Crystal structure of *N*,*N*-dimethylphosphoramidochloridic acid 4-methylphenyl ester, $ClP(O)[N(CH_3)_2][OC_6H_4(CH_3)]$

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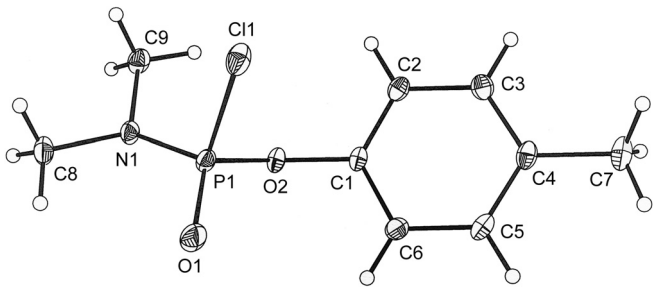

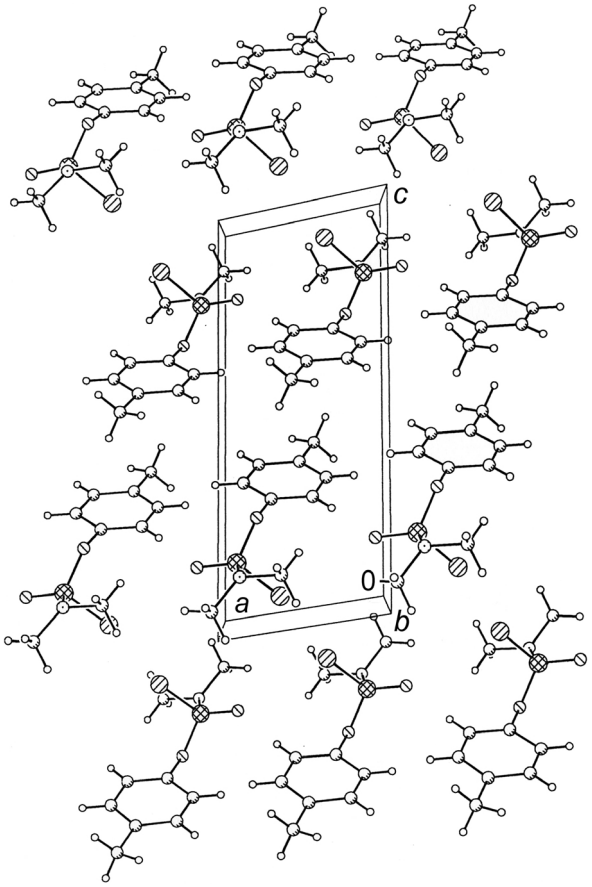

Abstract

$C_9H_{13}ClNO_2P$, triclinic, $P\bar{1}$ (no. 2), a = 6.056(1) Å, b = 6.858(1) Å, c = 14.370(3) Å, α = 98.111(5)°, β = 97.798(5)°, γ = 105.440(5)°, V = 560.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.032, $wR_{ref}(F^2)$ = 0.082, T = 100 K.

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Source of material

N,*N*-dimethylamine hydrochloride (16.3 g, 0.2 mol) and pyridine (31.6 g, 0.4 mol) was added to a solution of (4-tolyl)-dichlorophosphate (45.0 g, 0.2 mol) in 70 ml dry benzene at 0 °C. After 12 h stirring, the solvent was evaporated in vacuum. The flash gradient chromatography method was used for the purification of the product (silicagel, *n*-hexane/ethyl acetate 9:1). Single crystals of the product were obtained from a solution in CH_3CN after a slow evaporation at room temperature.

Discussion

Although a number of organic phosphorus (OP) compounds were synthesized in the 1800s, their development as insecticides only occurred in the late 1930s and early 1940s. Gerhard Schrader is credited for the discovery of the general chemical structure of anticholinestrase OP compounds [1]. Phosphoramidates are one class of OP compounds. Their extensive application in different areas such as medicine (treatment of cancer, AIDS and Alzheimer), agriculture (insecticides, herbicides and fungicides), industry (stabilizers, oxidants) and other interesting scientific fields has resulted in a lot of attention begin paid to their chemical properties [2-4].

