Crystal structure of *N*,*N*′,*N*′′-tris(2-pyridinyl)phosphoric triamide, $(NC_5H_4NH)_3PO$

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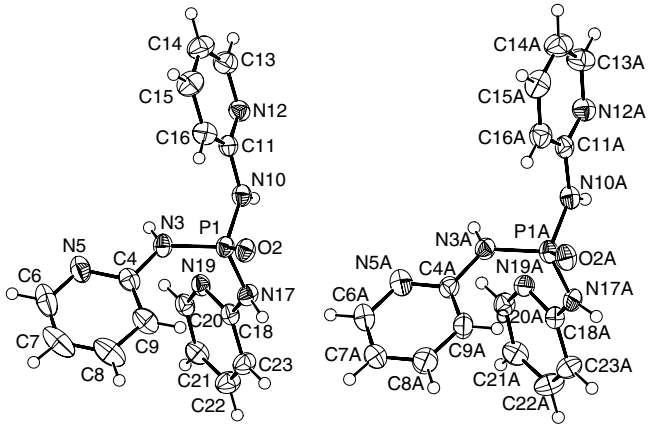

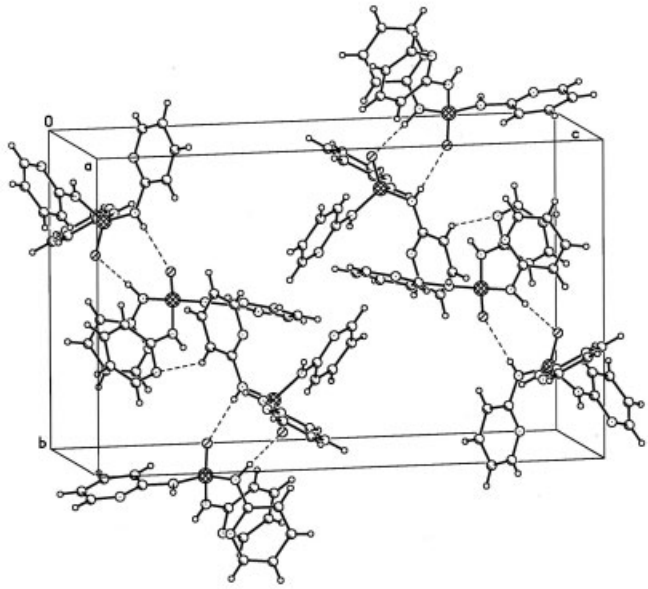

Abstract

$C_{15}H_{15}N_6OP$, monoclinic, $P12_1/n1$ (no. 14),
$a = 10.558(2)$ Å, $b = 13.448(2)$ Å, $c = 21.814(4)$ Å,
$\beta = 92.314(4)°$, $V = 3094.6$ Å^3, $Z = 8$,
$R_{gt}(F) = 0.051$, $wR_{ref}(F^2) = 0.101$, $T = 120$ K.

Source of material

The title compound was synthesized by the reaction of phosphoryl chloride (1 mmol) with 2-amino pyridine (6 mmol) in dry benzene (4 hours stirring at 343 K). The residue was washed with H_2O. The crystals of the product were obtained from a mixture of *n*-heptane, methanol and chloroform after slow evaporation at room temperature. Elemental analysis: found – C, 55.15 %; H, 4.64 %; N, 25.72 %; calc. for $C_{15}H_{15}N_6OP$ – C, 55.21 %; H, 4.63 %; N, 25.76 %.

Discussion

Of the numerous known phosphoric triamides with formula $OP[N(H)R]_3$, structures have been determined only for R = H, *m*-tol, *p*-tol, methyl and *tert*-butyl [1]. Here we report the 2-pyridinyl substituted compound $OP[N(H)C_5H_4N]_3$. The crystal structure of this compound consists of two symmetrically independent molecules (figure, top). All of the P—N bond lengths are in the region of 1.64 Å - 1.65 Å. They are significantly shorter than the typical P—N single bond length (1.77 Å) due to the conjugation of nitrogen lone pair with phosphoryl group [2]. The environments of the nitrogen atoms are practically planar. The sums of the surrounding angles for N(3), N(10) and N(17) are 358.6°, 358.0° and 354.4°, respectively. Similar results were obtained for three other nitrogen atoms N(3A), N(10A) and N(17A). The length of the P=O bond is directly caused to the nature of the substituents next to phosphorus atom. Therefore, the P(1)—O(2) and P(1A)—O(2A) bond lengths of the title compound are similar to values of previously synthesized phosphoric triamides [3]: 1.473(2) Å and 1.471(2) Å, respectively.

