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Favoured conformations of methyl isopropyl, ethyl isopropyl, methyl *tert*-butyl, and ethyl *tert*-butyl 2-(triphenylphosphoranylidene)malonate

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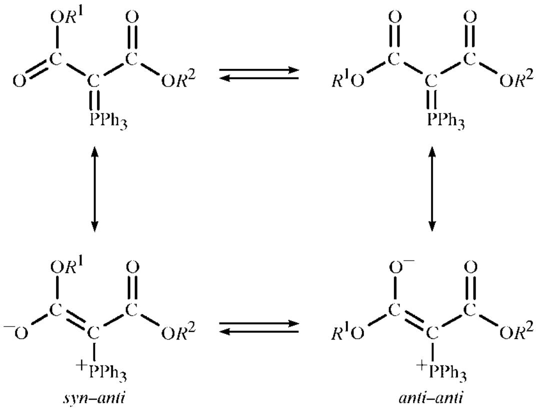
The conformations of organic compounds determined in the solid state are important because they can be compared with those in solution and/or from theoretical calculations. In this work, the crystal and molecular structures of four closely related diesters, namely methyl isopropyl 2-(triphenylphosphoranylidene)malonate, $C_{25}H_{25}O_4P$, ethyl isopropyl 2-(triphenylphosphoranylidene)malonate, $C_{26}H_{27}O_4P$, methyl *tert*-butyl 2-(triphenylphosphoranylidene)malonate, $C_{26}H_{27}O_4P$, and ethyl *tert*-butyl 2-(triphenylphosphoranylidene)malonate, $C_{27}H_{29}O_4P$, have been analysed as a preliminary step for such comparative studies. As a result of extensive electronic delocalization, as well as intra- and intermolecular interactions, a remarkably similar pattern of preferred conformations in the crystal structures results, *viz*. a *syn–anti* conformation of the acyl groups with respect to the P atom, with the bulkier alkoxy groups oriented towards the P atom. The crystal structures are controlled by nonconventional hydrogen-bonding and intramolecular interactions between cationoid P and acyl and alkoxy O atoms in *syn* positions.

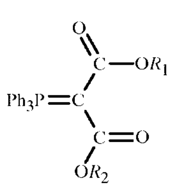
Comment

The conformations of crystalline triphenylphosphonium ylides stabilized by electron-withdrawing groups such as ester, keto or cyano depend on the balance between electronic delocalization and intra- and intermolecular nonbonding interactions (Castañeda *et al.*, 2003; Castañeda, Acuña *et al.*, 2007). The bond between P and the ylidic C atom allows free rotation at ambient temperatures on the NMR time scale, indicating the inadequacy of a structure with a classical C═P double bond (Bachrach & Nitsche, 1994). In ylides stabilized by a single keto or ester group, there is a strong interaction between cationoid phosphorus and the *syn* acyl O atom (Wilson & Tebby, 1972; Zeliger *et al.*, 1969), but *syn–syn* diesters have never been observed and are not shown, as in the first scheme for *syn–anti* and *anti–anti* mixtures. The crystal conformation is controlled by minor changes in the diester groups because the dimethyl ester is a 1:1 *anti–anti*/*syn–anti* mixture, in the methyl ethyl diester the acyl O atom of the methyl ester group is *syn* and that of the ethyl ester group is *anti* (Castañeda, Jullian *et al.*, 2007), and in the diethyl ester both acyl O atoms are *anti* to the P atom (Castañeda *et al.*, 2005). This limited evidence indicates that acyl groups can adopt either geometry, but the bulkier alkoxy group tends to be *syn* to P.



(I*a*) *syn*−*anti* R^1=Me, R^2=^{i}Pr (I*b*) *syn*−*anti* R^1=Et, R^2=^{i}Pr
(II*a*) *syn*−*anti* R^1=Me, R^2=^{t}Bu (II*a*) *syn*−*anti* R^1=Et, R^2=^{t}Bu

A series of diesters with methoxy, ethoxy, isopropoxy and *tert*-butoxy groups, namely the methyl isopropyl-, (I*a*), ethyl isopropyl-, (I*b*), methyl *tert*-butyl-, (II*a*), and ethyl *tert*-butyl 2-(triphenylphosphoranylidene)malonate diesters, (II*b*), $Ph_3P{=\!=}C(CO_2R_1)CO_2R_2$ (where R_1 = Me or Et and R_2 = ^{i}Pr or ^{t}Bu), have been prepared and their structures analysed. Figs. 1, 3, 5 and 7 show the molecular structures of the compounds, while Figs. 2, 4, 6 and 8 present the corresponding packing views. Selected bond distances for (I*a*), (I*b*), (II*a*) and (II*b*) are given in Tables 1, 3, 5 and 7, respectively. Tables 2, 4, 6, 8 and 9 show the nonbonding interactions and short contacts relevant to the packing discussion.



