(2R*,3R*,4R*)-tert-Butyl 2-(diethoxyphosphoryl)-4-nitro-3-(4-nitrophenyl)pentanoate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.072
wR factor = 0.207
Data-to-parameter ratio = 14.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{19}H_{29}N_2O_9P$, was isolated as a single diastereoisomer. The molecule adopts an extended conformation with the phosphoryl and 4-nitrophenyl groups placed in antiperiplanar positions.

Comment

We have recently demonstrated that primary and secondary 3-aryl-2-(diethoxyphosphoryl)-4-nitroalkanoic acids undergo spontaneous Nef reactions (Ballini & Petrini, 2004) leading to 3-(diethoxyphosphoryl)-1-hydroxysuccinimides and 2-(diethoxyphosphoryl)-4-oxoalkanoic acids (Krawczyk *et al.*, 2002; Krawczyk & Albrecht, 2005; Krawczyk *et al.*, 2006). The title compound, (I), was prepared as a single diastereoisomer and is a key substrate in this reaction. Its relative stereochemistry at all three stereogenic centers C5, C11 and C12 is 2R*,3R*,4R*, respectively (Fig. 1). The molecule adopts an extended conformation with the phosphoryl and 4-nitrophenyl groups placed in antiperiplanar positions. The latter group is *gauche* with respect to the methyl substituent. The main bond lengths are close to those observed in related compounds (Cambridge Structural Database, Version 5.27, April 2006 update; *ConQuest*, Version 1.8; *Mogul*, Version 1.1; Allen, 2002) In particular, the N1—C12 bond is much longer [1.509 (4) Å] than the N2—C17 bond [1.460 (4) Å]; the standard values (Allen *et al.*, 1992) are 1.509 and 1.468 Å, respectively. The shortening of C—C and C—O bonds in the diethoxphosphoryl groups (Table 1) has been observed in the crystal structures of organophosphorus compounds and may follow from high displacement parameters of the terminal C atoms. The latter are often prone to dynamic disorder (Wojciechowski & Wolf, 2006). However, an attempt to refine the C1/C2 ethyl group using a two-site disorder model gave unsatisfactory results.

(I)
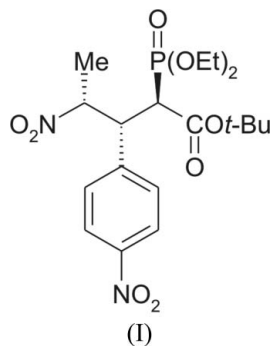
The P atom is located at the center of a distorted tetrahedron with valency angles ranging in value from 101.19 (14) to 116.47 (14)°. On average the O—P—O angles [114.7 (2)°]
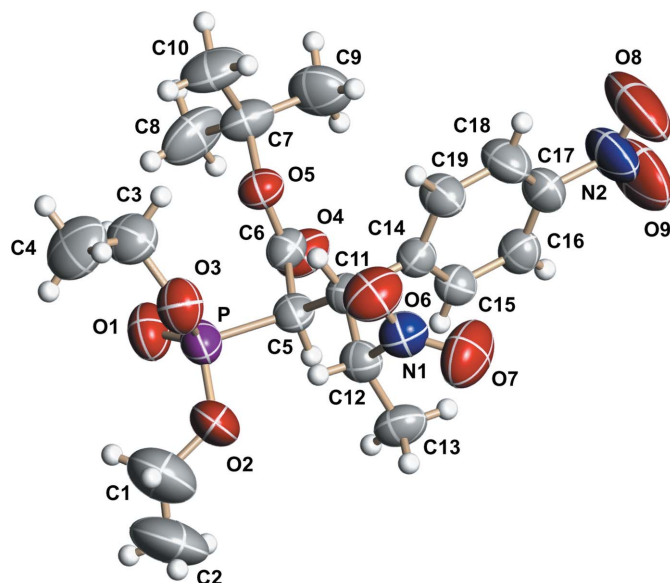
Figure 1
Molecular structure of the title compound (I). Displacement ellipsoids are drawn at the 50% probability level.

are larger than O—P—C [103.7 (2)°]. This is a general feature, often encountered in phosphorus compounds, indicating the significance of repulsive Coulombic type interactions between the O atoms bearing the negative charge (Gillespie & Popelier, 2001).

In the crystal structure, atoms O1, O4 and O6 are involved in close intermolecular contacts with the neighboring H atoms. According to the definition of Desiraju and Steiner (Steiner, 1997; Steiner & Desiraju, 1998), these contacts could be classified as weak C—H···O hydrogen bonds. Details are summarized in Table 2.

Experimental

Compound (I) was obtained by the Michael addition of nitroethane to *tert*-butyl 2-diethoxyphosphoryl-3-(4-nitrophenyl)acrylate in the presence of potassium *tert*-butoxide. Synthetic details are given by Krawczyk *et al.* (2006). Crystals suitable for the X-ray structure determination were grown at 293 K by slow evaporation of an ethanol–water (1:1) solution.

Crystal data

$C_{19}H_{29}N_2O_9P$
$M_r = 460.41$
Monoclinic, $P2_1/c$
$a = 12.3654$ (4) Å
$b = 9.7216$ (3) Å
$c = 20.4966$ (7) Å
$\beta = 105.814$ (2)°
$V = 2370.67$ (13) Å^3

$Z = 4$
$D_x = 1.290$ Mg m^{-3}
Cu $K\alpha$ radiation
$\mu = 1.47$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
$0.16 \times 0.13 \times 0.10$ mm

Data collection

Bruker SMART APEX diffractometer
ω scans
Absorption correction: multi-scan (*SHELXTL*; Bruker, 2003)
$T_{min} = 0.776$, $T_{max} = 0.867$

25754 measured reflections
4506 independent reflections
4262 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 70.7°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.072$
$wR(F^2) = 0.208$
$S = 0.96$
4506 reflections
304 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1223P)^2 + 1.8058P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.97$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P—O1	1.461 (3)	O3—C3	1.503 (5)
P—O2	1.554 (3)	N1—C12	1.509 (4)
P—O3	1.538 (2)	N2—C17	1.460 (4)
P—C5	1.819 (3)	C1—C2	1.256 (8)
O2—C1	1.365 (6)	C3—C4	1.442 (6)
O1—P—O2	115.82 (16)	O2—P—C5	101.19 (14)
O1—P—O3	116.47 (14)	O3—P—O2	101.82 (16)
O1—P—C5	111.91 (14)	O3—P—C5	108.10 (12)
O1—P—C5—C11	157.8 (2)	N1—C12—C11—C5	−173.1 (2)
P—C5—C11—C12	63.5 (3)	N1—C12—C11—C14	61.4 (3)
P—C5—C11—C14	−170.33 (17)	C13—C12—C11—C14	−62.7 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H51···O4^i	0.98 (3)	2.38 (4)	3.360 (3)	173 (2)
C16—H16···O1^i	0.91	2.58	3.293 (4)	135
C19—H19···O6^{ii}	0.96	2.52	3.408 (4)	154

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

The positional and isotropic displacement parameters of H atoms at stereogenic centers *i.e.* H51, H111 and H121, were allowed to refine freely. The positional parameters of all remaining H atoms were constrained [C—H = 0.84–1.09 Å and U_{iso}(H) = 1.2U_{eq}(C)].

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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