

# Differences in the crystal structures of two dialkyl diester triphenylphosphonium ylids

Fernando Castañeda,<sup>a\*</sup> Carolina Jullian,<sup>a</sup> Clifford A. Bunton,<sup>b</sup> María Teresa Garland<sup>c</sup> and Ricardo Baggio<sup>d</sup>

<sup>a</sup>Departamento de Química Orgánica y Físicoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile, <sup>b</sup>Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 931060, USA, <sup>c</sup>CIMAT, Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago de Chile, Chile, and <sup>d</sup>Departamento de Física, Comisión Nacional de Energía Atómica, Avenida Gral Paz 1499, 1650 Buenos Aires, Argentina  
Correspondence e-mail: fcastane@ciq.uchile.cl

Hydrogen bonding and crystal packing play major roles in determining the conformations of ethyl methyl 2-(triphenylphosphoranylidene)malonate,  $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_3$  or  $\text{C}_{24}\text{H}_{23}\text{O}_4\text{P}$ , (I), and dimethyl 2-(triphenylphosphoranylidene)malonate,  $\text{Ph}_3\text{P}=\text{C}(\text{CO}_2\text{CH}_3)_2$  or  $\text{C}_{23}\text{H}_{21}\text{O}_4\text{P}$ , (II). In (I), the acyl O atom of the ethyl ester group is *anti* to the P atom, while the O atom of the methyl ester group is *syn*. In (II), the dimethyl diester is a 1:1 mixture of *anti-anti* and *syn-anti* conformers.

## Comment

X-ray structures of stabilized phosphonium ylids possessing a substituent that conjugates with the  $\text{P}=\text{C}$  double bond have been reviewed by Bachrach & Nitsche (1994). Ylidic resonance is important in phosphonium ylids stabilized by electron-withdrawing substituents due to electronic delocalization between the  $\text{P}-\text{C}$  bond, the ylidic bond and an acyl group (Castañeda *et al.*, 2001, 2003), but it may be offset by inter- or intramolecular interactions. For example, in the crystalline diethyl diester (III) (see scheme), one ester group is significantly out of the ylidic plane and both anionoid acyl O atoms are *anti*, oriented away from the cationoid P atom (Castañeda *et al.*, 2005, 2007). It appears that conformations may differ in the solid state and in solution due to intermolecular interactions in the solid, and we now consider the crystal structures of the methyl ethyl and dimethyl diesters, (I) and (II), respectively, in comparison with that of (III). For simplicity, these ylids are represented in the scheme with a  $\text{P}=\text{C}$  double bond, but in solution the phenyl groups of stabilized ylids rapidly exchange positions and  $\text{P}-\text{C}$  bond lengths are intermediate between those typical of single and double bonds

(1.80–1.83 and 1.63–1.73 Å, respectively; Howells *et al.*, 1973). Some results given here show, unexpectedly, that replacement of ethyl by methyl groups can significantly affect the crystal structure. Several structural features are characteristic of stabilized phosphonium ylids, *e.g.* the P atoms are distorted tetrahedra with relatively long  $\text{P}-\text{C}$  bonds. There are, however, differences between the crystal structures of the phosphonium ylids (I), (II) and (III) which we shall consider in detail.

