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X-ray Structure Analysis Online

Synthesis and Crystal Structure of 5,5-Dimethyl-2-(*p*-methylanilino)-2-oxo-1,3,2-diazaphosphorinane

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The crystal structure of 5,5-dimethyl-2-(*p*-methylanilino)-2-oxo-1,3,2-diazaphosphorinane has been determined. The P–N bond lengths are significantly shorter than the P–N single bond. The P=O bond is placed in an equatorial position and is slightly longer than the PO double bond length. The molecule is obtained in the form of a two dimensional polymer *via* intermolecular –N–H···O=P– and –N–H···N– hydrogen bonds. A weak C–H···O hydrogen bond is also observed in the structure.

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Diazaphosphorinanes are an important class of organophosphorus compounds due to their biological significance.[1] In contrast to the numerous studies available concerning the conformation of diheterophosphorinanes containing oxygen, sulfur or NR, little attention has been devoted to the ones containing NH.[2] We report here on results of the reaction of N-4-methyl phenyl phosphoramidic dichloride (1 mmol) with 2,2-dimethylpropylenediamine (1 mmol in the presence of 2 mmol triethylamine as HCl scavenger) to form 5,5-dimethyl-2-(*p*-methylanilino)-2-oxo-1,3,2-diaza-phosphorinane, Fig. 1. The single crystals of the title compound were obtained from a solution of methanol and chloroform in the ratio 1:4 after slow evaporation at room temperature. 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.

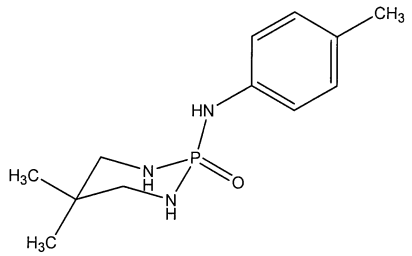

Fig. 1 Chemical structure.

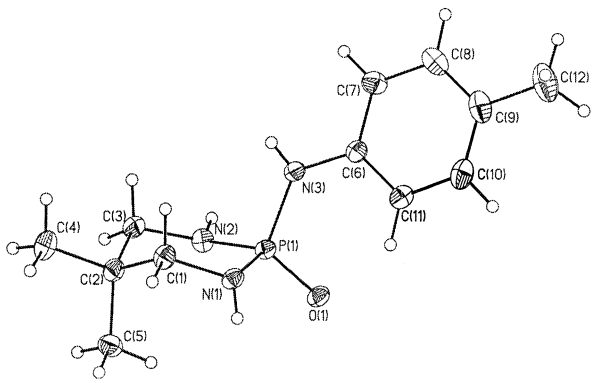

Fig. 2 Molecular structure of the title compound, showing the atom-labeling scheme and 50% probability level displacement ellipsoids.

The phosphorus atom is slightly distorted from tetrahedral configuration. The bond angles around P(1) are in the range of 115.17 – 104.25˚. The P(1)–O(1) bond length (1.4852(10)Å) is

Table 1 Crystal data and structure refinement for the title compound

Formula: $C_{12}H_{20}N_3OP$	
Formula weight = 253.28	
Crystal system: Monoclinic	
Space group: *C*2/*c*	$Z = 8$
$a = 28.1477(11)$Å	$\beta = 104.4530(10)^\circ$
$b = 10.8999(4)$Å	
$c = 9.1380(4)$Å	
$V = 2714.88(19)$Å^3	
$D_x = 1.238$ Mg/m^3	
No. of reflections used = 10132	
$2\theta_{max} = 60.02$ with Mo K_α	
$R = 0.0496$ [3265 refs. $I > 2\sigma(I)$]	
$(\Delta/\sigma)_{max} = 0.005$	
$(\Delta\rho)_{max} = 0.456$ eÅ^{-3}	
$(\Delta\rho)_{min} = -0.316$ 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 ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of non-hydrogen atoms