	R_1	R_2
(I*a*)	Me	$CHMe_2$
(I*b*)	Et	$CHMe_2$
(II*a*)	Me	CMe_3
(II*b*)	Et	CMe_3

In the crystals of these diesters, the bulkier alkoxy groups are oriented towards, and the smaller alkoxy groups away from, the P atom. The ester groups have *Z* conformations, as is typical of carboxylic esters (Eliel & Wilen, 1994), and are approximately in the ylidic plane. The ^{1}H and ^{13}C NMR spectra of these diesters indicate that the conformations are

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the same in solution and the solid state, as detailed elsewhere (Castañeda *et al.*, 2008). The geometries of the crystalline diesters are governed by the balance between ylidic resonance and intra- and intermolecular interactions. As is generally the case, the C$\overset{\cdots}{-}$P bond lengths are between those characteristic of single and double bonds (Howells *et al.*, 1973), and in solution the ^{1}H and ^{13}C NMR signals indicate free rotation about this bond. However, in the crystal structure, the orientations of the phenyl groups are similar in the four ylides and are apparently insensitive to the bulkiness of the alkoxy ester groups.

To a first approximation, the bonds between the ylidic and acyl C atoms are in the same plane, consistent with important ylidic resonance. Some angles at these C atoms differ from the expected 120°, but the sum of the angles is approximately 360°. In earlier observations of ylidic diesters with methoxy or ethoxy substituents, we found that the bulkier alkoxy group was oriented towards the P atom (Castañeda, Jullian *et al.*, 2007), and the present results fit this generalization. In the crystal structure, bulky alkoxy groups oriented away from the P atom would interfere both intra- and intermolecularly. Both isopropoxy and *tert*-butoxy groups are oriented towards the face of the phenyl group which is approximately orthogonal to the C$\overset{\cdots}{-}$P bond, as shown by the ^{1}H NMR signals in solution ($CDCl_3$). The bond lengths between ylidic and acyl C atoms are between those typical of single and double bonds, as are those in the acyl groups (Howells *et al.*, 1973).

Elsewhere, we show that computed interatomic distances and angles for isolated molecules are generally similar to those in the crystal structure (Castañeda, Jullian *et al.*, 2007). Computations indicate that the conformations of isolated ylidic diesters have minor effects on their computed energies, indicating the role of intermolecular interactions in controlling conformation. Intramolecular interactions in the crystal structure, and probably also in solution, involve interactions between cationoid P and acyl and alkyl O atoms in the *syn* position, which slightly lengthens the acyl group *syn* to P relative to the *anti*-acyl group, as shown by the relative lengths of O4—C3 and O2—C2. This generalization fails for the methyl *tert*-butyl diester, (II*a*). There are also, in some diesters, intramolecular interactions between methyl H atoms and *anti* acyl O atoms. There are always intermolecular interactions between phenyl H atoms and the acyl O atoms of an adjacent molecule (Desiraju & Steiner, 1999). These interactions between phenyl H atoms and acyl O atoms are generally important and play key roles in determining the conformations of individual molecules and crystal structures (Castañeda, Jullian *et al.*, 2007).

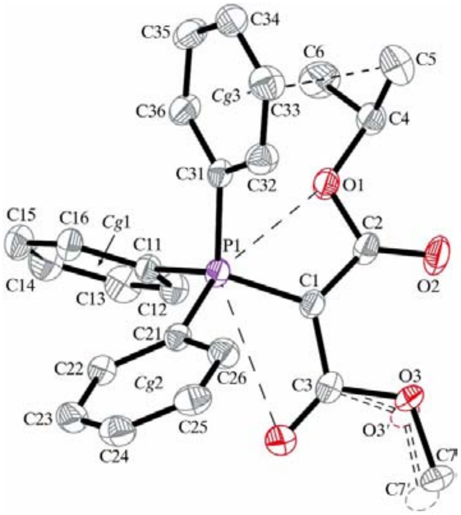

Figure 1
A molecular diagram of (I*a*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. *Cg*1, *Cg*2 and *Cg*3 denote ring centroids. Intramolecular interactions (P···O contacts and C—H···π bonds) are shown as single dashed lines. The minor component of the disordered methyl group is shown by double dashed bonds and dashed ellipsoids.

