

CRYSTAL AND MOLECULAR STRUCTURE OF 1,3-BIS(TRIMETHYLSILYL)-2 λ^3 ,4 λ^3 -BIS(2,2,6,6-TETRAMETHYLPYPERIDINO)DIAZADIPHOSPHETIDINE

V. Ya. Antosyak and V. N. Biyushkin

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An x-ray diffraction structural analysis using λ Mo radiation for a total of 2042 reflections and least squares refinement anisotropically for nonhydrogen atoms and isotropically for hydrogen atoms ($R = 0.050$) yielded the crystal structure of 1,3-bis(trimethylsilyl)-2 λ^3 ,4 λ^3 -(bis(2,2,6,6-tetramethylpyperidino)diazadiphosphetidine. The unit cell parameters of the orthorhombic crystals are as follows: $a = 10.992(5)$, $b = 21.143(6)$, $c = 12.942(5)$ Å, $d_{\text{calc}} = 1.141$ g/cm³, $Z = 4$, space group Pbca. The molecule has trans configuration. The central diazadiphosphetidine ring is planar. The P—N bonds in this ring differ in length and have values of 1.733(3) and 1.747(3) Å.

The structure of four-membered P_2N_2 rings in 1,3,2,4-diazadiphosphetidines depends significantly on the nature of the substituents [1]. We have carried out an x-ray diffraction structural analysis of 1,3-bis(trimethylsilyl)-2 λ^3 ,4 λ^3 -bis(2,2,6,6-tetramethylpyperidino)diazadiphosphetidine. The synthesis of this compound was described by Romanenko et al. [2] who ascribed trans configuration of the substituents at the phosphorus atom on the basis of spectral data.

The unit cell parameters of the colorless, orthorhombic prisms are as follows: $a = 10.992(5)$, $b = 21.143(6)$, $c = 12.942(5)$ Å, space group Pbca, $d_{\text{calc}} = 1.141$ g/cm³, $Z = 4$, $\mu(\text{MoK}_\alpha) = 2.02$ cm⁻¹. A 1.0-mm-long cylindrical sample with 0.2 mm diameter was prepared for the x-ray diffraction structural analysis. The intensities of 2042 independent reflections with $I > 2\sigma$ were measured on a DAR-UMB diffractometer using MoK α radiation and a graphite monochromator. Corrections for absorption were not introduced.

The structure was solved by the heavy atom method and refined by the method of least squares anisotropically to $R = 0.050$ using the YANX programs [3]. The positions of the hydrogen atoms were determined from the electron density difference map. The temperature factor for the hydrogen atoms in the refinement was taken to be 0.06 Å². The coordinates of all the atoms are given in Table 1, while the bond lengths and angles of the nonhydrogen atoms are given in Table 2. The projection of the structure onto the xy plane is given in Fig. 1.

RESULTS AND DISCUSSION

The trans isomer is found in this structure. The tetramethylpyperidine fragments are oriented trans relative to the planar four-membered P_2N_2 ring. The molecule is centrosymmetric. Its geometric center coincides with the crystallographic center of symmetry (see Fig. 1). The phosphorus atoms in the diazadiphosphetidine ring have pyramidal configuration, while the nitrogen atoms have plane trigonal configuration.

As in other phosphetidines, the orientation of the bonds at the phosphorus atom in this structure differs significantly from the bond orientation in proper tetrahedral configuration. Thus, the bond angles involving the phosphorus atom with a piperidine nitrogen atom are close to tetrahedral (108.7 and 112.2°), while the endocyclic angle between the P—N1 and P—N1' bonds are only 82.5°. Bond angles close to 82.5° were found in cis-1,3-(tert-butyl)-2,4-dichloro-1,3,2,4-diazadiphosphetidine [4,5] and trans-1,3-bis(trimethylsilyl)-2,4-bis[di(trimethylsilyl)amino]-1,3,2,4-diazadiphosphetidine [6].

