Crystal Structure of *N*-Benzoyl-*N'*,*N''*-bis(2-ethylhexyl)phosphoric triamide

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N-Benzoyl-*N'*,*N''*-bis(2-ethylhexyl)phosphoric triamide crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.9333(16)\text{\AA}$, $b = 10.5356(17)\text{\AA}$, $c = 12.343(2)\text{\AA}$, $\alpha = 77.34(0)^\circ$, $\beta = 85.68(0)^\circ$, $\gamma = 85.09(0)^\circ$ and $Z = 2$. The crystal structure indicates disorder in two amine groups that are connected to a phosphor atom. The molecule is obtained in the form of a one-dimensional polymer *via* intermolecular N-H...O hydrogen bonds. The environment of the three nitrogen atoms is planar, and the P-N bond lengths are significantly shorter than the P-N single bond.

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The very rapid development of organophosphorus chemistry during the last three decades has given rise to the synthesis of many compounds bonded by phosphorus and nitrogen.^{1,2} Organophosphorus compounds with the C(O)N(H)P(O) skeleton have attracted attention because of their properties as ligands, antitumor agents and ureas inhibitors.^{3,4} The existence of racemic or chairal amines in such molecules enables the existence of different isomers in the crystal structure. Herein we report on the crystal structure of a new phosphoric triamide containing two racemic amines (Fig. 1).

The *N*-benzoyl-*N'*,*N''*-bis(2-ethylhexyl)phosphoric triamide was prepared from the reaction of *N*-benzoyl-phosphoramidic dichloride with D,L-2-ethylhexyl amine, as previously reported.⁵ Slow evaporation of a solution of chloroform and heptane (with ratio 6/1) of the title compound at room temperature yielded suitable crystals for X-ray analysis by full-matrix least squares using the program SHELXTL-97.

The corresponding crystal data and structure refinements are summarized in Table 1. The structure was solved by direct methods. The positions of the hydrogen bonds were obtained from a difference Fourier map. The atomic coordinates for non-hydrogen atoms are listed in Table 2, and selected inter atomic parameters are collected in Table 3.

In this molecule we have a centrosymmetric structure. The formation of the centrosymmetric crystal structure is because the initial reagent was racemic, and there was no spontaneous resolution during crystallization. In any case there would be racemate in the crystal. The title compound indicates disorder in two amine groups that are connected to phosphor atom (Fig.

2). The disordered molecule comprises both enantiomers in both chiral atoms (C9 and C22). Two components of the disordered molecule are equally disordered (in a ratio of 0.5:0.5). In this structure the P(O) and C(O) groups are at anti-position to each other. The coordination environment around the phosphorus atom of the compound is approximately tetrahedral, since the average of six angles involving P is 109.45° . The P-N bond lengths are P1-N1, 1.679(4); P1-N2, 1.608(6); and P1-N3, 1.604(6)Å. All of these bonds are shorter than the typical P-N single bond length (1.77 Å for NaHPO₃NH₂).¹ The environment of the amine nitrogen atoms is nearly planar. The sum of the N atom bond angles is 360.0, 357.2 and 357.1° for N1, N2 and N3, respectively. The P=O

Table 1 Crystal data and structure refinement for the title compound

Empirical formula: C ₂₃ H ₄₂ N ₃ O ₂ P	
Formula weight = 423.57	
Crystal structure: triclinic	
Space group: $P\bar{1}$	$Z = 2$
$a = 9.9333(16)\text{\AA}$	$\alpha = 77.342(4)^\circ$
$b = 10.5356(17)\text{\AA}$	$\beta = 85.677(4)^\circ$
$c = 12.343(2)\text{\AA}$	$\gamma = 85.088(3)^\circ$
$V = 1253.6(4)\text{\AA}^3$	
Calculated density = 1.122 Mg/m ³	
Absorption coefficient/mm ⁻¹ = 0.132	
$F(0\ 0\ 0) = 464$	
Crystal size = 0.25 × 0.25 × 0.20 mm	
No. of reflection used = 10191	
No. of parameters = 245	
$\theta_{\max} = 26.00^\circ$ with Mo- K_α	
$R1 = 0.0932 [I \geq 2\sigma(I)]$	
$wR2 = 0.1859$	
Goodness-of-fit on $F^2 = 1.016$	
$(\Delta\sigma) = 0.003$	
$(\Delta\rho)_{\max} = 0.602\text{ e\AA}^{-3}$	
$(\Delta\rho)_{\min} = 0.219\text{ e\AA}^{-3}$	
Measurement: Bruker SMART 1000 CCD	
Program system: SADABS	
Structure determination: SHELXTL	
Refinement: full-matrix least-squares on F^2	
CCDC deposition number: 292739

Fig. 1 Chemical structure of the title compound.