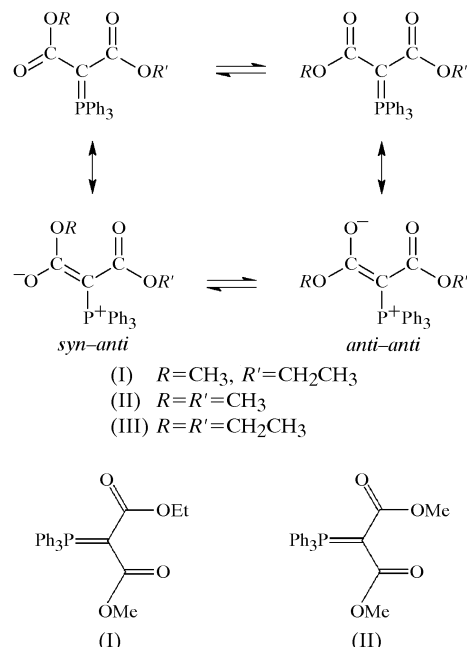
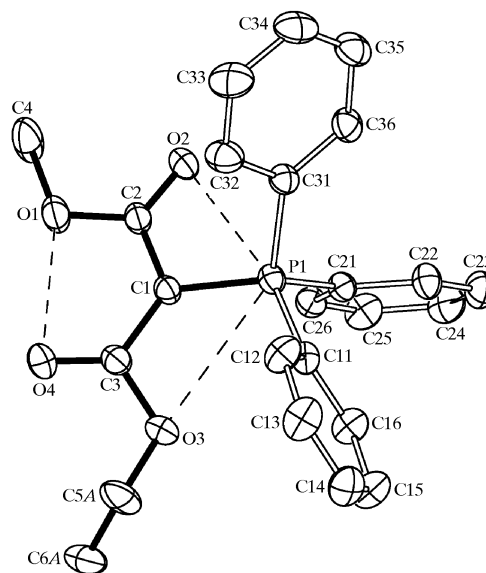
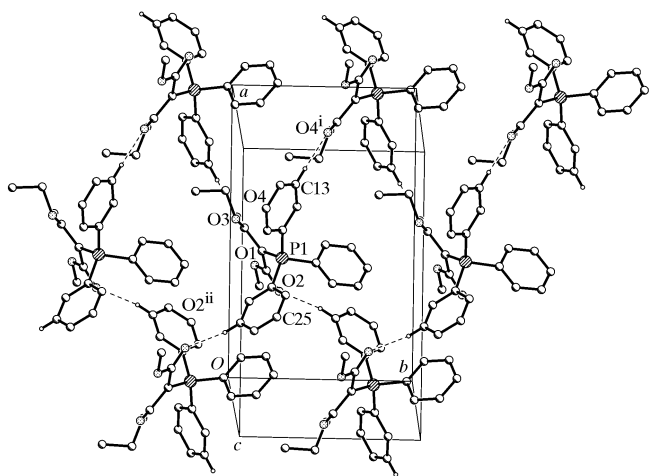


Fig. 1 presents a molecular view of the methyl ethyl diester ylid, (I), while selected geometric parameters are presented in Table 1. The O1–C4 methoxy group is *anti* and acyl atom O2

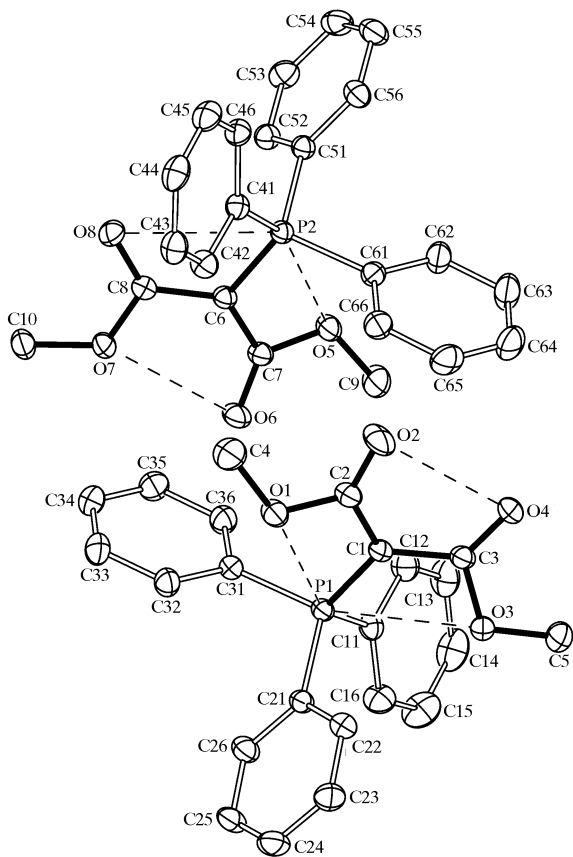


**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme used, as well as the short intramolecular contacts (dashed lines) listed in Table 1. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity. Only the main part of the disordered ethyl group is shown [occupancy 0.804 (6)].

