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Diethyl [(*Z*)-1-iodo-2-phenyl-1-hexenyl]phosphonate

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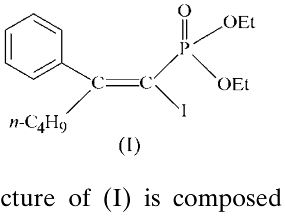
The crystal structure of the title compound, $C_{16}H_{24}IO_3P$, is composed of independent molecules, in which one of the phosphonate ethoxy groups is disordered over two positions. The other ethoxy group lies sandwiched between two phenyl rings and, as a result, is ordered. This constrained environment also leads to two C—H···centroid interactions, one intra- and one intermolecular. Examination of the extended structure reveals the presence of chains of molecules held together by I···O interactions.

Comment

For the last three decades there has been considerable interest in the synthesis and characterization of alkenylphosphonates due to their wide range of applications as polymer additives, flame retardants and intermediates for drugs, and as a useful tool in organic transformations (Minami & Motoyoshiya, 1992). However, very few vinylphosphonate structures have been characterized by X-ray crystallography to date. As part of an ongoing study of phosphoorganic biomolecules, we previously reported a facile procedure for the stereoselective preparation of alkenylphosphonates by carbocupration of 1-alkynylphosphonates in diethyl ether, followed by hydrolysis or reaction with various electrophiles (Cristau *et al.*, 1994, 1997). We report here the structure of the title compound, (I), which has been determined by X-ray crystallographic methods.



(I)

The crystal structure of (I) is composed of independent molecules, in which the phosphonate ethoxy group facing the I atom is disordered over two orientations. In contrast, the other ethoxy group (atoms C13 and C14) does not exhibit disorder. This is due to restraints placed on it by the geometry of the molecule, in particular the arrangement of O atoms around the C1—P bond, leading to it facing the phenyl ring (Fig. 1). In addition, extrapolating the structure indicates that this ethoxy group is sandwiched between two phenyl rings (one intra- and one intermolecular), preventing disorder (Fig. 2). This constrained environment also leads to two C—H···*Cg* interactions (*Cg* is the centroid of the C7–C12 ring). One of these (C14—H14*C*···*Cg*; Table 1) acts in an intramolecular manner between the ethoxy group and the phenyl ring of the molecule, while the other (C14—H14*B*···Cg^{i}; Table 1 and Fig. 2) occurs between the same ethoxy group and phenyl ring but as an intermolecular interaction.

Despite the rotational restraint imposed by the double bond (C1═C2), the deviations from zero in the torsion angles I—C1—C2—C3 [−6.7 (5)°] and P—C1—C2—C7 [−5.6 (5)°] indicate that there is some deviation from planarity around C1═C2. This is most probably due to some steric interaction between I and C3, and P and C7.

Examining the crystal packing of (I) indicates that molecules related by the twofold screw axis are held together by an I···O interaction [$I\cdots O1^{ii}$ = 3.076 (3) Å, $C1—I\cdots O1^{ii}$ = 176.17 (12)° and $I\cdots O1^{ii}—P^{ii}$ = 143.20 (16)°; symmetry code: (ii) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$]. This leads to a chain of molecules running along the *b* axis (Fig. 3). While many examples of general I···O interactions can be found in the Cambridge Structural Database (CSD, Version 5.25, update 3 of July 2004; Allen, 2002), very few examples involving C—I···O—P interactions exist. A search of the CSD for an interaction between C—I and O—P yielded only 16 hits with I···O distances less than 4 Å. Only two of these have I···O distances less than 3.3 Å [2.921 Å in ICYGET10 (Jain *et al.*, 1977) and 2.941 Å in HXMIPX (Balthazor *et al.*, 1978)], and both structure determinations date back to the 1970's. In general, the effect of I···O interactions has not been widely discussed

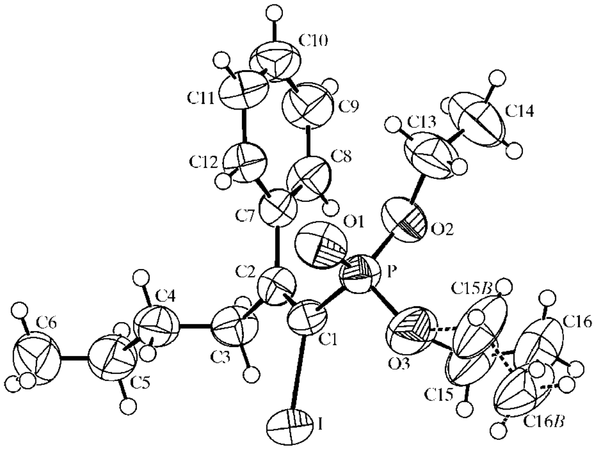


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown with arbitrary radii. The disordered component is shown with dashed bonds.