The endocyclic P—N1 and P—N1' bonds are close in length to a P—N single bond (1.77 Å) but differ from each other by $\sim 5\sigma(d)$ (1.733(3) and 1.747(3) Å). An analogous difference in the endocyclic P—N bonds was found in

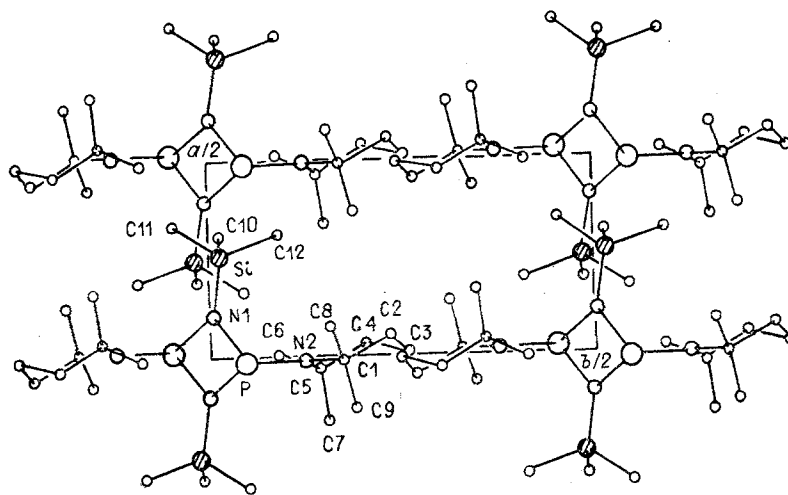


Fig. 1. Projection of the structure on the xy plane.

trans-1,3-bis(ethoxyphosphoryl)-2,4-bis(diethylamino)-1,3,2,4-diazadiphosphetidine [8], in which the central diaza-diphosphetidine ring is nonplanar with extrusion of its component atoms from the mean plane by 0.15 Å. The P—N bond lengths in this ring are 1.749(2) and 1.760(2) Å and are somewhat longer than the P—N bonds in the compound studied. The same values (1.751(2) and 1.760(2) Å) for the P—N bond were found in the four-membered ring in 1,3,2- λ^3 -diazaphosphetidine [9]. On the other hand, the difference in the ring P—N bonds in the trans isomers of 1,3-dimethyl-2,4-bis(tert-butyl)-1,3,2,4-diazadiphosphetidine [10], 1,3-diphenyl-2,4-dimethoxy-1,3,2,4-diazadiphosphetidine [11], and 1,3-bis(trimethylsilyl)-2,4-bis[di(trimethylsilyl)amino]-1,3,2,4-diazadiphosphetidine [6] with planar diazadiphosphetidine rings is less pronounced and does not exceed 2σ . Some contraction of these bonds is noted in these latter compounds. Analogous behavior is found for the cis isomers of 1,3-diphenyl-2-[di(phenylamino)phosphino]phenyl-4-phenylamino-1,3,2,4-diazadiphosphetidine [12] and bis(1,3-diphenyl-4-phenylamino)phenylamine [13], in which, however, the diazadiphosphetidine rings are planar as in the trans isomers. The endocyclic P—N bonds in cis-1,3-bis(tert-butyl)-2,4-bis(diphenylphosphinomethylamino)-1,3,2,4-diazadiphosphetidine [14], in which the heterocycle is nonplanar and the displacement of the atoms from the mean plane is 0.13 Å, are also identical. Alternation of the P—N bonds in the diazadiphosphetidine ring is somewhat more pronounced in cis-2,4-dipiperidine-1,3-di-tert-butyl-diazadiphosphetidine [15], in which these bond lengths are 1.720(2), 1.722(2), 1.747(2), and 1.750(2) Å, while the P_2N_2 ring is nonplanar and the component atoms are extruded from the mean plane by 0.13 Å.

