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Crystal Structure of *N*-Benzoyl-*N′*,*N″*-bis(pyrrolidinyl) phosphoric triamide

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The crystal structure of *N*-benzoyl-*N′*,*N″*-bis(pyrrolidinyl)phosphoric triamide has been determined. The P–N bond lengths are significantly shorter than the P–N single bond, and the nitrogen atoms are relatively planar. The molecule is obtained in the form of a dimmeric aggregate via two (symmetry independent) hydrogen bonds, which constitutes an asymmetric unit and two crystallographically independent molecules that are present based on the conformational forms of pyrrolidinyl groups.

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Phosphoric triamides have found widespread use in organic and bio-chemistry.[1] The strong donor properties and Lewis basicity make them excellent ligands for small and hard metal ions. Some derivatives of these compounds are used in clinical practice as anticancer preparations.

We report here on results of the reaction of *N*-benzoyl phosphoramidic dichloride with pyrrolidine to form a phosphorus compound, *N*-benzoyl-*N′*,*N″*-bis(pyrrolidinyl)-phosphoric triamide. The investigated compound (Fig. 1) was synthesized according to a well-established method.[2] A single crystal of title compound was obtained from a solution of heptane and chloroform in the ratio (1:4) after slow evaporation at room temperature. The structure was obtained in the form of a dimmeric aggregate (Fig. 2). The crystal and experimental data are given in Table 1. The structure was solved by direct methods. The positions of the hydrogen atoms were obtained from a difference Fourier map. The atomic coordinates for non-hydrogen atoms are listed in Table 2. Selected bond lengths and angles are given in Table 3. The occupancy factors of disordered atoms C(9), C(9′), C(14), and C(14′) were refined by a least-squares method.

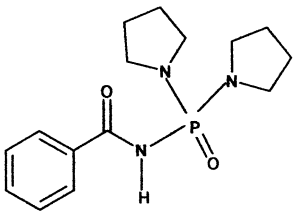

Fig. 1 Chemical structure.

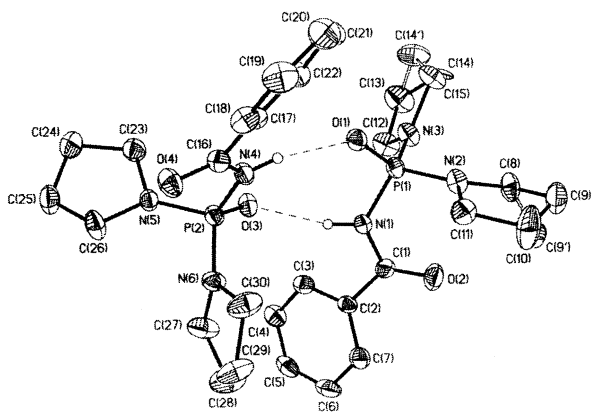

Fig. 2 Molecular structure of the title compound, showing the atom-labeling scheme and 50% probability level displacement ellipsoids.

The P(1)–N(1), P(1)–N(2) and P(1)–N(3) bond lengths are 1.679(4), 1.618(4) and 1.615(4)Å, respectively. They are significantly shorter than the typical P–N single bond length (1.77Å)[3]. The share of the partial multiple bond in P(1)–N(1) is less than that in P(1)–N(2) and P(1)–N(3) based on the conjugation of the nitrogen lone pair with a carbonyl group. Similar data were obtained for the P(2)–N(4), P(2)–N(5) and P(2)–N(6) bond lengths (see Table 3).

The angles C(8)–N(2)–P(1), C(11)–N(2)–P(1),

Table 1 Crystal data and structure refinement for *N*-benzoyl-*N′*,*N″*-bis(pyrrolidinyl)phosphoric triamide

Formula: $C_{15}H_{22}N_3O_2P$	
Formula weight = 307.33	
Crystal system: triclinic	
Space group: $P\bar{1}$	$Z = 4$
$a = 8.673(4)$Å	$\alpha = 101.857(10)^\circ$
$b = 12.576(5)$Å	$\beta = 90.515(10)^\circ$
$c = 16.179(7)$Å	$\gamma = 109.775(10)^\circ$
$V = 1619.3(12)$Å^3	
$D_x = 1.261$ Mg/m^3	
No. of reflections used = 11541	
$2\theta_{max} = 52.04$ with Mo K_α	
$R = 0.0794$	
$(\Delta/\sigma)_{max} = 0.000$	
$(\Delta/\rho)_{max} = 0.292$ eÅ^3	
$(\Delta/\rho)_{min} = -0.285$ eÅ^3	
Measurement: Bruker SMART 1000 CCD	
Program system: SADABS	
Structure determination: SHELXTL	
Refinement: full-matrix least-squares on F^2	

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Table 2 Fractional coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) of non hydrogen atoms.

