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Fused 1,3,2-dioxaborinanes, derivatives of 4-diphenylphosphino- and 4-diphenylphosphoryl-4H-1,3-dioxa-2-boraphenanthrenes, and their complexes with amines have been synthesized. According to X-ray diffraction data, the complex of 2-phenyl-4-diphenylphosphoryl-4H-1,3-dioxa-2-boraphenanthrene with butylamine exists as a dimer due to the formation of intermolecular hydrogen bonds.

Key words: fused 4-diphenylphosphino-1,3,2-dioxaborinanes, complexes with amines; X-ray diffraction analysis.

Intramolecular nonvalent electronic interactions affect the spatial structure and reactivity of organic compounds. For example, the dipole-dipole interactions of lone electron pairs of heteroatoms determine the spatial orientation of substituents in 1,3-diheterophosphorinanes,¹ while donor-acceptor $n-\sigma^*$ interactions affect the reactivity of the P and B atoms in dioxaboraphosphorinanes.² We recently demonstrated³ the existence of intramolecular electronic interaction between one of the phenyl substituents at P atom in 4-diphenylphosphino-5,6-benzo-2-phenyl-1,3,2-dioxaborinane (1) and the planar heterocyclic dioxaborinane moiety. This interaction, which is of the "stacking effect" type, manifests itself in solutions as a shift of the signal in the ³¹P NMR spectrum. One of the conditions necessary in order for the stacking effect to occur is the presence of a planar 1,3,2-dioxaborinane moiety in these compounds.^{3,4} In a continuation of the studies on intramolecular interactions in P,B-containing compounds, we synthesized a series of novel diphenylphosphino-2-phenyl-1,3,2dioxaborinanes.

1,3,2-Dioxaborinane 2, which incorporates an exocyclic phosphino group and a planar heterocyclic moiety, was obtained in analogy to compound 1 according to Scheme 1 (*cf.* Ref. 3).

Dioxaborinane 2 is a white crystalline compound, whose IR spectrum contains a band corresponding to B^{III} —O bond vibrations (1350 cm⁻¹). The mass spectrum of compound 2 displays two intense peaks with m/z 444 and 460. The former peak corresponds to the molecular ion, $[M]^{+}$, of 1,3,2-dioxaborinane 2, while the latter peak relates to its oxidated form. This agrees with the variation in the intensity ratio of the above peaks during recording of the mass spectrum. The precise m/z values measured for the former peak is 444.14209, which is in accord with the value of 444.14495 calculated from the elemental composition $(C_{29}H_{22}^{-11}BO_2P)$.



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The ³¹P NMR spectrum of a solution of dioxaborinane 2 in benzene recorded immediately after dissolution contains one signal at δP 7.3, which is shifted somewhat downfield in comparison with the usual position of signals of tertiary phosphines containing two aromatic substituents; the chemical shift is close to that observed for compound 1 (δP 10).³ In pyridine, the signal is shifted upfield by 5 ppm (δP 2). A similar effect has also been observed³ for dioxaborinane 1. This is explained by the formation of a complex with pyridine through the B atom; in this case, dispersion interaction becomes impossible. The dioxaborinane ring in compound 2 should be planar, like in compound 1, due to the presence of a fused aromatic ring; the diphenylphosphino group has to adopt a pseudoaxial orientation relative to the plane of the heterocycle. Due to the free rotation around the P-C bond, one of the phenyl rings can be located under the dioxaborinane ring, and the resulting attractive dispersion interaction stabilizes the structure of this rotamer.

