C4	0.4070 (7)	−0.0675 (3)	0.8923 (2)	0.0284 (7)
C5	0.6045 (7)	−0.1319 (3)	0.8503 (2)	0.0295 (7)
C6	0.0956 (7)	0.1186 (3)	0.8591 (2)	0.0272 (7)
O7	0.2367 (5)	0.1971 (2)	0.92455 (13)	0.0284 (6)
C8	0.4232 (7)	0.2779 (2)	0.8981 (2)	0.0254 (7)
O8	0.4685 (5)	0.2888 (2)	0.82381 (13)	0.0305 (6)
C9	0.5695 (10)	0.3479 (3)	0.9704 (2)	0.0393 (9)
C21	0.4430 (8)	0.0862 (3)	0.6898 (2)	0.0318 (8)
O21	0.6045 (6)	0.0738 (2)	0.63177 (15)	0.0456 (7)

Table 2. *Selected geometric parameters* (Å, °)

N1—C5	1.351 (4)	C4—C5	1.370 (5)
N1—C2	1.377 (4)	C6—O7	1.464 (4)
C2—C3	1.389 (4)	O7—C8	1.344 (4)
C2—C21	1.433 (4)	C8—O8	1.209 (4)
C3—C4	1.402 (4)	C8—C9	1.490 (5)
C3—C6	1.502 (4)	C21—O21	1.225 (4)
C5—N1—C2	109.0 (3)	N1—C5—C4	109.1 (3)
N1—C2—C3	107.4 (3)	O7—C6—C3	111.5 (3)
N1—C2—C21	121.9 (3)	C8—O7—C6	116.7 (2)
C3—C2—C21	130.6 (3)	O8—C8—O7	122.6 (3)
C2—C3—C4	107.2 (3)	O8—C8—C9	125.2 (3)
C2—C3—C6	127.1 (3)	O7—C8—C9	112.2 (3)
C4—C3—C6	125.7 (3)	O21—C21—C2	124.5 (3)
C5—C4—C3	107.3 (3)		
C2—C3—C6—O7	−107.1 (3)	C6—O7—C8—C9	−176.3 (3)
C4—C3—C6—O7	70.0 (4)	N1—C2—C21—O21	−4.4 (5)
C3—C6—O7—C8	79.4 (3)	C3—C2—C21—O21	172.3 (3)
C6—O7—C8—O8	2.1 (4)		

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dimethyl [α-(Benzylamino)-*p*-chlorobenzyl]phosphonate

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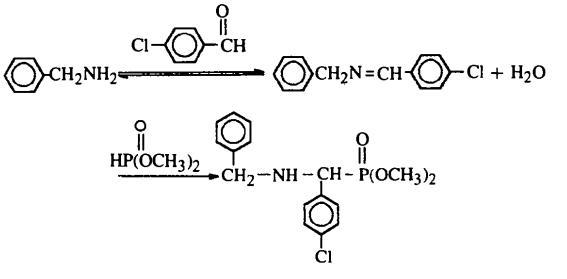
Abstract

The title compound, $C_{16}H_{19}ClNO_3P$, is one of a series of α-substituted aminomethyl phosphonates. There are two independent molecules in the asymmetric unit and in each the P atom adopts a tetrahedral configuration. The P═O double-bond length and the mean P—O single-bond length are 1.425 (5) and 1.560 (5) Å for molecule (1) and 1.417 (6) and 1.562 (5) Å for molecule (2), respectively. The P═O double-bond lengths in both molecules are shorter than those in 1,3,2-oxazaphospholidine derivatives and caged bicyclic phosphorus compounds.

Comment

α-Substituted aminomethyl phosphonates have been investigated (Li, Wang, Zhang, Miao, Liu, Cao & Guo, 1988; Li, Wang, Han, Liu, Cao, Jiang, Miao & Liu, 1988) because of their potential biological activity. The title compound, (I), was synthesized and its crystal structure is presented here.