The phosphorus atoms P(1) and P(1A) have slightly distorted tetrahedral configuration. The bond angles around P(1) are in the range of 115.5° - 102.8°. The maximum and minimum values of angles are observed for ∠O(2)–P(1)–N(10) and ∠N(3)–P(1)–N(10), respectively. In the other molecule, they are in the region of 115.1° and 103.5° for the angles of ∠O(2A)–P(1A)–N(3A) and ∠N(3A)–P(1A)–N(10A). In this structure, molecules are connected by six different kinds of intermolecular hydrogen bonds and they exist in the polymeric chains in crystalline lattice produced by hydrogen bonding between the amino protons with pyridinic nitrogen and phosphorilic oxygen atoms (figure, bottom).

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.3 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.92 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	21118, 5845
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4355
$N(param)_{refined}$:	421
Programs:	SADABS [4], SHELXTL [5]

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

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.5394	0.8027	0.7591	0.039
H(3A)	4*e*	0.7457	0.6874	0.4316	0.035
H(6)	4*e*	0.8038	0.6616	0.6473	0.070
H(6A)	4*e*	0.5304	0.5452	0.5707	0.062
H(7A)	4*e*	0.3631	0.6515	0.5858	0.064
H(7)	4*e*	0.8211	0.7577	0.5616	0.076
H(8)	4*e*	0.7047	0.9041	0.5534	0.069
H(8A)	4*e*	0.3380	0.7881	0.5240	0.069
H(9A)	4*e*	0.4868	0.8254	0.4525	0.049
H(9)	4*e*	0.5772	0.9496	0.6333	0.054
H(10)	4*e*	0.3224	0.9092	0.8197	0.037
H(10A)	4*e*	0.8213	0.7701	0.3098	0.032
H(13)	4*e*	0.4443	0.8656	1.0054	0.048
H(13A)	4*e*	1.2186	0.8163	0.3256	0.051
H(14)	4*e*	0.6586	0.8896	1.0144	0.055

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(14A)	4*e*	1.2599	0.8997	0.4157	0.056
H(15A)	4*e*	1.0912	0.9356	0.4784	0.053
H(15)	4*e*	0.7636	0.9414	0.9284	0.055
H(16)	4*e*	0.6495	0.9684	0.8367	0.044
H(16A)	4*e*	0.8873	0.8890	0.4463	0.046
H(17)	4*e*	0.3328	0.9911	0.6722	0.026
H(17A)	4*e*	0.5318	0.8208	0.3095	0.027
H(20)	4*e*	0.2001	0.6447	0.7204	0.037
H(20A)	4*e*	0.6410	0.4622	0.3203	0.039
H(21)	4*e*	0.0690	0.6467	0.6347	0.043
H(21A)	4*e*	0.4505	0.4222	0.2714	0.047
H(22)	4*e*	0.0560	0.7913	0.5759	0.049
H(22A)	4*e*	0.3151	0.5514	0.2419	0.053
H(23A)	4*e*	0.3702	0.7135	0.2655	0.045
H(23)	4*e*	0.1802	0.9267	0.6046	0.044