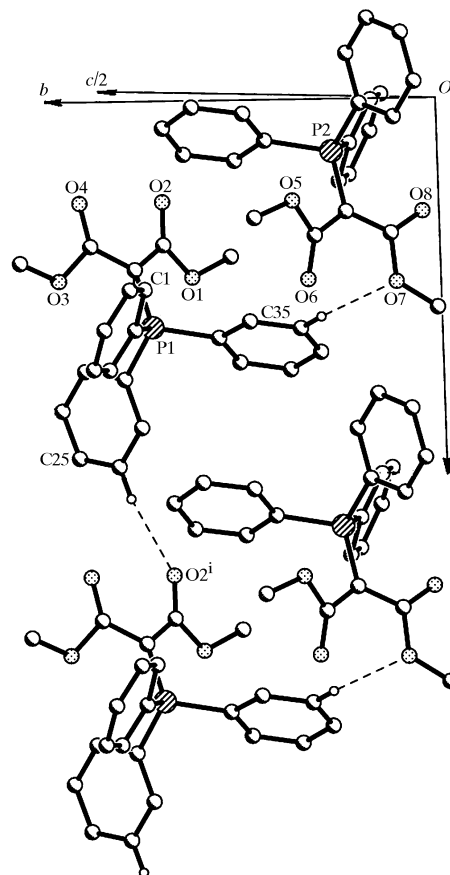
is *syn* to atom P1, while the O3—C5—C6 ethoxy group is *syn*, probably because this bulkier group interferes more with neighbouring molecules. Acyl atom O4 is *anti* to atom P1 and



**Figure 2**  
A packing diagram for (I), displaying the weakly connected two-dimensional structure resulting from hydrogen bonding (dashed lines). (Symmetry codes as in Table 2.)



**Figure 3**  
The two independent molecules of (II), showing the atom-numbering scheme used, as well as the short intramolecular contacts (dashed lines) listed in Table 3. Displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.



**Figure 4**  
A packing diagram for (II), displaying the hydrogen-bonded (dashed lines) P1 chain running along [100], with pendant P2 ylid units. The cell outline has been omitted for convenience, being replaced by the *a*, *b* and *c/2* vectors. (Symmetry codes as in Table 4.)

both acyl groups are modestly out of the plane defined by the near trigonal ylidic atom C1 [atom O3 by  $-0.52(1)$  Å and atom O4 by  $0.43(1)$  Å]. This geometry allows a degree of electronic delocalization in the near-planar ylidic system and favourable interactions between the cationoid P1 and anionoid O2 atoms, as in other stabilized ylids, but dipole–dipole interactions involving *anti* atoms O1 and O4 are destabilizing. The positions of ethoxy atoms C5 and C6 are disordered (see *Experimental*).

Each ylid unit of (I) interacts through two weak non-conventional C—H···O hydrogen bonds (Desiraju & Steiner, 1999) with four nearest neighbours, to define a two-dimensional structure parallel to (001) (Fig. 2 and Table 2)

The structure of (II) (Fig. 3 and Table 3) presents two independent ylid molecules in the asymmetric unit, one with both acyl atoms O2 and O4 *anti* to atom P1, and the other with acyl atom O8 *syn* and acyl atom O6 *anti* to atom P2. Crystallization involves the close association of *anti–anti* and *syn–anti* conformers, defined in terms of the orientations of the acyl O atoms relative to the P atom.

The two independent ylidic groups are not in very close proximity but there are, as in (I), a couple of weak non-conventional C—H···O hydrogen bonds, leading to a chain of

P1 units running along [100] with pendant and relatively free P2 ylid groups at the side (Fig. 4 and Table 4)

The melting points of the compounds are quite different, that for the dimethyl diester (465 K) being unexpectedly much higher than that of the methyl ethyl diester (395 K). The melting points of most triphenylphosphonium ylides are *ca* 400 K, despite significant differences in their crystal structures. The ylidic groups of each unit in crystalline (II) are approximately planar and the torsion angles relating the orientations of the O atoms relative to atoms P1 or P2 permit favourable ylidic resonance (see relevant parameters in Table 3).