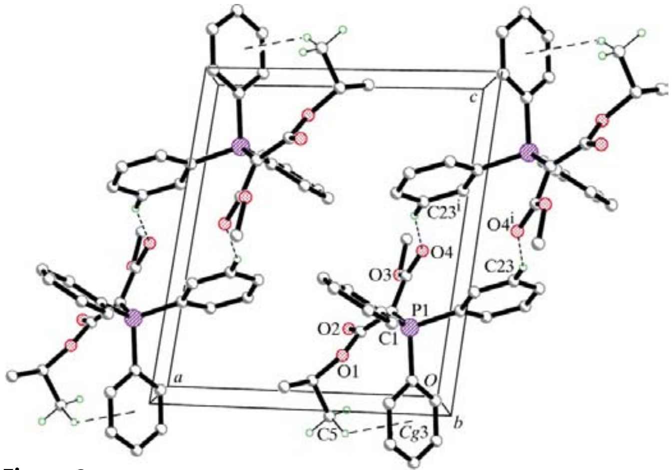

Figure 2
A packing diagram for (I*a*), showing the weakly connected dimeric structure. Intermolecular C—H···O and intramolecular C—H···π bonds are shown as dashed lines. The symmetry codes are as in Table 2.

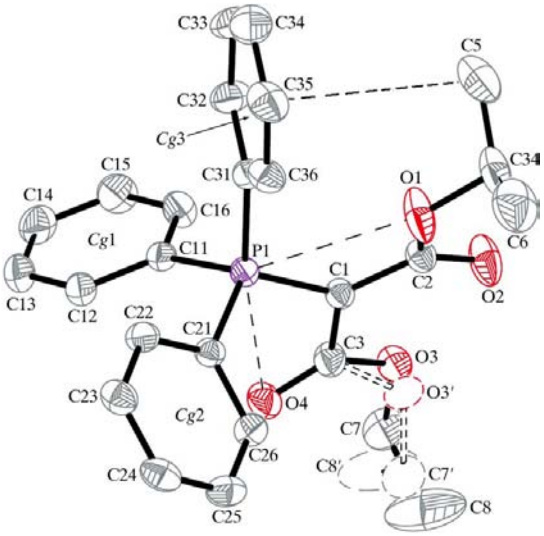

Figure 3
A molecular diagram of (I*b*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. *Cg*1, *Cg*2 and *Cg*3 denote ring centroids. Intramolecular interactions (P···O contacts and C—H···π bonds) are shown as single dashed lines. The minor component of the disordered ethyl group is shown by double dashed bonds and dashed ellipsoids.

In the crystal structure of (I*b*) (Fig. 4), one alkoxy group *syn* to P is directed towards the face of a phenyl group which is approximately orthogonal to the ylidic C—P bond. The consequent C—H$\cdots\pi$ interaction should be modestly stabilizing (Nishio *et al.*, 1995; Nishio & Hirota, 1989) and is seen in a variety of diesters and keto esters. In the other ester residue, the *syn*-acyl group is oriented between two phenyl groups, and independent evidence indicates that for some diester ylides the geometries are similar for isolated molecules and in the crystal structure.

Due to the common skeleton, all four ylides exhibit analogous weak intramolecular interactions, *viz.* two short P$\cdots$O contacts and one further C—H$\cdots\pi$ hydrogen bond between the terminal methyl H atom (C5—H5*C*) and the phenyl ring C31–C36 (*Cg*3) (entries 1–3 in Tables 2, 4, 6 and 8). There are, however, differences in the intermolecular interactions and the derived packing schemes. In (I*a*) and (I*b*), there is one nonconventional intermolecular C—H$\cdots$O bond between the C21–C26 phenyl ring (*Cg*2) and atom O4, but it

