

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.003$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$wR(F^2) = 0.129$	$\Delta\rho_{\min} = -0.22$ e Å^{-3}
$S = 1.10$	Extinction correction: *SHELXL97*
3880 reflections	Extinction coefficient: 0.0202 (15)
272 parameters	
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.059P)^2 + 1.0148P]$ where $P = (F_o^2 + 2F_c^2)/3$	

H atoms were placed at idealized positions (C—H = 0.93 Å for CH atoms, 0.97 Å for CH$_2$ atoms and 0.96 Å for CH$_3$ atoms), with $U_{\rm iso}$(H) values of $xU_{\rm eq}$(C), having $x = 1.5$ for methyl H atoms and $x = 1.2$ for the remainder. Methyl H atoms were allowed to rotate about the C—C axis. The monoclinic character of (II) [$\beta = 90.12$ (2)°] was originally checked through the agreement between equivalents [$R_{\rm int}$(monoclinic) = 0.027 and $R_{\rm int}$(orthorhombic) = 0.545].

For both compounds, data collection: *P3/P4-PC* (Siemens, 1991); cell refinement: *P3/P4-PC*; data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1259). Services for accessing these data are described at the back of the journal.

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