(I)

The asymmetric unit contains two independent molecules. The P atom adopts a distorted tetrahedral configuration; the bond angles around the P atom are in the range 100.9 (2)–116.1 (3)° for molecule (1) and 97.8 (3)–119.3 (3)° for molecule (2). The mean P—O

single-bond lengths [1.560 (5) and 1.562 (5) Å for molecules (1) and (2), respectively] are in good agreement with the values in $C_{11}H_{12}O_5NP$ [1.556 (3) Å], $C_{12}H_{13}O_6NP$ [1.564 (5) Å], $C_{12}H_{13}O_7P$ [1.570 (4) Å] and $C_{11}H_{10}O_8NP$ [1.560 (5) Å] (Liu, Sun, Miao, Li, Wang, Han & Xu, 1992); the P=O double-bond lengths [1.425 (4) for molecule (1) and 1.417 (6) Å for molecule (2)] are shorter than those in the above compounds [1.452 (3), 1.449 (3), 1.439 (4) and 1.448 (5) Å, respectively], in the diazaphospholidine derivative [1.479 (1) Å] (Liu, Sun, Miao, Feng & Chen, 1992), and in the diazaphosphabicyclo[3.2.1]octane derivative (1.490 Å) (Liu, Miao, Liu & Chen, 1991). The P—C bond length [1.806 (6) Å] compares well with data reported by Marre, Sanchez, Wolf, Jaud & Galy (1984), and Perales & Garcia-Blanco (1977). The dihedral angles between the two benzene ring planes are 50.3 (2) and 56.2 (2)° for molecules (1) and (2), respectively.

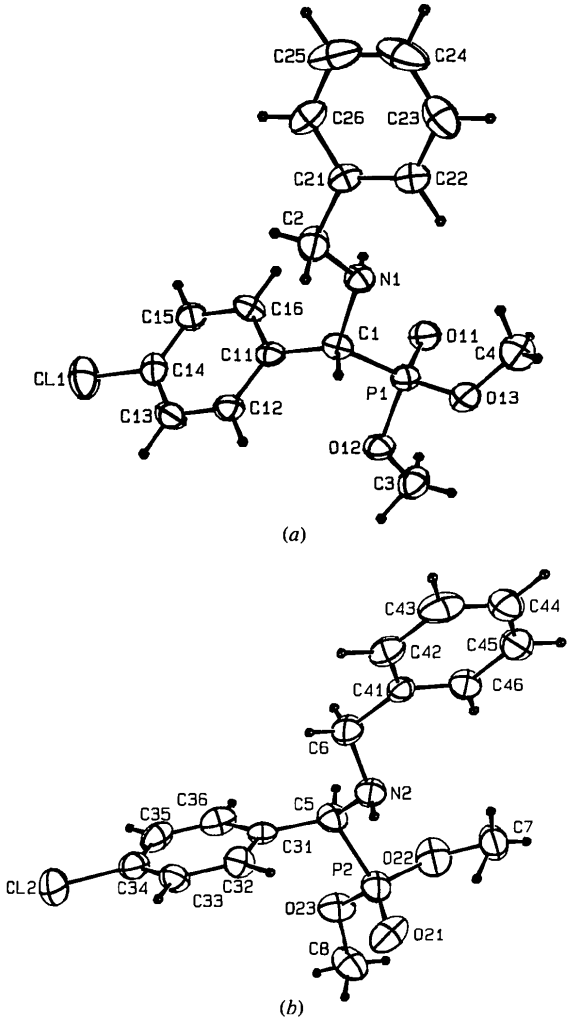


Fig. 1. Perspective drawings of (*a*) molecule (1) and (*b*) molecule (2) of the title compound, with the atomic numbering. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

Benzylamine in benzene was added dropwise to *p*-chlorobenzaldehyde dissolved in benzene with a catalytic amount of toluenesulfonic acid at room temperature, and then refluxed for 6 h to obtain *N*-(*p*-chlorobenzylidene)benzylamine. A mixture of this product and dimethyl phosphonate was heated to 313 K for 0.5 h to yield the title compound (see scheme above). The product was recrystallized from a mixed solvent of chloroform, ether and petroleum ether (1:2:2).