In the title crystal structure, the four different groups linked to P atom make a distorted tetrahedral configuration (figure, top). The bond angles around P atom are in the range of 101.71(7)° (∠O2–P1–N1) to 117.24(7)° (∠O1–P1–O2). The oxygen atom (of 4-CH_3–C_6H_4–O moiety) has sp^2 character (∠C1–O2–P1 = 122.3(1)°). The P1—O2 bond length (1.581(1) Å) is smaller than the P—O single bond length (1.64 Å [3]). Also, the P—N bond length (1.621(1) Å) is shorter than the P—N single bond length (1.77 Å [3]). The C8–C9–P1–N1 torsion angle is 18.6° which indicates that the nitrogen atom is deviated from the plane defined by the respective atoms. Furthermore, the sum of the surrounding angles around N atom is 352.1° which is less than that of the sp^2 angle. Besides the Cl···Cl electrostatic interaction, there are bifurcated weak hydrogen bonds in the crystal structure resulting in a layered packing parallel (001) (figure, bottom). Each molecule in network is surrounded by five neighboring molecules via these two types of interactions.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.20 × 0.30 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.59 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX II CCD, φ/ω
$2\theta_{max}$:	54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5532, 2372
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2076
$N(param)_{refined}$:	130
Program:	SHELXTL [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	2*i*	0.3399	0.2018	0.2678	0.022
H(3A)	2*i*	0.2045	–0.1007	0.3279	0.024
H(5A)	2*i*	0.8681	–0.0863	0.4251	0.026
H(6A)	2*i*	1.0060	0.2184	0.3671	0.024
H(7A)	2*i*	0.3166	–0.4213	0.3715	0.041
H(7B)	2*i*	0.3664	–0.2896	0.4772	0.041
H(7C)	2*i*	0.5652	–0.3745	0.4386	0.041

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(8A)	2*i*	1.0261	0.9024	0.1163	0.040
H(8B)	2*i*	0.9267	0.7033	0.0331	0.040
H(8C)	2*i*	1.1511	0.7239	0.1110	0.040
H(9A)	2*i*	0.6419	0.8344	0.1739	0.032
H(9B)	2*i*	0.5267	0.6073	0.1918	0.032
H(9C)	2*i*	0.5427	0.6463	0.0854	0.032

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	2*i*	0.63440(8)	0.20255(6)	0.08801(3)	0.0396(3)	0.0171(2)	0.0176(2)	0.0059(2)	0.0031(2)	0.0031(1)
P(1)	2*i*	0.87282(7)	0.43169(6)	0.18602(3)	0.0189(2)	0.0165(2)	0.0177(2)	0.0080(2)	0.0046(2)	0.0073(2)
O(1)	2*i*	1.1024(2)	0.4004(2)	0.19026(9)	0.0251(7)	0.0359(7)	0.0369(7)	0.0180(6)	0.0113(5)	0.0201(6)
O(2)	2*i*	0.7617(2)	0.4207(2)	0.27927(8)	0.0256(6)	0.0139(5)	0.0172(5)	0.0069(5)	0.0057(4)	0.0059(4)
N(1)	2*i*	0.8496(2)	0.6497(2)	0.1614(1)	0.0191(7)	0.0151(6)	0.0219(7)	0.0063(5)	0.0055(5)	0.0083(5)
C(1)	2*i*	0.6834(3)	0.2342(2)	0.3127(1)	0.0234(8)	0.0133(7)	0.0145(7)	0.0062(6)	0.0049(6)	0.0048(5)
C(2)	2*i*	0.4466(3)	0.1433(2)	0.3001(1)	0.0233(8)	0.0177(8)	0.0181(7)	0.0106(7)	0.0051(6)	0.0048(6)
C(3)	2*i*	0.3673(3)	–0.0367(3)	0.3358(1)	0.0216(8)	0.0192(8)	0.0206(8)	0.0054(7)	0.0070(6)	0.0039(6)
C(4)	2*i*	0.5220(3)	–0.1244(2)	0.3829(1)	0.0310(9)	0.0161(7)	0.0152(7)	0.0083(7)	0.0073(6)	0.0040(6)
C(5)	2*i*	0.7603(3)	–0.0278(3)	0.3936(1)	0.0291(9)	0.0213(8)	0.0186(8)	0.0123(7)	0.0032(6)	0.0078(6)
C(6)	2*i*	0.8435(3)	0.1529(3)	0.3590(1)	0.0193(8)	0.0229(8)	0.0195(8)	0.0076(7)	0.0027(6)	0.0063(6)
C(7)	2*i*	0.4349(4)	–0.3195(3)	0.4209(1)	0.042(1)	0.0188(8)	0.0235(9)	0.0090(8)	0.0101(7)	0.0085(7)
C(8)	2*i*	1.0010(3)	0.7535(3)	0.1004(1)	0.0258(9)	0.0280(9)	0.0313(9)	0.0075(7)	0.0103(7)	0.0178(7)
C(9)	2*i*	0.6213(3)	0.6876(3)	0.1524(1)	0.0239(9)	0.0208(8)	0.0247(8)	0.0119(7)	0.0067(6)	0.0087(6)

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