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)	4*e*	0.45919(6)	0.94907(4)	0.74559(3)	0.0300(3)	0.0210(3)	0.0318(3)	0.0004(2)	0.0009(2)	–0.0002(2)
P(1A)	4*e*	0.68298(6)	0.80953(4)	0.37618(3)	0.0350(3)	0.0232(3)	0.0290(3)	–0.0001(3)	0.0025(2)	0.0026(2)
O(2)	4*e*	0.5245(2)	1.0442(1)	0.73583(8)	0.0350(9)	0.0241(9)	0.040(1)	–0.0001(7)	0.0001(7)	0.0008(7)
O(2A)	4*e*	0.6591(2)	0.9124(1)	0.39567(8)	0.046(1)	0.0249(9)	0.037(1)	0.0005(8)	0.0058(8)	0.0014(7)
N(3)	4*e*	0.5485(2)	0.8507(2)	0.7365(1)	0.033(1)	0.022(1)	0.038(1)	0.0003(8)	0.0035(9)	0.0012(9)
N(3A)	4*e*	0.6910(2)	0.7274(2)	0.43174(9)	0.031(1)	0.028(1)	0.032(1)	0.0050(9)	0.0015(8)	0.0037(8)
C(4A)	4*e*	0.5949(2)	0.7056(2)	0.4718(1)	0.033(1)	0.034(1)	0.025(1)	–0.003(1)	–0.0024(9)	0.001(1)
C(4)	4*e*	0.6209(2)	0.8294(2)	0.6862(1)	0.029(1)	0.030(1)	0.038(1)	–0.006(1)	0.001(1)	–0.010(1)
N(5)	4*e*	0.6852(2)	0.7445(2)	0.6911(1)	0.033(1)	0.038(1)	0.052(2)	0.003(1)	–0.001(1)	–0.016(1)
N(5A)	4*e*	0.6092(2)	0.6228(2)	0.5050(1)	0.048(1)	0.047(1)	0.042(1)	–0.001(1)	0.005(1)	0.010(1)
C(6)	4*e*	0.7578(3)	0.7205(3)	0.6444(2)	0.039(2)	0.057(2)	0.079(2)	0.008(1)	0.005(2)	–0.031(2)
C(6A)	4*e*	0.5219(3)	0.6026(3)	0.5471(1)	0.049(2)	0.061(2)	0.044(2)	–0.002(2)	0.006(1)	0.022(2)
C(7A)	4*e*	0.4208(3)	0.6651(3)	0.5558(1)	0.039(2)	0.081(2)	0.042(2)	0.001(2)	0.009(1)	0.020(2)
C(7)	4*e*	0.7687(3)	0.7774(3)	0.5927(2)	0.056(2)	0.078(3)	0.058(2)	–0.019(2)	0.022(2)	–0.035(2)
C(8)	4*e*	0.7002(3)	0.8642(3)	0.5880(2)	0.062(2)	0.062(2)	0.050(2)	–0.022(2)	0.021(2)	–0.018(2)
C(8A)	4*e*	0.4075(3)	0.7466(3)	0.5197(2)	0.044(2)	0.080(2)	0.049(2)	0.015(2)	0.010(1)	0.016(2)
C(9A)	4*e*	0.4952(2)	0.7690(2)	0.4770(1)	0.044(2)	0.045(2)	0.033(1)	0.009(1)	0.007(1)	0.012(1)
C(9)	4*e*	0.6245(3)	0.8913(2)	0.6354(1)	0.051(2)	0.041(2)	0.043(2)	–0.009(1)	0.012(1)	–0.007(1)
N(10)	4*e*	0.4055(2)	0.9324(2)	0.81497(9)	0.029(1)	0.026(1)	0.035(1)	0.0001(8)	0.0011(8)	–0.0014(9)
N(10A)	4*e*	0.8198(2)	0.7967(1)	0.34315(9)	0.037(1)	0.025(1)	0.027(1)	–0.0037(8)	0.0013(8)	–0.0012(9)
C(11A)	4*e*	0.9383(2)	0.8262(2)	0.3665(1)	0.036(1)	0.020(1)	0.034(1)	–0.000(1)	0.001(1)	0.006(1)
C(11)	4*e*	0.4798(2)	0.9252(2)	0.8691(1)	0.037(1)	0.020(1)	0.032(1)	0.001(1)	0.000(1)	–0.002(1)
N(12A)	4*e*	1.0345(2)	0.8037(2)	0.3311(1)	0.036(1)	0.027(1)	0.041(1)	–0.0028(9)	0.0010(9)	–0.0013(9)