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Table 2 Fractional coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) of non-hydrogen atoms

	x	y	z	U_{eq}
P(1)	-2752(1)	4173(1)	5(2)	101(1)
O(1)	-4074(3)	3625(3)	6(4)	128(2)
O(2)	-975(3)	6238(3)	35(3)	99(1)
N(1)	-3132(3)	5746(3)	48(4)	97(2)
N(2)	-1747(4)	4067(5)	-1060(6)	114(2)
N(3)	-1823(4)	3509(4)	1013(6)	105(2)
C(1)	-2184(4)	6585(4)	83(5)	93(2)
C(2)	-2643(3)	7887(3)	314(5)	144(3)
C(3)	-1730(3)	8853(4)	45(5)	133(3)
C(4)	-2068(4)	10065(3)	303(5)	222(6)
C(5)	-3320(5)	10311(4)	830(5)	181(4)
C(6)	-4233(4)	9345(5)	1098(4)	163(3)
C(7)	-3894(3)	8134(4)	841(4)	147(3)
C(8)	-2097(10)	4599(10)	-2166(11)	199(5)
C(9)	-1695(11)	3691(13)	-2936(12)	216(5)
C(10A)	-2720(20)	4000(40)	-3810(20)	350(20)
C(11A)	-4150(30)	4230(30)	-3330(20)	262(13)
C(12A)	-175(15)	3840(20)	-3120(20)	227(11)
C(13A)	290(30)	2840(30)	-3820(30)	321(16)
C(14A)	1680(20)	2320(30)	-3420(20)	265(13)
C(15A)	3030(20)	1900(20)	-3953(17)	203(8)
C(10B)	-2920(20)	2890(20)	-2720(20)	298(14)
C(11B)	-3820(30)	3440(30)	-3670(20)	260(12)
C(12B)	-689(17)	2536(16)	-2880(20)	222(9)
C(13B)	490(20)	3410(20)	-3180(20)	228(10)
C(14B)	1230(20)	2630(50)	-3970(40)	430(30)
C(15B)	2610(20)	3010(20)	-3729(19)	211(9)
C(21)	-2200(8)	3508(10)	2123(11)	187(4)
C(22)	-1832(11)	2274(12)	2957(11)	218(5)
C(23A)	-2470(20)	1920(30)	4131(15)	260(11)
C(24A)	-3850(20)	1360(20)	4180(20)	213(8)
C(25A)	-311(12)	2290(13)	3073(14)	133(5)
C(26A)	587(17)	1065(15)	3538(17)	180(7)
C(27A)	2070(19)	1300(20)	3430(20)	218(10)
C(28A)	2950(30)	40(20)	3570(20)	306(14)
C(23B)	-3180(20)	1700(50)	2960(60)	580(40)
C(24B)	-4390(30)	2430(30)	3440(30)	309(16)
C(25B)	-774(17)	1190(20)	2880(30)	286(14)
C(26B)	456(18)	1928(17)	2920(16)	154(6)
C(27B)	1540(20)	800(20)	3200(20)	264(13)
C(28B)	2920(20)	1290(20)	2770(18)	208(8)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

Table 3 Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for the compound

P(1)-O(1)	1.479(3)	O(2)-C(1)	1.226(5)
P(1)-N(3)	1.604(6)	N(1)-C(1)	1.354(5)
P(1)-N(2)	1.608(6)	N(2)-C(8)	1.414(10)
P(1)-N(1)	1.679(4)	N(3)-C(21)	1.393(11)
O(1)-P(1)-N(3)	116.3(3)	N(2)-P(1)-N(1)	110.1(2)
O(1)-P(1)-N(2)	114.6(3)	C(1)-N(1)-P(1)	123.2(3)
N(3)-P(1)-N(2)	101.9(3)	C(8)-N(2)-P(1)	123.0(5)
O(1)-P(1)-N(1)	104.94(17)	C(21)-N(3)-P(1)	123.5(5)
N(3)-P(1)-N(1)	109.0(2)	O(2)-C(1)-N(1)	120.9(4)

bond length in this molecule is 1.479(3) $\text{\AA}$ which is slightly longer than the PO double bond length (1.45 $\text{\AA}$ for POCl_3).¹ A packing diagram of the title compound shows two molecules in

Fig. 2 Disordered pattern of the molecule. The dashed lines represent the bond between the disordered atoms (a) and a packing diagram of the crystal structure, in which the hydrogen bonds are shown as dashed lines (b). Hydrogens are omitted for clarity.

Table 4 Hydrogen-bond D-H...A for the compound [$\text{\AA}$ and $^\circ$]

D-H	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle\text{DHA}$	A
N(1)-H(1)N	0.90	1.91	2.800(4)	169	O1[-x-1,-y+1,-z]
N(2)-H(2)N	0.90	2.25	3.034(5)	146	O2[-x,-y+1,-z]
N(3)-H(3)N	0.90	2.12	2.984(6)	160	O2[-x,-y+1,-z]

a unit cell. The compound produces a one-dimensional polymeric chain from intermolecular N1-H1...O1, N2-H2...O2 and N3-H3...O2 hydrogen bonds (Fig. 2, Table 4).

References

1. D. E. C. Corbridge, "Phosphorus, an outline of its chemistry, Biochemistry and technology", 5th ed., **1995**, Elsevier, Amsterdam.
2. M. L. Helm, S. A. Katz, T. W. Imieczny, R. M. Hands, and A. O. Norman, *Inorg. Chem.*, **1999**, 38, 3167.
3. E. A. Trush, V. A. Ovchynikov, K. V. Domasevitch, J. S. Wiatek-kozłowska, V. Y. Zub, and V. m. Amirkhanov, *Z. Naturforsch.*, **2002**, 57b, 746.
4. K. Jaroslav and F. Swerdlhoff, U.S.Pat. 4,517,003, **1985**.
5. K. Gholivand, H. Mostaanzadeh, Z. Shariatnia, and N. Oroujzadeh, *Main Group Met. Chem.*, **2006**, 5, 95.