In structure (I), acyl atom O4 is *anti* to atom P1, but the loss of this charge stabilization is partially offset by the interaction of ethoxy atom O3 with atom P1. In these diesters, the P—C bond lengths are intermediate between those typical of single and double bonds, and the structures of stabilized phosphonium ylides are sometimes written with a double bond between the ylidic and acyl C atoms, but this model is inadequate for diesters in view of the conformations of the *syn* and *anti* groups in the crystalline dimethyl diester, (II).

The observations that in the crystalline diethyl diester, (III), both acyl O atoms are *anti* to the P atom and one is out of the ylidic plane, that in the methyl ethyl diester, (I), one acyl O atom is *syn* to the P atom and the other is *anti*, with the ethoxy O atom *syn* to the P atom, and that the dimethyl diester, (II), is a 1:1 mixture of *syn-anti* and *anti-anti* diesters, show that, in the crystalline state, resonance and P—O interactions are not as important as hydrogen bonding and crystal packing in determining conformation.

## Experimental

For the preparation of the ethyl methyl diester ylid, (I), methyl chloroformate (9 mmol) in benzene (10 ml) was added dropwise to a stirred solution of (ethoxycarbonylmethylene)triphenylphosphorane (18 mmol) in benzene (40 ml) at room temperature under nitrogen. The reaction was complete in 8 h and a white solid, namely (ethoxycarbonylmethyl)triphenylphosphonium chloride, was separated. After filtration, most of the solvent was removed by rotary evaporation and the remaining solution, about 10 ml, was diluted with cyclohexane to precipitate (I), which was then crystallized from ethyl acetate. Diester ylid (I) was also obtained with practically the same yield by a similar reaction of the homologous (methoxycarbonylmethylene)triphenylphosphorane with ethyl chloroformate (yield 85%; m.p. 395 K). Analysis calculated for C<sub>24</sub>H<sub>25</sub>O<sub>4</sub>P: C 70.93, H 5.70%; found: C 71.13, H 5.55%. The dimethyl diester ylid, (II), was prepared according to the methods of Horner & Oediger (1958) and Castañeda *et al.* (2005) (yield 80%; m.p. 465 K). Analysis calculated for C<sub>23</sub>H<sub>21</sub>O<sub>4</sub>P: C 70.40, H 5.39%; found: C 70.68, H 5.59%.

### Compound (I)

#### Crystal data

C <sub>24</sub> H <sub>25</sub> O <sub>4</sub> P	$V = 2101.0$ (4) Å <sup>3</sup>
$M_r = 406.39$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 14.3378$ (17) Å	$\mu = 0.16$ mm <sup>-1</sup>
$b = 9.1666$ (11) Å	$T = 295$ (2) K
$c = 16.2696$ (19) Å	$0.20 \times 0.18 \times 0.14$ mm
$\beta = 100.711$ (2)°	

#### Data collection

Bruker SMART CCD area-detector diffractometer	4717 independent reflections
17124 measured reflections	2769 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.061$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$	272 parameters
$wR(F^2) = 0.153$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.32$ e Å <sup>-3</sup>
4717 reflections	$\Delta\rho_{\text{min}} = -0.32$ e Å <sup>-3</sup>

**Table 1**

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

P1—C1	1.741 (3)	O4—C3	1.203 (3)
O1—C2	1.345 (3)	C1—C2	1.428 (4)
O1—C4	1.477 (4)	C1—C3	1.440 (4)
O2—C2	1.219 (3)	P1—O2	2.789 (2)
O3—C3	1.356 (3)	P1—O3	3.004 (2)
O3—C5A	1.4982 (10)	O1—O4	2.755 (3)
P1—C1—C2—O2	10.2 (4)	P1—C1—C3—O4	154.2 (3)

**Table 2**

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C13—H13 $\cdots$ O4 <sup>i</sup>	0.93	2.48	3.376 (4)	162
C25—H25 $\cdots$ O2 <sup>ii</sup>	0.93	2.49	3.392 (4)	162