N(12)	4*e*	0.4186(2)	0.8970(2)	0.91845(9)	0.038(1)	0.028(1)	0.031(1)	–0.0012(9)	0.0021(9)	–0.0017(9)
C(13)	4*e*	0.4868(3)	0.8852(2)	0.9709(1)	0.053(2)	0.033(1)	0.034(2)	–0.003(1)	0.002(1)	0.002(1)
C(13A)	4*e*	1.1514(2)	0.8315(2)	0.3503(1)	0.033(1)	0.036(2)	0.059(2)	–0.003(1)	0.002(1)	–0.004(1)
C(14)	4*e*	0.6149(3)	0.8999(2)	0.9771(1)	0.050(2)	0.042(2)	0.043(2)	–0.005(1)	–0.013(1)	0.003(1)
C(14A)	4*e*	1.1774(3)	0.8811(2)	0.4042(2)	0.039(2)	0.039(2)	0.062(2)	–0.007(1)	–0.009(1)	–0.003(1)
C(15A)	4*e*	1.0770(3)	0.9028(2)	0.4412(1)	0.057(2)	0.031(1)	0.045(2)	–0.005(1)	–0.011(1)	–0.005(1)
C(15)	4*e*	0.6765(3)	0.9306(2)	0.9259(1)	0.037(1)	0.048(2)	0.051(2)	–0.006(1)	–0.007(1)	0.002(1)
C(16)	4*e*	0.6095(2)	0.9455(2)	0.8712(1)	0.038(1)	0.034(1)	0.037(2)	–0.008(1)	0.002(1)	–0.000(1)
C(16A)	4*e*	0.9559(3)	0.8751(2)	0.4223(1)	0.044(2)	0.032(1)	0.038(2)	–0.003(1)	–0.000(1)	0.002(1)
N(17)	4*e*	0.3323(2)	0.9444(2)	0.69884(9)	0.037(1)	0.021(1)	0.035(1)	–0.0021(8)	–0.0007(9)	0.0037(9)
N(17A)	4*e*	0.5735(2)	0.7756(2)	0.32465(9)	0.034(1)	0.026(1)	0.034(1)	0.0047(9)	–0.0004(9)	0.0075(9)
C(18)	4*e*	0.2603(2)	0.8618(2)	0.6811(1)	0.031(1)	0.024(1)	0.031(1)	0.001(1)	0.004(1)	–0.003(1)
C(18A)	4*e*	0.5404(2)	0.6794(2)	0.3076(1)	0.033(1)	0.027(1)	0.026(1)	0.002(1)	0.0021(9)	0.001(1)
N(19A)	4*e*	0.6224(2)	0.6067(2)	0.32173(9)	0.030(1)	0.027(1)	0.033(1)	0.0007(8)	0.0008(8)	0.0024(8)
N(19)	4*e*	0.2677(2)	0.7802(1)	0.71530(9)	0.033(1)	0.024(1)	0.032(1)	0.0018(8)	0.0046(8)	–0.0007(8)
C(20)	4*e*	0.1958(2)	0.7023(2)	0.6968(1)	0.037(1)	0.025(1)	0.033(1)	0.000(1)	0.009(1)	–0.000(1)
C(20A)	4*e*	0.5859(2)	0.5135(2)	0.3087(1)	0.036(1)	0.025(1)	0.036(1)	0.002(1)	0.002(1)	0.002(1)
C(21)	4*e*	0.1166(2)	0.7025(2)	0.6457(1)	0.039(1)	0.031(1)	0.037(1)	–0.009(1)	0.005(1)	–0.006(1)
C(21A)	4*e*	0.4720(2)	0.4881(2)	0.2794(1)	0.041(1)	0.032(1)	0.045(2)	–0.006(1)	0.004(1)	–0.007(1)
C(22)	4*e*	0.1097(3)	0.7882(2)	0.6108(1)	0.043(2)	0.040(2)	0.039(2)	–0.003(1)	–0.007(1)	0.000(1)
C(22A)	4*e*	0.3918(3)	0.5649(2)	0.2627(1)	0.035(1)	0.047(2)	0.051(2)	0.002(1)	–0.010(1)	–0.012(1)
C(23A)	4*e*	0.4242(2)	0.6613(2)	0.2765(1)	0.034(1)	0.037(1)	0.042(2)	0.008(1)	–0.003(1)	–0.003(1)
C(23)	4*e*	0.1825(2)	0.8687(2)	0.6279(1)	0.043(1)	0.029(1)	0.037(1)	–0.001(1)	–0.004(1)	0.005(1)

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