Refinement of the crystal structure of *N*-4-nitrophenylphosphoramidic acid dimethyl ester, $(CH_3O)_2PONHC_6H_4NO_2$, *at 120 K*

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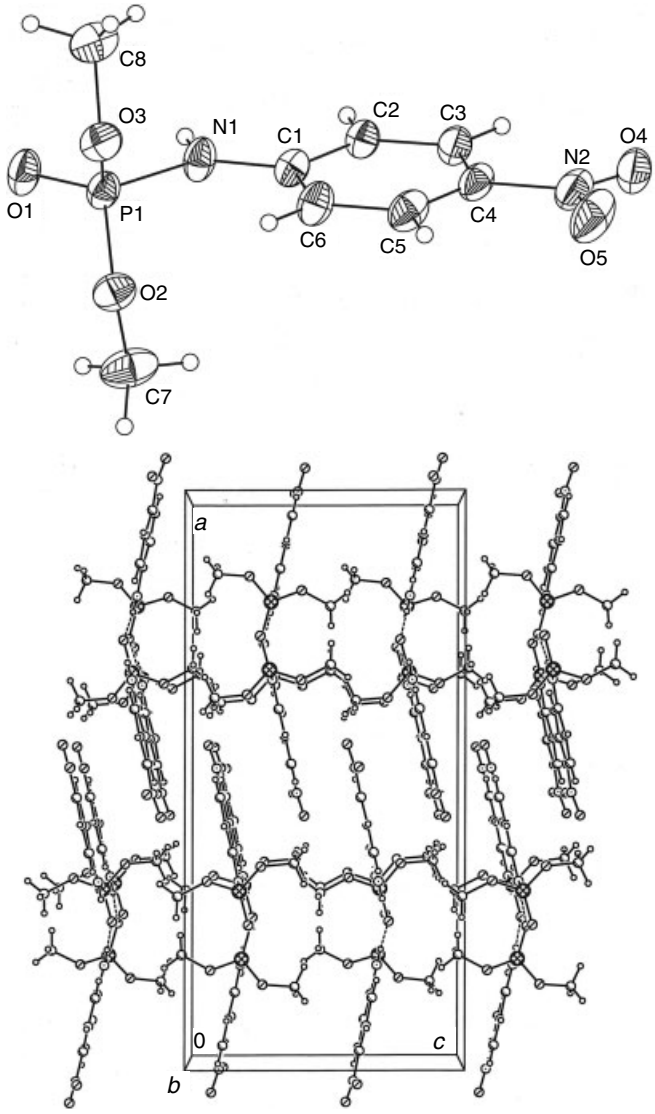
Received November 8, 2004, accepted and available on-line January 5, 2005; CCDC no. 1267/1426



Abstract

$C_8H_{11}N_2O_5P$, orthorhombic, *Pbcn* (no. 60), $a = 24.714(5)$ Å, $b = 7.330(1)$ Å, $c = 11.980(2)$ Å, $V = 2170.3$ Å^3, $Z = 8$, $R_{gt}(F) = 0.054$, $wR_{ref}(F^2) = 0.128$, $T = 120$ K.

Source of material

The title compound was synthesized according to a well-established method [1,2]. Crystals were obtained from a mixture of *n*-heptane and methanol after slow evaporation at room temperature.

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Elemental analysis: found – C, 38.95 %; H, 4.46 %; N, 11.41 %; calc. for $C_8H_{11}N_2O_5P$ – C, 39.03 %; H, 4.50 %; N, 11.38 %.

Discussion

Phosphoramidic acid esters have attracted attention due to their synthetic and biological applications [3,4]. So far, the structures have been determined only for a few molecules of this series [5]. Here, we report the crystal structure of *N*-4-nitrophenyl phosphoramidic acid dimethyl ester at 120 K which confirms the result at 283 K – 303 K [1]. Methoxy groups in this structure (figure, top) have *syn* orientation to each other. Molecule is obtained as polymeric chain produced by –P=O···H–N– hydrogen bond (figure, bottom). Furthermore, there are C2–H2A···O1′ and C7–H7A···O4′ weak hydrogen bonds in the crystal with d(C2···O1′) = 3.352 Å, ∠C2–H2A···O1′ = 135.9° and d(C7···O4′) = 3.302 Å, ∠C7–H7A···O4′ = 133.6°, respectively. Another feature of the structure is the electrostatic interaction between N2–O4 in one molecule with O4′–N2′ in neighboring molecule (two equivalent N2···O4 interactions with distances that are equal to 2.966 Å).

The P1—O2 and P1—O3 bond lengths are 1.563(2) Å and 1.571(2) Å, respectively, which are smaller than the P—O single bond length (1.64 Å [6]). The bond angles C7–O2–P1 and C8–O3–P1 are 120.1(1)° and 121.0(1)°, respectively, corresponding to sp^2 hybridization bond angles. Also, the P—N bond length (1.639(2) Å) is shorter than the P—N single bond length (1.77 Å [6]) and the nitrogen atom is nearly planar. The deviation from planarity can be supported by the torsion angle H1N–P1–C1–N1 being about 0.4°. The sum of the angles around nitrogen atom is 360.0°. The angles C1–N1–H1N and P1–N1–C1 are 122.8° and 128.9°, respectively and the angle P1–N1–H1N is smaller (108.4°). The phosphorus atom has a distorted tetrahedral coordination. The surrounding angles of P1 are in the range of 96.5° – 116.9°. The minimum and maximum values of angles are observed for angles O2–P1–O3 and O1–P1–O2, respectively.