As in other phosphetidines [6-9,12-15], the bond of phosphorus with the exocyclic nitrogen atom in the compound studied is shortened relative to the exocyclic P—N bonds. This value is in accord with the lengths of the exocyclic P—N bonds in the compounds cited above containing similar bonds and falls in the range 1.649–1.712 Å at its upper boundary [6,8,9,12-15]. The endocyclic angle at N1 is 97.2°, while the exocyclic bond angles at this atom are 129.4° (P—N1—Si) and 133.2° (P'—N1—Si). The N1—Si bond length is equal to 1.736 Å. A similar value (1.744 Å) was obtained for the corresponding bond in trans-1,3-bis(trimethylsilyl)-2,4-bis(di(trimethylsilyl)amino)-1,3,2,4-diazadiphosphetidine [6]. It is shorter than the Si—C bond lengths, which differ between themselves (1.850, 1.859, and 1.882 Å). The angle between the N1—Si bond and N1—N1' direction is 175.7°. The trimethylsilyl fragment is almost symmetrically oriented related to the central diazadiphosphetidine fragment. The C11—Si—N1—P torsion angle is 178.4°. The other two torsion angles involving the other carbon atoms, C10—Si—N1—P and C12—Si—N1—P are 57.9 and 60.6°, respectively. A significant difference is noted in the N1—Si—C bond angles, which have the following values: N1SiC11, 106.6; N1SiC10, 109.1; and N1SiC12, 113.1°. The expansion of the N2SiC12 bond angle is dictated by the steric interaction between C12 and N2. The compensating effect of this slant of the trimethylsilyl fragment and the above-mentioned deviation of the N1—Si bond from symmetrical arrangement provides for approximately equal short contacts of the methyl groups of this fragment with the other atoms of the molecule, which are not bonded to it: C10—N1, 2.93; C11—N1, 2.93; C11—P'(I), 3.58; C12—N1, 3.02; C12—N2, 3.65 Å. The configuration of the bond

TABLE 1. Coordinates of the Basis Atoms with Standard Deviations

Atom	x	y	z	Atom	x	y	z
Si	0,2601(4)	0,0167(4)	0,0121(4)	H6	0,125(5)	0,194(2)	-0,126(4)
P	-0,0137(1)	0,0483(1)	0,0617(1)	H7	-0,049(5)	0,057(2)	-0,177(4)
N1	0,1041(3)	0,0044(2)	0,0063(3)	H8	0,092(5)	0,080(2)	-0,161(4)
N2	-0,0143(4)	0,1220(2)	0,0078(3)	H9	0,007(5)	0,114(2)	-0,244(4)
C1	-0,0149(5)	0,1737(2)	0,0895(4)	H10	-0,212(5)	0,183(2)	-0,071(4)
C2	0,0467(7)	0,2345(3)	0,0483(6)	H11	-0,220(5)	0,109(2)	-0,115(4)
C3	0,0027(7)	0,2560(2)	-0,0555(5)	H12	-0,186(4)	0,179(2)	-0,187(4)
C4	0,0302(6)	0,2020(2)	-0,1281(4)	H13	0,028(5)	0,120(2)	0,223(4)
C5	-0,0388(5)	0,1412(2)	-0,1015(4)	H14	0,085(5)	0,203(2)	0,212(4)
C6	0,0078(5)	0,0910(2)	-0,1767(3)	H15	0,158(5)	0,142(2)	0,161(4)
C7	-0,1750(6)	0,1500(3)	-0,1218(5)	H16	-0,191(5)	0,206(2)	0,079(4)
C8	0,0698(7)	0,1559(3)	0,1807(5)	H17	-0,119(5)	0,211(2)	0,193(4)
C9	-0,1404(6)	0,1867(3)	0,1310(6)	H18	-0,181(5)	0,150(2)	0,172(4)
C10	0,3091(5)	0,0170(3)	0,1496(5)	H19	0,379(4)	0,019(2)	0,158(4)
C11	0,3393(5)	-0,0443(3)	-0,0652(5)	H20	0,284(5)	-0,022(2)	0,181(4)
C12	0,3082(5)	0,0949(3)	-0,0440(5)	H21	0,268(5)	0,044(2)	0,189(4)
H1	0,025(5)	0,269(2)	0,043(4)	H22	0,425(5)	-0,038(2)	-0,053(4)
H2	0,134(4)	0,223(2)	0,096(4)	H23	0,327(5)	-0,044(2)	-0,135(4)
H3	-0,090(4)	0,259(2)	-0,047(4)	H24	0,321(5)	-0,089(2)	-0,042(4)
H4	0,042(5)	0,294(2)	-0,071(4)	H25	0,271(5)	0,103(2)	-0,113(4)
H5	0,007(5)	0,213(2)	-0,195(4)	H26	0,401(4)	0,110(2)	-0,042(4)
				H27	0,271(5)	0,129(2)	0,008(4)

TABLE 2. Bond Lengths d (Å) and Bond Angles ω (deg)