Atom	x × 10^4	y × 10^4	z × 10^4	U(eq) × 10^3
P(1)	8542(2)	4608(1)	2554(1)	53(1)
P(2)	6636(2)	717(1)	2225(1)	56(1)
O(1)	7053(4)	3879(2)	2887(2)	65(1)
O(2)	12181(5)	4978(3)	2251(3)	103(1)
O(3)	7179(4)	1451(2)	1597(2)	65(1)
O(4)	4715(4)	61(3)	3701(2)	84(1)
N(1)	9554(5)	3729(3)	2130(2)	55(1)
N(2)	9650(5)	5678(3)	3296(2)	61(1)
N(3)	8270(5)	5189(3)	1789(2)	69(1)
N(4)	5896(4)	1480(3)	3002(2)	59(1)
N(5)	5267(5)	-518(3)	1781(2)	60(1)
N(6)	8034(5)	396(3)	2690(2)	67(1)
C(1)	11173(7)	4012(4)	1992(3)	66(1)
C(2)	11679(6)	3088(4)	1431(3)	54(1)
C(3)	10635(6)	2288(4)	775(3)	64(1)
C(4)	11175(8)	1513(4)	223(3)	76(2)
C(5)	12744(9)	1521(5)	333(4)	87(2)
C(6)	13781(7)	2282(5)	1010(4)	88(2)
C(7)	13264(7)	3080(4)	1550(3)	73(1)
C(8)	10817(7)	6811(4)	3185(4)	87(2)
C(9)	11438(12)	7479(6)	4076(6)	104(3)
C(9′)	12210(40)	7030(20)	3750(20)	76(9)
C(10)	11336(11)	6626(5)	4564(4)	145(3)
C(11)	10070(7)	5492(4)	4118(3)	78(2)
C(12)	8451(8)	4808(5)	901(3)	88(2)
C(13)	7680(10)	5416(6)	434(4)	117(2)
C(14)	7580(40)	6350(30)	1060(30)	65(10)
C(14′)	6602(13)	5836(11)	985(8)	109(4)
C(15)	7215(8)	5943(5)	1877(3)	92(2)
C(16)	5013(6)	1046(4)	3631(3)	59(1)
C(17)	4471(5)	1879(4)	4266(3)	60(1)
C(18)	4153(6)	1646(4)	5058(3)	72(1)
C(19)	3651(7)	2386(6)	5666(4)	98(2)
C(20)	3431(8)	3333(5)	5483(4)	99(2)
C(21)	3678(7)	3559(4)	4685(4)	90(2)
C(22)	4231(6)	2861(4)	4085(3)	71(1)
C(23)	3938(6)	-592(4)	1184(3)	79(2)
C(24)	2779(8)	-1816(5)	1056(5)	124(3)
C(25)	3683(7)	-2474(4)	1345(4)	94(2)
C(26)	4898(7)	-1648(4)	2027(3)	88(2)
C(27)	9167(8)	-53(5)	2218(4)	102(2)
C(28)	10600(9)	191(7)	2800(5)	136(3)
C(29)	10061(8)	397(6)	3667(4)	114(2)
C(30)	8733(8)	883(6)	3586(3)	104(2)

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

C(15)–N(3)–P(1), C(12)–N(3)–P(1) and C(16)–N(4)–P(2) are 128.5(3)˚, 121.0(3)˚, 120.6(3)˚, 127.1(3)˚ and 125.1(3)˚, which confirm sp^2 hybridization for amino and amidic nitrogens in the title compound.

N-Benzoyl-*N*′,*N*″-bis(pyrrolidinyl)phosphoric triamide appears as two crystallographically independent molecules.

Table 3 Selected bond lengths (Å) and angles (deg) for title compound.

P(1)-N(1)	1.679(4)	C(1)-N(1)	1.360(5)
P(1)-N(2)	1.618(4)	C(9)-C(10)	1.437(9)
P(1)-N(3)	1.615(4)	C(9′)-C(10)	1.61(3)
O(2)-C(1)	1.217(5)	C(13)-C(14)	1.42(4)
P(1)-O(1)	1.487(3)	C(13)-C(14′)	1.451(12)
O(1)-P(1)-N(1)	106.77(17)	C(11)-N(2)-P(1)	121.0(3)
O(1)-P(1)-N(2)	110.86(18)	C(12)-N(3)-P(1)	127.1(3)
O(1)-P(1)-N(3)	117.6(2)	C(15)-N(3)-P(1)	120.6(3)
N(3)-P(1)-N(2)	105.16(19)	C(16)-N(4)-P(2)	125.1(3)
N(2)-P(1)-N(1)	112.8(2)	C(23)-N(5)-P(2)	121.1(3)
N(3)-P(1)-N(1)	103.66(18)	C(26)-N(5)-P(2)	128.0(3)
O(3)-P(2)-N(5)	110.48(18)	C(27)-N(6)-P(2)	121.9(4)
O(3)-P(2)-N(6)	117.1(2)	C(30)-N(6)-P(2)	125.9(3)
N(5)-P(2)-N(6)	105.02(19)	C(13)-C(14)-C(15)	108.3(18)
O(3)-P(2)-N(4)	106.11(17)	C(13)-C(14′)-C(15)	107.0(8)
N(5)-P(2)-N(4)	112.2(2)	C(10)-C(9)-C(8)	105.8(6)
N(6)-P(2)-N(4)	105.97(19)	C(8)-C(9′)-C(10)	101.0(18)
C(1)-N(1)-P(1)	128.5(3)	C(9′)-C(8)-C(9)	43.8(12)
C(8)-N(2)-P(1)	126.7(3)	N(2)-C(8)-C(9)	103.8(5)

Table 4 Hydrogen bond D-H...A for the title compound.

D-H…A	d(D-H)	d(H…A)	d(D…A)	∠DHA
N(1)-H(1A)…O(3)	0.86(6)	2.01(5)	2.855(6)	167(5)
N(4)-H(4A)…O(1)	0.86(6)	2.04(6)	2.886(5)	166(5)

This is based on the conformational forms of the pyrrolidinyl groups and the orientation of the phenyl ring. The pyrrolidinyl ring is planar in one conformer, but in another one is deformed due to a disorder of the C(9), C(9′), C(14), and C(14′) atoms (see Fig. 2). The dimmeric aggregate in the structure is not centrosymmetric. These two independent molecules are linked into the dimmeric aggregate *via* two (symmetry independent) hydrogen bonds (see Fig. 2 and Table 4). Because the whole dimmeric aggregate actually constitutes an asymmetric unit, this is not a centrosymmetric aggregate. However, in other molecules with one “active” hydrogen atom, centrosymmetric dimmers have usually been observed.[2]

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