Table 1. Data collection and handling.

Crystal:	light yellow prism, size 0.20 × 0.28 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.62 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	16467, 3153
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2254
$N(param)_{refined}$:	147
Program:	SHELXTL [7]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1N)	8*d*	0.2972	–0.0632	0.2031	0.056
H(2A)	8*d*	0.3466	–0.3442	0.1856	0.034
H(3A)	8*d*	0.4267	–0.4956	0.1490	0.039
H(5A)	8*d*	0.5022	–0.0142	0.1075	0.042
H(6A)	8*d*	0.4215	0.1385	0.1421	0.040
H(7A)	8*d*	0.3830	0.3398	0.4279	0.070
H(7B)	8*d*	0.3741	0.1352	0.3944	0.070
H(7C)	8*d*	0.3243	0.2584	0.4247	0.070
H(8A)	8*d*	0.3253	0.3107	–0.0787	0.069
H(8B)	8*d*	0.2686	0.3250	–0.0205	0.069
H(8C)	8*d*	0.2991	0.1375	–0.0243	0.069

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}
P(1)	8*d*	0.31166(2)	0.21461(7)	0.19758(5)	0.0215(2)	0.0241(2)	0.0372(3)	–0.0000(2)	–0.0024(2)	0.0012(2)
O(1)	8*d*	0.25467(5)	0.2336(2)	0.2297(1)	0.0211(6)	0.0307(7)	0.0542(9)	0.0038(5)	0.0005(6)	0.0007(7)
O(2)	8*d*	0.35437(6)	0.3094(2)	0.2744(1)	0.0289(7)	0.0341(7)	0.0350(8)	–0.0072(6)	–0.0034(6)	0.0021(6)
O(3)	8*d*	0.32954(6)	0.3097(2)	0.0860(1)	0.0351(7)	0.0313(7)	0.0349(8)	–0.0033(6)	–0.0046(6)	0.0032(6)
O(4)	8*d*	0.52296(7)	–0.5309(3)	0.1162(1)	0.0455(9)	0.060(1)	0.0397(9)	0.0275(8)	–0.0042(7)	–0.0057(8)
O(5)	8*d*	0.56206(6)	–0.2734(3)	0.0769(2)	0.0271(8)	0.090(1)	0.043(1)	0.0152(8)	0.0096(7)	0.0139(9)
N(1)	8*d*	0.32587(6)	–0.0034(2)	0.1900(2)	0.0196(7)	0.0243(7)	0.049(1)	–0.0001(6)	0.0010(7)	0.0029(7)
N(2)	8*d*	0.52200(7)	–0.3637(3)	0.1041(2)	0.0311(9)	0.068(1)	0.0263(9)	0.0180(9)	–0.0004(7)	0.0002(9)
C(1)	8*d*	0.37564(7)	–0.0875(3)	0.1677(2)	0.0225(8)	0.0311(9)	0.031(1)	0.0020(7)	–0.0008(7)	0.0026(8)
C(2)	8*d*	0.37775(7)	–0.2779(3)	0.1697(2)	0.0233(8)	0.0294(9)	0.032(1)	0.0017(7)	0.0005(7)	0.0015(8)
C(3)	8*d*	0.42544(8)	–0.3688(3)	0.1482(2)	0.0297(9)	0.037(1)	0.031(1)	0.0085(8)	–0.0013(8)	–0.0001(8)
C(4)	8*d*	0.47160(8)	–0.2667(3)	0.1253(2)	0.0250(9)	0.052(1)	0.0224(9)	0.0113(8)	0.0012(7)	0.0017(8)
C(5)	8*d*	0.47079(8)	–0.0794(3)	0.1230(2)	0.0230(9)	0.048(1)	0.033(1)	–0.0001(8)	0.0027(8)	0.0062(9)
C(6)	8*d*	0.42256(7)	0.0117(3)	0.1439(2)	0.0240(8)	0.034(1)	0.041(1)	0.0007(8)	0.0027(8)	0.0071(9)
C(7)	8*d*	0.3594(1)	0.2562(4)	0.3901(2)	0.037(1)	0.071(2)	0.034(1)	–0.018(1)	–0.004(1)	0.006(1)
C(8)	8*d*	0.3035(1)	0.2672(4)	–0.0180(2)	0.044(1)	0.054(1)	0.041(1)	–0.002(1)	–0.009(1)	–0.000(1)

Acknowledgments. Support of this investigation by Tarbiat Modarres University is gratefully acknowledged. We thank the Institute of Organoelement Compounds of the Russian Academy of Science for determining the crystal structure.

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