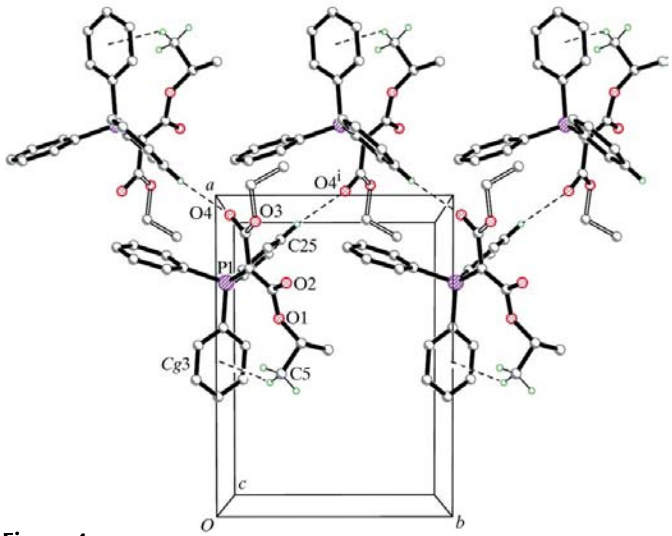

Figure 4
A packing diagram for (I*b*), showing the weakly connected chains running along the *b* axis. Intermolecular C—H$\cdots$O and intramolecular C—H$\cdots\pi$ bonds are shown as dashed lines. The symmetry codes are as in Table 4.

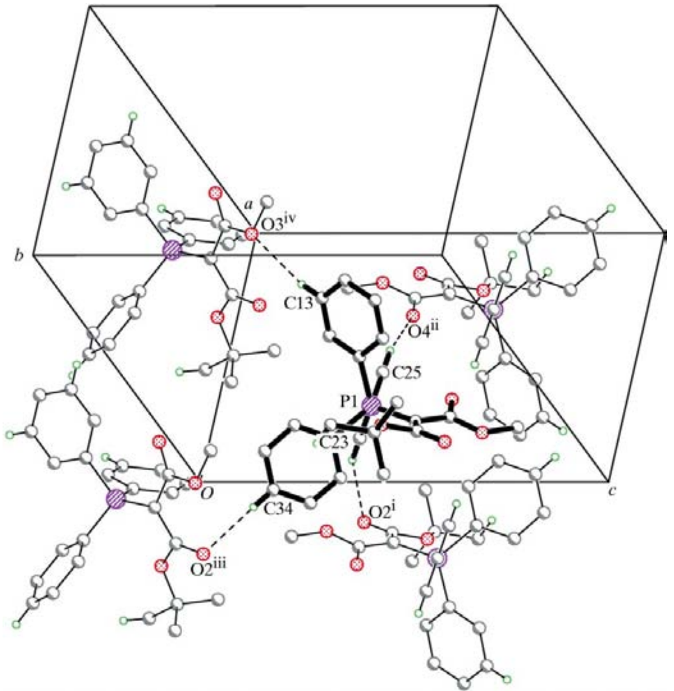

Figure 6
A packing diagram for (II*a*), showing the three-dimensional structure. Intermolecular C—H$\cdots$O bonds are shown as dashed lines. Intramolecular hydrogen bonds have been omitted for clarity. The symmetry codes are as in Table 6.

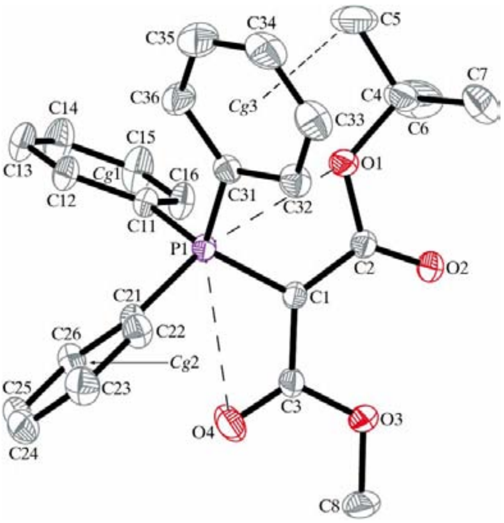

Figure 5
A molecular diagram of (II*a*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. *Cg*1, *Cg*2 and *Cg*3 denote ring centroids. Intramolecular interactions (P$\cdots$O contacts and C—H$\cdots\pi$ bonds) are shown as dashed lines.