Bond	d	Bond	d
Si—C(10)	1,859(6)	C(1)—C(8)	1,550(8)
Si—C(11)	1,850(6)	C(1)—C(9)	1,506(9)
Si—C(12)	1,881(6)	C(3)—C(2)	1,498(10)
Si—N(1)	1,736(3)	C(3)—C(4)	1,510(8)
P—N(1)	1,747(3)	C(5)—C(4)	1,533(7)
P—N(2)	1,708(3)	C(5)—C(6)	1,529(7)
C(1)—N(2)	1,521(6)	C(5)—C(7)	1,531(8)
C(1)—C(2)	1,548(8)	C(5)—N(2)	1,496(6)
Bond angle	ω	Bond angle	ω
C(10)SiC(11)	112,6(3)	N(2)C(1)C(9)	112,6(4)
C(10)SiC(12)	106,6(3)	C(2)C(1)C(8)	101,6(5)
C(10)SiN(1)	109,2(2)	C(2)C(1)C(9)	111,8(5)
C(11)SiC(12)	105,7(3)	C(8)C(1)C(9)	108,9(5)
C(11)SiN(1)	109,7(2)	C(1)C(2)C(3)	114,9(6)
C(12)SiN(1)	113,1(2)	C(2)C(3)C(4)	105,3(5)
C(12)N(1)P	129,4(2)	C(3)C(4)C(5)	113,3(5)
N(1)PN(2)	108,6(2)	C(4)C(5)N(2)	110,6(4)
PN(2)C(1)	111,8(3)	C(4)C(5)C(6)	105,8(4)
PN(2)C(5)	129,4(3)	C(4)C(5)C(7)	110,1(4)
C(1)N(2)C(5)	117,5(3)	N(2)C(5)C(6)	110,7(4)
N(2)C(1)C(2)	110,8(4)	N(2)C(5)C(7)	111,8(4)
N(2)C(1)C(8)	110,6(4)	C(6)C(5)C(7)	107,6(4)

angles of the piperidine nitrogen atom, N2, is planar trigonal. The sum of the bond angles at this atom is 358.7°.

The piperidine ring has chair conformation. However, N2 and C3, which is in the position para to N2, are nonuniformly displaced from the mean plane of the remaining atoms, C1C2C4C5, which are located in a plane to $\pm 0.02^\circ$. Atom N2 is 0.485 Å from this plane, while C3 is 0.734 Å from this plane. The C1C2C4C5 plane forms dihedral angles with C1N2C5 and C2C3C4 of 38.4 and 53.6°, respectively.

The configuration of the carbon atoms in the ring are slightly displaced from ideal. The bonds of C3 with the carbon atoms (C3—C2, 1.498; C3—C4, 1.509 Å) are somewhat shorter than the standard C—C single bond length (1.544 Å) and the other ring C—C bonds equal to 1.548 and 1.532 Å. On the other hand, the bonds of N2 with carbon atoms (N2—C1, 1.521 and N2—C5, 1.496 Å) are somewhat longer than the standard N—C single bond length (1.475 Å).

The piperidine ring is approximately perpendicular to the plane of the central diazadiphosphetidine fragment. The piperidine ring plane forms an angle of 95° with the plane of the four-membered ring. However, the piperidine ring is asymmetrically oriented relative to the P—N2 bond. The P—N2—C1 bond angle is 111.8°, while the P—N2—C5 bond angle is expanded to 129.4°. Such an orientation of the piperidine ring leads to the circumstance that the equatorial methyl group at C1 is much closer to the phosphorus atom directly bound to piperidine nitrogen N2 than the other equatorial methyl group at C5 to the opposite side of the ring. The C8—P distance is 2.897 Å, while the C6—P distance is 3.224 Å. The expansion of the P—N2—C5 bond angle is a consequence of the repulsion of the equatorial methyl group at C5 from the atoms of heterocycle not bonded to the piperidine fragment: C6—N1', 3.176; C6—N1'', 3.230; C6—P', 3.300 Å.

The packing of the molecules in the crystal is a function of van der Waals interactions.

This structure indicates that nonidentical endocyclic P—N bonds in a diazadiphosphetidine ring are also observed in trans-planar isomers and, thus, the relationship of the lengths of these bonds is independent of the planarity of this ring and on the cis or trans orientation of the exocyclic substituents at the pyramidal phosphorus atoms.

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