Refinement of the crystal structure of *N*-4-nitrophenylphosphoramidic acid dimethyl ester, $(\text{CH}_3\text{O})_2\text{PONHCH}_6\text{H}_4\text{NO}_2$, at 120 K

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Elemental analysis: found – C, 38.95 %; H, 4.46 %; N, 11.41 %; calc. for $\text{C}_8\text{H}_{11}\text{N}_2\text{O}_5\text{P}$ – 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 $-\text{P}=\text{O} \cdots \text{H}-\text{N}-$ hydrogen bond (figure, bottom). Furthermore, there are $\text{C}2-\text{H}2\text{A} \cdots \text{O}1'$ and $\text{C}7-\text{H}7\text{A} \cdots \text{O}4'$ weak hydrogen bonds in the crystal with $d(\text{C}2 \cdots \text{O}1') = 3.352 \text{ \AA}$, $\angle \text{C}2-\text{H}2\text{A} \cdots \text{O}1' = 135.9^\circ$ and $d(\text{C}7 \cdots \text{O}4') = 3.302 \text{ \AA}$, $\angle \text{C}7-\text{H}7\text{A} \cdots \text{O}4' = 133.6^\circ$, respectively. Another feature of the structure is the electrostatic interaction between $\text{N}2-\text{O}4$ in one molecule with $\text{O}4'-\text{N}2'$ in neighboring molecule (two equivalent $\text{N}2 \cdots \text{O}4$ interactions with distances that are equal to $2.966 \text{ \AA}$).

The $\text{P}1-\text{O}2$ and $\text{P}1-\text{O}3$ bond lengths are $1.563(2) \text{ \AA}$ and $1.571(2) \text{ \AA}$, respectively, which are smaller than the $\text{P}-\text{O}$ single bond length ($1.64 \text{ \AA}$ [6]). The bond angles $\text{C}7-\text{O}2-\text{P}1$ and $\text{C}8-\text{O}3-\text{P}1$ are $120.1(1)^\circ$ and $121.0(1)^\circ$, respectively, corresponding to sp^2 hybridization bond angles. Also, the $\text{P}-\text{N}$ bond length ($1.639(2) \text{ \AA}$) is shorter than the $\text{P}-\text{N}$ single bond length ($1.77 \text{ \AA}$ [6]) and the nitrogen atom is nearly planar. The deviation from planarity can be supported by the torsion angle $\text{H}1\text{N}-\text{P}1-\text{C}1-\text{N}1$ being about 0.4° . The sum of the angles around nitrogen atom is 360.0° . The angles $\text{C}1-\text{N}1-\text{H}1\text{N}$ and $\text{P}1-\text{N}1-\text{C}1$ are 122.8° and 128.9° , respectively and the angle $\text{P}1-\text{N}1-\text{H}1\text{N}$ is smaller (108.4°). The phosphorus atom has a distorted tetrahedral coordination. The surrounding angles of $\text{P}1$ are in the range of $96.5^\circ - 116.9^\circ$. The minimum and maximum values of angles are observed for angles $\text{O}2-\text{P}1-\text{O}3$ and $\text{O}1-\text{P}1-\text{O}2$, respectively.

Table 1. Data collection and handling.

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

Abstract

$\text{C}_8\text{H}_{11}\text{N}_2\text{O}_5\text{P}$, orthorhombic, *Pbcn* (no. 60), $a = 24.714(5) \text{ \AA}$, $b = 7.330(1) \text{ \AA}$, $c = 11.980(2) \text{ \AA}$, $V = 2170.3 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.054$, $wR_{\text{ref}}(F^2) = 0.128$, $T = 120 \text{ K}$.

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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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1N)	8d	0.2972	−0.0632	0.2031	0.056
H(2A)	8d	0.3466	−0.3442	0.1856	0.034
H(3A)	8d	0.4267	−0.4956	0.1490	0.039
H(5A)	8d	0.5022	−0.0142	0.1075	0.042
H(6A)	8d	0.4215	0.1385	0.1421	0.040
H(7A)	8d	0.3830	0.3398	0.4279	0.070

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(7B)	8d	0.3741	0.1352	0.3944	0.070
H(7C)	8d	0.3243	0.2584	0.4247	0.070
H(8A)	8d	0.3253	0.3107	−0.0787	0.069
H(8B)	8d	0.2686	0.3250	−0.0205	0.069
H(8C)	8d	0.2991	0.1375	−0.0243	0.069

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
P(1)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)	8d	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)

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