Crystal data

$C_{16}H_{19}ClNO_3P$
$M_r = 339.76$
Triclinic
$P\bar{1}$
$a = 10.857\ (3)$ Å
$b = 11.445\ (2)$ Å
$c = 13.916\ (3)$ Å
$\alpha = 87.51\ (2)°$
$\beta = 80.91\ (2)°$
$\gamma = 73.42\ (3)°$
$V = 1636.5\ (7)$ Å^3
$Z = 4$
$D_x = 1.379$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 0.34$ mm^{-1}
$T = 294$ K
Prism
0.30 × 0.28 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6186 measured reflections
5512 independent reflections
2646 observed reflections [$F > 3\sigma(F)$]
$R_{int} = 0.020$
$\theta_{max} = 25°$
$h = 0 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity decay: 8.1%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.056$
$S = 1.51$
2646 reflections
513 parameters
Only coordinates of H atoms refined
Unit weights applied
$(\Delta/\sigma)_{max} = 0.55$ (H703 *z*)
$\Delta\rho_{max} = 0.863$ e Å^{-3}
$\Delta\rho_{min} = -0.105$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	B_{eq}
Cl1	0.1130 (2)	1.1414 (2)	1.4363 (1)	6.52 (6)
P1	0.4506 (2)	1.2441 (2)	0.9970 (1)	3.39 (4)
N1	0.2981	1.1286 (4)	0.9467 (4)	3.4 (1)
O11	0.5566 (4)	1.1367 (4)	0.9975 (3)	4.3 (1)
O12	0.4379 (4)	1.3423 (4)	1.0749 (3)	3.9 (1)
O13	0.4555 (4)	1.3209 (4)	0.9017 (3)	4.5 (1)
C11	0.2463 (5)	1.1987 (5)	1.1229 (4)	3.0 (1)
C12	0.1677 (6)	1.2933 (5)	1.1821 (5)	3.6 (2)
C13	0.1269 (6)	1.2776 (6)	1.2780 (5)	4.3 (2)
C14	0.1636 (6)	1.1642 (6)	1.3143 (5)	4.0 (2)
C15	0.2387 (6)	1.0687 (5)	1.2583 (5)	4.0 (2)
C16	0.2806 (6)	1.0865 (5)	1.1622 (5)	3.8 (2)

C21	0.1760 (5)	1.0348 (5)	0.8555 (4)	3.3 (1)
C22	0.2227 (6)	1.0665 (5)	0.7650 (5)	3.9 (2)
C23	0.2152 (7)	1.0068 (7)	0.6848 (5)	5.6 (2)
C24	0.1645 (7)	0.9121 (7)	0.6929 (6)	6.9 (2)
C25	0.1165 (7)	0.8795 (6)	0.7817 (7)	6.5 (2)
C26	0.1257 (6)	0.9393 (6)	0.8630 (5)	4.6 (2)
C1	0.2910 (5)	1.2205 (5)	1.0172 (4)	3.0 (1)
C2	0.1747 (6)	1.1057 (6)	0.9427 (5)	4.6 (2)
C3	0.5505 (7)	1.3749 (6)	1.0918 (5)	4.9 (2)
C4	0.4959 (7)	1.2698 (7)	0.8089 (5)	5.0 (2)
Cl2	0.1226 (2)	0.5555 (2)	0.9267 (1)	6.68 (6)
P2	0.4439 (2)	0.2835 (2)	0.4959 (1)	4.38 (4)
N2	0.2973 (5)	0.4817 (5)	0.4377 (4)	4.1 (1)
O21	0.5484 (5)	0.3330 (4)	0.5011 (4)	6.1 (1)
O22	0.4467 (6)	0.2061 (5)	0.4020 (4)	6.5 (2)
O23	0.4263 (4)	0.1882 (4)	0.5725 (4)	4.9 (1)
C31	0.2406 (5)	0.4366 (5)	0.6145 (4)	3.2 (1)
C32	0.2834 (6)	0.5246 (6)	0.6521 (5)	4.0 (2)
C33	0.2460 (6)	0.5614 (6)	0.7466 (5)	4.1 (2)
C34	0.1671 (6)	0.5091 (6)	0.8072 (5)	4.2 (2)
C35	0.1226 (6)	0.4234 (6)	0.7718 (5)	5.0 (2)
C36	0.1585 (6)	0.3861 (6)	0.6777 (5)	4.4 (2)
C41	0.1784 (5)	0.6327 (5)	0.3341 (4)	3.4 (1)
C42	0.1248 (6)	0.7554 (6)	0.3265 (5)	4.3 (2)
C43	0.1216 (7)	0.8085 (6)	0.2358 (6)	5.2 (2)
C44	0.1713 (7)	0.7397 (7)	0.1550 (5)	5.1 (2)
C45	0.2241 (7)	0.6200 (6)	0.1611 (5)	4.6 (2)
C46	0.2277 (6)	0.5672 (5)	0.2492 (5)	4.0 (2)
C5	0.2848 (7)	0.3922 (6)	0.5110 (5)	4.2 (2)
C6	0.1771 (7)	0.5722 (6)	0.4291 (5)	5.0 (2)
C7	0.4898 (8)	0.2384 (7)	0.3084 (5)	6.1 (2)
C8	0.5382 (8)	0.0978 (6)	0.5947 (6)	5.9 (2)