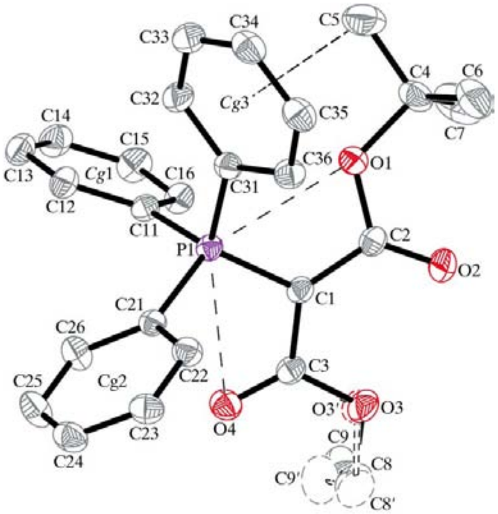

Figure 7
A molecular diagram of (II*b*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. *Cg*1, *Cg*2 and *Cg*3 denote ring centroids. Intramolecular interactions (P$\cdots$O contacts and C—H$\cdots\pi$ bonds) are shown as dashed lines. The minor component of the disordered ethyl group is shown by double dashed bonds and dashed ellipsoids.

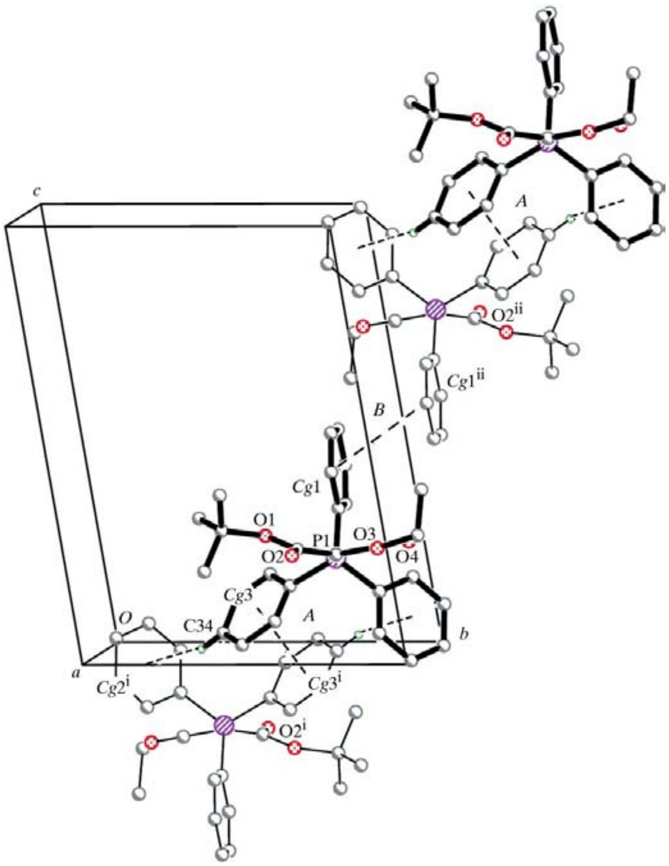

Figure 8
A packing diagram for (II*b*), showing the dimeric structures (at site *A*) connected into chains (at site *B*). Intermolecular C—H$\cdots\pi$ and π–π interactions are shown as dashed lines. Intramolecular interactions have been omitted for clarity. The symmetry codes are as in Tables 8 and 9.

gives dissimilar packing schemes: in (I*a*), hydrogen-bonded dimers are built up around a group of symmetry centres (Fig. 2), while for (I*b*) it results in the formation of a chain around the screw axis running along the unique *b* axis (Fig. 4). In ylides (II*a*) and (II*b*), these interactions differ, *viz*. in (II*a*) the preferred intermolecular contacts are nonconventional C—H$\cdots$O bonds (Table 6), while in (II*b*) they are mainly C—H$\cdots\pi$ (Table 8) and π–π bonds (Table 9), and the crystal structures differ. In (II*a*), the predominant C—H$\cdots$O bonds are spread uniformly in four directions (Fig. 6), generating a homogeneously connected three-dimensional structure. In (II*b*), dimeric structures are built up around a group of symmetry centres [at $(0, \frac{1}{2}, 0)$, zone *A* in Fig. 8], connected into [111] chains by rather weak π–π bonds around the inversion centre at $(\frac{1}{2}, 1, \frac{1}{2})$ (*B* in Fig. 8). Finally, weak hydrogen bonds with atom O2 as an acceptor link these chains, with their [100] translated homologues, into a two-dimensional structure parallel to the (011) plane.