Dioxaborinane 2 is more stable than its benzo-analog 1. For example, it can be recrystallized from an acetonitrile-DMF mixture (3 : 1) without protection from atmospheric oxygen; it undergoes hydrolysis in solution more slowly; despite the presence of a tricoordinated P atom, this compound is stable in storage. On the other hand, blocking of the B atom due to complexing with pyridine results in a decrease in the stability of the diphenylphosphino group to oxidation, so only a complex of pyridine with phosphine oxide 3 can be isolated from the solution. In this case, one can see an analogy between the behavior of these compounds and that of P,B-compounds of another type, namely, 1,3,2,5-dioxaboraphosphorinanes (which, like compounds 1-3, contain the P-C-O-B fragment); it has been shown that in these compounds the reactivity of one heteroatom depends on the state of the other heteroatom. This was explained^{2,5} by the existence of intramolecular donor-acceptor $n-\sigma^*$ interaction between the tricoordinated P and B atoms along the P-C-O-B bond system.

The intramolecular dispersion interactions in compounds 1 and 2 involve the π -system of one of the phenyl substituents at the P atom. To expand the range of the possible interacting fragments, attempts were made to obtain 1,3,2-dioxaborinanes containing exocyclic phosphorane substituents, which incorporate, in addition to the phenyls, some other π -system. Furthermore, the pentacoordinated P atom, due to its configuration, should be more suitable for a plane-parallel orientation of the interacting π -systems. To obtain these compounds, dioxaborinane 2 was treated with 1,2-naphthoquinone and 2,3-di(N-butylimino)butane (Scheme 2). However, the reaction of compound 2 with 1,2-naphthoquinone resulted in 2-phenyl-4-diphenylphosphinoyl-4H-1,3-dioxa-2-boraphenanthrene (4), while that with 2,3-di(*N*-butylimino)butane gave a crystalline compound; based on the ¹H, ¹³C NMR, and IR spectroscopic data, the structure of complex 5, which incorporates butylamine coordinated to the B atom, was ascribed to the compound obtained. Obviously, the phosphoranes formed in the first step are hydrolyzed with traces of water to give phosphine oxides. Complex 5 results from the ready hydrolysis of the corresponding 2,3-diamino-2-butene, which is initially formed due to phosphorane decomposition.

Scheme 2



The chemical shifts of the signals in the ³¹P NMR spectra of compounds **3** and **4** were equal (δ P 27.3), whereas the signal of complex **5** was shifted 6 ppm downfield relative to the signals of its closest structural analogs, **3** and **4**. Furthermore, the band of the P=O vibrations in the IR spectrum of compound **5** is also shifted in comparison with the similar band of oxide **4** (1154 and 1190 cm⁻¹, respectively). All of these phenomena may result from additional intra- or intermolecular interactions appearing both in the crystal and in solution.

In order to determine the exact structure and to establish the nature of additional nonvalent interactions, we carried out an X-ray diffraction analysis of the crystals of 5. The geometrical structure of complex 5 is shown in Fig. 1, and the location of molecules in the



Fig. 1. Structure of complex 5.

crystal appears in Fig. 2. The coordinates and isotropic thermal parameters of the nonhydrogen atoms are given

in Table 1, while the bond lengths and bond angles are given in Tables 2 and 3, respectively.

Table 1. Coordinates of nonhydrogen atoms (×10⁴) and their equivalent isotropic thermal parameters (U_{eq} ×10³) in molecule 5