Table 2. *Selected geometric parameters* (Å, °)

Cl1—C14	1.733 (6)	Cl2—C34	1.720 (7)
P1—O11	1.425 (4)	P2—O21	1.417 (6)
P1—O12	1.558 (5)	P2—O22	1.602 (6)
P1—O13	1.561 (5)	P2—O23	1.522 (5)
P1—C1	1.806 (6)	P2—C5	1.805 (6)
N1—C1	1.448 (8)	N2—C5	1.432 (8)
N1—C2	1.446 (9)	N2—C6	1.434 (8)
O12—C3	1.430 (9)	O22—C7	1.384 (9)
O13—C4	1.394 (8)	O23—C8	1.420 (8)
C11—C1	1.507 (8)	C31—C5	1.506 (9)
C21—C2	1.49 (1)	C41—C6	1.465 (9)
O11—P1—O12	116.1 (3)	O21—P2—O22	119.3 (3)
O11—P1—O13	114.6 (2)	O21—P2—O23	115.5 (3)
O11—P1—C1	115.5 (3)	O21—P2—C5	115.2 (3)
O12—P1—O13	100.9 (2)	O22—P2—O23	97.8 (3)
O12—P1—C1	102.5 (2)	O22—P2—C5	104.1 (3)
O13—P1—C1	105.5 (3)	O23—P2—C5	102.3 (3)
C1—N1—C2	113.8 (4)	C5—N2—C6	113.6 (5)
P1—O12—C3	120.1 (4)	P2—O22—C7	122.7 (6)
P1—O13—C4	123.6 (4)	P2—O23—C8	118.7 (5)
C12—C11—C1	120.8 (5)	C32—C31—C5	122.5 (6)
C16—C11—C1	121.1 (5)	C36—C31—C5	120.8 (6)
Cl1—C14—C13	118.5 (5)	Cl2—C34—C33	119.4 (6)
Cl1—C14—C15	119.7 (5)	Cl2—C34—C35	121.5 (5)
C22—C21—C2	121.4 (6)	C42—C41—C6	121.1 (6)
C26—C21—C2	121.1 (6)	C46—C41—C6	121.2 (5)
P1—C1—N1	104.6 (3)	P2—C5—N2	103.6 (4)
P1—C1—C11	112.4 (4)	P2—C5—C31	112.0 (5)
N1—C1—C11	118.5 (5)	N2—C5—C31	117.2 (5)
N1—C2—C21	113.1 (5)	N2—C6—C41	112.7 (5)

The structure was solved by direct methods and refined by full-matrix least-squares calculation on F, with anisotropic displacement parameters for non-H atoms and fixed isotropic displacement parameters for H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *MolEN* (Fair, 1990). Data reduction: *MolEN*. Program(s) used to solve structure: *MolEN*; *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *MolEN*.

This work was supported by the Key Discipline Fund of Tianjin Higher Education, People's Republic of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1259). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,3,5-Tricyanobenzene

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Abstract

The crystal of the title compound (1,3,5-benzenetricarbonitrile, $C_9H_3N_3$) consists of C—H···N hydrogen-bonded helices which when projected down the helix axis result in a quasi-hexagonal network.