Experimental

The title isopropyl and *tert*-butyl diesters of triphenylphosphonium ylides, *viz*. (I*a*), (I*b*), (II*a*) and (II*b*), were synthesized by transylidation (Cristau & Plénat, 1994). The general procedure was as follows. A solution of methyl or ethyl chloroformate (20 mmol) in dry benzene (8 ml) was added slowly to isopropyl or *tert*-butyl 2-(triphenylphosphoranylidene)acetate ($Ph_3P{=}CH{-}CO_2R$, R = ^{i}Pr or ^{t}Bu; 40 mmol) in dry benzene (100 ml) under a dry atmosphere. The resulting solution was stirred for 4 h at room temperature and a white solid separated. The carboalkoxy methyltriphenylphosphonium chloride ($Ph_3P^+{-}CH_2{-}CO_2R\ Cl^-$; R = ^{i}Pr or ^{t}Bu) was removed by filtration and the solvent evaporated, giving a solid or an oil. Recrystallization from ethyl acetate gave the title novel diester ylides. For methyl isopropyl 2-(triphenylphosphoranylidene)malonate, (I*a*): yield 82%; m.p. 393 K; analysis calculated for $C_{25}H_{25}O_4P$: C 71.42, H 5.99%; found: C 71.70, H 6.22%. For ethyl isopropyl 2-(triphenylphosphoranylidene)malonate, (I*b*): yield 78%; m.p. 397 K; analysis calculated for $C_{26}H_{27}O_4P$: C 71.88, H 6.26%; found: C 72.15, H 6.35%. For methyl *tert*-butyl 2-(triphenylphosphoranylidene)malonate, (II*a*): yield 70%; m.p. 460 K; analysis calculated for $C_{26}H_{27}O_4P$: C 71.88, H 6.26%; found: C 72.12, H 6.30%. For ethyl *tert*-butyl 2-(triphenylphosphoranylidene)malonate, (II*b*): yield 65%; m.p. 412 K; analysis calculated for $C_{27}H_{29}O_4P$: C 72.31, H 6.52%; found: C 72.45, H 6.80%. ^{1}H NMR spectra in solution were monitored on a Bruker DRX 300 spectrometer referenced to trimethylsilane. IR spectra were obtained with a KBr disk on a Bruker IFS 56 FT spectrometer. Elemental analyses were carried out with a Fison EA 1108 analyser. Spectroscopic data are available in the archived CIF.

Compound (I*a*)

Crystal data

$C_{25}H_{25}O_4P$
M_r = 420.42
Triclinic, $P\overline{1}$
a = 9.8033 (6) Å
b = 10.4492 (7) Å
c = 11.2169 (7) Å
α = 100.573 (2)°
β = 94.878 (2)°
γ = 102.446 (3)°
V = 1093.64 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 273 (2) K
0.20 × 0.17 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
9176 measured reflections
4675 independent reflections
3133 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.134
S = 1.01
4675 reflections
282 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.27 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.17 e Å^{-3}

Table 1
Selected bond lengths (Å) for (I*a*).

P1—C1	1.7388 (19)	C1—C3	1.436 (3)
O2—C2	1.208 (2)	C1—C2	1.443 (3)
O4—C3	1.211 (2)		

Table 2
Hydrogen-bond geometry (Å, °) for (I*a*).

*Cg*3 is the centroid of the C31–C36 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
P1$\cdots$O1			2.799 (2)	
P1$\cdots$O4			3.030 (2)	
C5—H5*C*$\cdots$*Cg*3	0.96	2.89	3.657 (3)	138
C23—H23$\cdots$O4$^{\rm i}$	0.93	2.56	3.430 (3)	156

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

Compound (I*b*)

Crystal data

$C_{26}H_{27}O_4P$
M_r = 434.45
Monoclinic, $P2_1/c$
a = 12.5175 (16) Å
b = 9.1555 (12) Å
c = 20.351 (3) Å
β = 96.342 (2)°
V = 2318.0 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 140 (5) K
0.18 × 0.16 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
19001 measured reflections
5252 independent reflections
2713 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.140
S = 0.86
5252 reflections
300 parameters
7 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.33 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.27 e Å^{-3}

Table 3
Selected bond lengths (Å) for (I*b*).

P1—C1	1.741 (2)	C1—C3	1.425 (3)
O2—C2	1.188 (3)	C1—C2	1.441 (3)
O4—C3	1.228 (3)		

Table 4
Hydrogen-bond geometry (Å, °) for (I*b*).