Atom	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$U(\mathrm{eq}) \times 10^3$
P(1)	2613(1)	4026(1)	1865(1)	17(1)
O(1)	2814(1)	3936(1)	512(1)	20(1)
N(1)	2361(1)	2705(1)	2132(1)	19(1)
C(1)	1982(1)	2710(1)	2999(2)	21(1)
N(2)	2182(1)	5058(1)	1759(1)	19(1)
C(2)	1565(1)	3621(1)	2376(2)	20(1)
N(3)	3042(1)	4419(1)	3381(1)	20(1)
C(3)	1779(1)	4917(1)	2515(2)	20(1)
C(4)	1198(1)	3563(2)	3354(2)	28(1)
C(5)	1309(1)	3317(2)	739(2)	25(1)
C(6)	3534(1)	4032(1)	3802(2)	19(1)
C(7)	3852(1)	4587(2)	5049(2)	24(1)
C(8)	4340(1)	4234(2)	5490(2)	30(1)
C(9)	4529(1)	3329(2)	4718(2)	31(1)
C(10)	4210(1)	2794(2)	3478(2)	29(1)
C(11)	3720(1)	3133(2)	3014(2)	23(1)
C(12)	5056(1)	2922(2)	5236(3)	46(1)

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

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

P(1)-O(1)	1.4852(10)	C(1)-C(2)	1.536(2)
P(1)-N(1)	1.6502(12)	N(1)-C(1)	1.4776(18)
P(1)-N(2)	1.6402(13)	N(2)-C(3)	1.4764(18)
P(1)-N(3)	1.6496(13)	N(3)-C(6)	1.4071(18)
O(1)-P(1)-N(1)	109.42(6)	N(1)-C(1)-C(2)	113.01(11)
O(1)-P(1)-N(2)	115.17(6)	C(3)-N(2)-P(1)	122.97(10)
O(1)-P(1)-N(3)	111.51(6)	C(6)-N(3)-P(1)	127.96(10)
N(2)-P(1)-N(3)	104.25(6)	N(2)-C(3)-C(2)	113.04(11)
N(2)-P(1)-N(1)	105.51(6)	C(11)-C(6)-N(3)	122.70(13)
N(3)-P(1)-N(1)	110.75(7)	C(7)-C(6)-N(3)	118.72(13)
C(1)-N(1)-P(1)	118.11(10)	C(3)-C(2)-C(1)	108.45(12)

slightly longer than the PO double bond length (1.45 Å).[3] This bond is placed in an equatorial position, Fig. 2. The equatorial preference for the P=O bond was previously observed by Bentrude[4] and was attributed to the overlap of the endocyclic nitrogen p-orbital with P–N(exocyclic) anti-bonding orbital. The P(1)–N(1), P(1)–N(2) and P(1)–N(3) bond lengths are 1.6502(12), 1.6402(13) and 1.6496(13)Å which are shorter than the single bond length (1.77 Å).[3]

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

D-H...A	d(D-H)Å	d(H...A)Å	d(D...A)Å	∠DHA(˚)
N(1)-H(1N)…O(1)^{i}	0.79	2.16	2.946(2)	170
N(2)-H(2N)…N(1)^{ii}	0.82	2.43	3.218(2)	162
N(3)-H(3N)…O(1)^{iii}	0.78	2.06	2.836(2)	175

Symmetry operations i) 1/2 – x, 1/2 – y, –z; ii) 1/2 – x, 1/2 + y, 1/2 – z; iii) x, 1 – y, 1/2 + z

The nitrogen environment of *p*-methylaniline moiety is practically planar, but the endocyclic N(1) and N(2) atoms are not. Sums of the surrounding angles of N(1), N(2) and N(3) atoms are 344.4˚, 347.7˚ and 360˚, respectively.

The structure was obtained in the form of a two dimensional polymer *via* –N–H···O=P– and –N–H···N– hydrogen bonds (Table 4). The concept of H-bonds has been extended to C–H···Y bonding (where Y is an electronegative atom). Previous studies have suggested that C–H···O hydrogen bonds occur in the ranges of 3.0 – 4.0 Å for C···O distances and of more than 110˚ for the bond angles.[5] In the network of this structure, there is one C–H···O hydrogen bond, C(7)–H(7)···O(1) with C(7)···O(1) = 3.455 Å and ∠C(7)–H(7)···O(1) = 134.19˚.

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