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in the literature and is sufficiently rare that it is highlighted by current *Acta Crystallographica* validation programs as an unlikely interaction. However, the effect of I$\cdots$O interactions, together with other weak interactions, on the crystal packing of some iodonitroarenesulfonamides and iodonitroanilines has been discussed in detail by Kelly *et al.* (2002) and Garden *et al.* (2002).

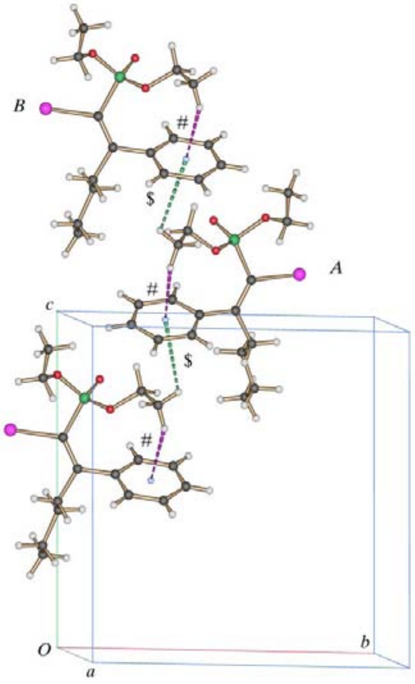

Figure 2
The weak C—H$\cdots\pi$ interactions in the structure of (I). The intra- and intermolecular C—H$\cdots\pi$ interactions are indicated by a hash (#) and a dollar sign ($), respectively. Molecules *A* and *B* are at the symmetry positions ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$) and ($1 + x, y, 1 + z$), respectively.

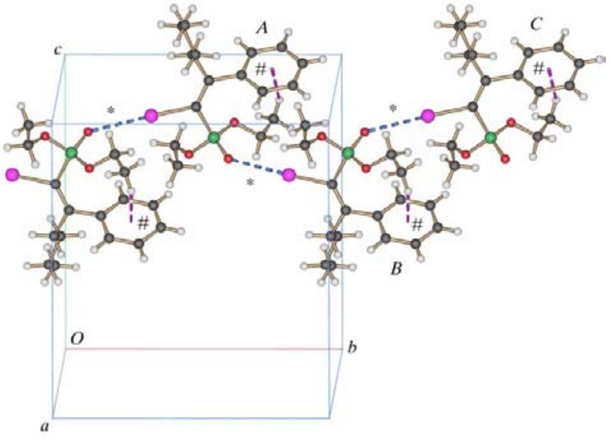

Figure 3
Part of the structure of (I), showing the chain of molecules held together by I$\cdots$O interactions, which are indicated by an asterisk (*). The intramolecular C—H$\cdots\pi$ interactions are indicated with hashes (#). Molecules *A*, *B* and *C* are at the symmetry positions ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$), ($x, 1 + y, z$) and ($\frac{1}{2} - x, \frac{3}{2} + y, \frac{3}{2} - z$), respectively.

Experimental

The title compound was obtained as described previously by Cristau *et al.* (1997). Crystallization from Et$_2$O/*n*-hexane yielded single crystals of (I) suitable for X-ray diffraction.

Crystal data

$C_{16}H_{24}IO_3P$
$M_r = 422.22$
Monoclinic, $P2_1/n$
$a = 11.7324$ (18) Å
$b = 12.3985$ (19) Å
$c = 13.228$ (2) Å
$\beta = 101.817$ (3)°
$V = 1883.4$ (5) Å^3
$Z = 4$
$D_x = 1.489$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1006 reflections
$\theta = 2.4$–27.4°
$\mu = 1.79$ mm^{-1}
$T = 293$ (2) K
Irregular, colourless
0.48 × 0.42 × 0.26 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-Plus*; Bruker, 1999)
$T_{\min} = 0.480$, $T_{\max} = 0.653$
10 404 measured reflections
3693 independent reflections
2988 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 26.0°$
$h = -13 \rightarrow 14$
$k = -13 \rightarrow 15$
$l = -12 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.086$
$S = 1.05$
3693 reflections
212 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 1.3932P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.70$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0031 (4)

Table 1
Hydrogen-bonding geometry (Å, °).

Cg is the centroid of the C7–C12 benzene ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C14—H14*C*$\cdots$*Cg*	0.96	3.38	4.077 (7)	131
C14—H14*B*$\cdots$*Cg*$^{\rm i}$	0.96	3.36	3.870 (7)	116

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

One of the phosphonate ethoxy groups exhibits orientational disorder and was refined over two positions using SADI and DFIX restraints (*SHELXTL*; Bruker, 1999); the final occupancy was 0.64 (1) for C15/C16 and 0.36 (1) for C15*B*/C16*B*. H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H distances of 0.93 (aromatic CH), 0.97 (CH$_2$) or 0.96 Å (CH$_3$), and with $U_{\rm iso}$(H) values equal to 1.2 (CH and CH$_2$) or 1.5 (CH$_3$) times $U_{\rm eq}$(C).

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003) and *SCHAKAL97* (Keller, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1218). Services for accessing these data are described at the back of the journal.

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