*Cg*3 is the centroid of the C31–C36 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
P1⋯O1			2.953 (2)	
P1⋯O4			2.809 (2)	
C5—H5*C*⋯*Cg*3	0.96	2.93	3.663 (4)	134
C25—H25⋯O4$^{\rm i}$	0.93	2.40	3.323 (3)	172

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

Compound (II*a*)

Crystal data

$C_{26}H_{27}O_4P$
M_r = 434.45
Monoclinic, $P2_1/n$
a = 9.8140 (7) Å
b = 15.889 (2) Å
c = 15.404 (2) Å
β = 90.413 (2)°
V = 2402.0 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 140 (5) K
0.16 × 0.16 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer
19840 measured reflections
5292 independent reflections
4501 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.144
S = 1.04
5292 reflections
284 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.59 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.45 e Å^{-3}

Table 5
Selected bond lengths (Å) for (II*a*).

P1—C1	1.7451 (16)	C1—C3	1.434 (2)
O2—C2	1.211 (2)	C1—C2	1.447 (2)
O4—C3	1.188 (2)		

Table 6
Hydrogen-bond geometry (Å, °) for (II*a*).

*Cg*3 is the centroid of the C31–C36 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
P1⋯O1			2.729 (2)	
P1⋯O4			2.986 (2)	
C5—H5*C*⋯*Cg*3	0.96	2.99	3.788 (3)	141
C23—H23⋯O2$^{\rm i}$	0.93	2.56	3.424 (2)	154
C25—H25⋯O4$^{\rm ii}$	0.93	2.39	3.255 (3)	155
C34—H34⋯O2$^{\rm iii}$	0.93	2.59	3.511 (3)	171
C13—H13⋯O3$^{\rm iv}$	0.93	2.54	3.455 (3)	166

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

Compound (II*b*)

Crystal data

$C_{27}H_{29}O_4P$
M_r = 448.47
Triclinic, $P\overline{1}$
a = 8.9616 (7) Å
b = 10.3589 (8) Å
c = 14.5644 (11) Å
α = 97.388 (2)°
β = 107.705 (3)°
γ = 105.338 (2)°
V = 1209.55 (16) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 140 (5) K
0.20 × 0.18 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
10154 measured reflections
5183 independent reflections
3919 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.136
S = 1.03
5183 reflections
299 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.35 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.16 e Å^{-3}

Table 7
Selected bond lengths (Å) for (II*b*).

P1—C1	1.7383 (14)	C1—C3	1.429 (2)
O2—C2	1.2080 (18)	C1—C2	1.448 (2)
O4—C3	1.2174 (19)		

Table 8
Hydrogen-bond geometry (Å, °) for (II*b*).

*Cg*2 is the centroid of the C21–C26 ring and *Cg*3 is the centroid of the C31–C36 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
P1⋯O1			2.877 (2)	
P1⋯O4			2.877 (2)	
C5—H5*C*⋯*Cg*3	0.96	3.07	3.944 (2)	152
C34—H34⋯*Cg*2$^{\rm i}$	0.93	2.90	3.712 (2)	146
C12—H12⋯O2$^{\rm ii}$	0.93	2.57	3.168 (2)	123

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

Table 9
π–π contacts (Å, °) for (II*b*).

*Cg*1 and *Cg*3 are as defined in Fig. 7. DA is the mean slippage angle, IPD is the mean interplanar distance and CCD is the centre-to-centre distance (for details, see Janiak, 2000).

Group 1	Group 2	DA (°)	IPD (Å)	CCD (Å)
*Cg*1	$Cg1^{ii}$	0	3.386	3.974 (2)
*Cg*3	$Cg3^{i}$	0	3.663	3.937 (2)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 2-y, 1-z$.

H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C—H = 0.93 (aromatic), 0.97 (CH_2) or 0.96 Å (CH_3), and with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H and CH_2, or $1.5U_{eq}(C)$ for CH_3.

Some terminal groups were disordered over two different orientations and accordingly were refined with a geometrically restrained split model; these were the methoxy group in (I*a*) and the ethoxy groups in (I*b*) and (II*b*). The refinements converged to final occupancies of 0.66 (2)/0.34 (2), 0.616 (4)/384 (4) and 0.747 (4)/0.253 (4) using two, seven and three restraints, respectively.

For all four compounds, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2001); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-NT* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3152). Services for accessing these data are described at the back of the journal.

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