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

### Compound (II)

#### Crystal data

C <sub>23</sub> H <sub>21</sub> O <sub>4</sub> P	$V = 3968.1$ (5) Å <sup>3</sup>
$M_r = 392.37$	$Z = 8$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.1031$ (8) Å	$\mu = 0.17$ mm <sup>-1</sup>
$b = 14.6961$ (11) Å	$T = 273$ (2) K
$c = 26.756$ (2) Å	$0.18 \times 0.18 \times 0.16$ mm
$\beta = 92.7340$ (10)°	

#### Data collection

Bruker SMART CCD area-detector diffractometer	8973 independent reflections
33032 measured reflections	6466 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.040$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	509 parameters
$wR(F^2) = 0.145$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.44$ e Å <sup>-3</sup>
8973 reflections	$\Delta\rho_{\text{min}} = -0.23$ e Å <sup>-3</sup>

H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic, C—H = 0.97 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for CH<sub>2</sub>, and C—H = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms. The ethyl group in (I) was found to be disordered over two different orientations and was accordingly refined with a split model to final occupancies of 0.804 (6) and 0.196 (6).

For both 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, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick,

**Table 3**

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

P1—C1	1.738 (2)	P2—C6	1.7408 (19)
O1—C2	1.361 (2)	O5—C7	1.361 (2)
O1—C4	1.429 (3)	O5—C9	1.434 (3)
O2—C2	1.204 (2)	O6—C7	1.208 (2)
O3—C3	1.369 (2)	O7—C8	1.353 (2)
O3—C5	1.434 (3)	O7—C10	1.433 (2)
O4—C3	1.204 (2)	O8—C8	1.220 (2)
C1—C2	1.430 (3)	C6—C8	1.432 (3)
C1—C3	1.443 (3)	C6—C7	1.443 (3)
P1—O3	2.8396 (15)	P2—O5	2.8355 (14)
P1—O1	2.8784 (15)	P2—O8	2.9985 (15)
O2—O4	2.864 (2)	O6—O7	2.729 (2)
P1—C1—C2—O2	−162.0 (2)	P2—C6—C7—O6	154.6 (2)
P1—C1—C3—O4	158.20 (19)	P2—C6—C8—O8	8.8 (3)

**Table 4**

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C25—H25...O2 <sup>1</sup>	0.93	2.46	3.326 (3)	155
C35—H35...O7	0.93	2.49	3.377 (3)	159

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

1997); molecular graphics: *SHELXTL-NT* (Bruker, 2001); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

The authors acknowledge CONICYT-FONDAP (grant No. 11980002) and the Spanish Research Council (CSIC) for providing a free-of-charge license to the Cambridge Structural Database.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3064). Services for accessing these data are described at the back of the journal.

## References

- Bachrach, S. M. & Nitsche, C. I. (1994). *The Chemistry of Organophosphorus Compounds*, edited by F. R. Hartley, Vol. 3, ch. 4, pp. 273–299. Chichester: Wiley.
- Bruker (2001). *SMART-NT* (Version 5.624), *SAINTE-NT* (Version 6.04) and *SHELXTL-NT* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Castañeda, F., Aliaga, C., Bunton, C. A., Garland, M. T. & Baggio, R. (2005). *Acta Cryst.* **C61**, o496–o499.
- Castañeda, F., Aliaga, C., Garland, M. T., Hu, J., Gillitt, N. D. & Bunton, C. A. (2007). *Phosphorus Sulfur Silicon Relat. Elem.* **182**, 1–10.
- Castañeda, F., Terraza, C. A., Bunton, C. A., Gillitt, N. D. & Garland, M. T. (2003). *Phosphorus Sulfur Silicon Relat. Elem.* **178**, 1973–1985.
- Castañeda, F., Terraza, C. A., Garland, M. T., Bunton, C. A. & Baggio, R. F. (2001). *Acta Cryst.* **C57**, 180–184.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*, pp. 152–157. Oxford University Press.
- Horner, L. & Oediger, H. (1958). *Chem. Ber.* **91**, 437–442.
- Howells, M. A., Howells, R. D., Baenziger, N. C. & Burton, D. J. (1973). *J. Am. Chem. Soc.* **95**, 5366–5370.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.