Atom	x	у	z	$U_{\rm eq}/~{\rm \AA}^2$	Atom	x	у	z	$U_{\rm eq}/$ Å ²
P(1)	595(1)	2331(1)	6434(1)	37(1)	C(15)	239(6)	3244(5)	9965(4)	81(2)
O(1)	679(3)	1096(2)	6338(2)	49(1)	C(16)	970(6)	3923(4)	9194(4)	74(2)
O(2)	-816(3)	2882(2)	4766(2)	39(1)	C(17)	1109(5)	3661(4)	8136(3)	58(2)
O(3)	-1965(3)	1061(2)	5128(2)	45(1)	C(18)	2017(4)	3024(3)	5655(3)	39(1)
N(1)	157(3)	1147(2)	3965(2)	45(1)	C(19)	2032(4)	4169(3)	5368(3)	51(1)
B(1)	-1216(4)	1859(3)	4320(3)	37(1)	C(20)	3122(5)	4636(4)	4724(4)	66(2)
C(1)	-944(4)	2962(3)	5895(3)	38(1)	C(21)	4187(5)	3976(5)	4323(4)	74(2)
C(2)	-2263(4)	2450(3)	6420(3)	39(1)	C(22)	4201(5)	2851(5)	4600(4)	69(2)
C(3)	-2704(4)	1514(3)	5980(3)	42(1)	C(23)	3141(4)	2362(4)	5262(4)	54(2)
C(4)	-3962(4)	980(3)	6385(3)	54(1)	C(24)	1135(5)	1687(4)	3111(4)	66(2)
C(5)	-4751(4)	1436(4)	7216(4)	61(2)	C(25)	1567(6)	936(4)	2222(4)	75(2)
C(6)	-4371(4)	2418(4)	7667(3)	56(2)	C(26)	2732(6)	1389(5)	1437(4)	82(2)
C(7)	-5250(5)	2931(5)	8494(4)	78(2)	C(27)	3122(9)	586(6)	561(5)	120(3)
C(8)	-4862(7)	3888(6)	8913(4)	87(2)	C(28)	-2041(4)	2096(3)	3286(3)	40(1)
C(9)	-3628(6)	4392(4)	8566(4)	75(2)	C(29)	-2576(5)	1239(3)	2763(3)	56(2)
C(10)	-2730(5)	3928(4)	7769(3)	58(2)	C(30)	-3331(5)	1424(4)	1899(4)	70(2)
C(11)	-3108(4)	2943(3)	7285(3)	46(1)	C(31)	-3572(6)	2519(5)	1542(4)	73(2)
C(12)	531(4)	2709(3)	7815(3)	43(1)	C(32)	-3063(5)	3376(4)	2030(4)	67(2)
C(13)	-177(6)	2016(4)	8602(4)	69(2)	C(33)	-2308(5)	3177(3)	2896(3)	55(2)
C(14)	-340(7)	2298(6)	9656(4)	86(2)					



Fig. 2. Location of molecules in the crystal of 5 (dashed lines indicate the hydrogen bonds).

							-
Table	2.	Bond	lengths	(d)	in	molecule	5

Bond	d/Å	Bond	d/Å	
P(1) - O(1)	1.486(3)	O(2) - C(1)	1.414(4)	
O(2) - B(1)	1.442(5)	O(3) - C(3)	1.356(4)	
O(3) - B(1)	1.490(5)	C(1) - C(2)	1.504(5)	
N(1) - B(1)	1.619(5)	C(2) - C(3)	1.366(5)	
P(1) - C(1)	1.854(4)			

Table 3. Bond angles (ω) in molecule 5

Angle	ω/deg	Angle	ω/deg
O(1) - P(1) - C(1)	112.9(2)	O(1) - P(1) - C(12)	111.8(2)
C(1) - P(1) - C(12)	106.7(2)	O(1) - P(1) - C(18)	111.1(2)
C(1) - P(1) - C(18)	104.5(2)	C(12) - P(1) - C(18)	109.4(2)
B(1) - O(2) - C(1)	119.4(3)	B(1) - O(3) - C(3)	116.7(3)
B(1) - N(1) - C(24)	115.9(3)	O(2) - B(1) - O(3)	113.6(3)
O(2) - B(1) - N(1)	108.5(3)	O(3) - B(1) - N(1)	101.3(3)
O(2) - B(1) - C(28)	112.2(3)	O(3) - B(1) - C(28)	111.6(3)
N(1)-B(1)-C(28)	108.8(3)	P(1) - C(1) - O(2)	109.1(2)
P(1) - C(1) - C(2)	112.8(2)	O(2) - C(1) - C(2)	111.6(3)
C(1) - C(2) - C(3)	116.6(3)	C(1)-C(2)-C(11)	123.5(3)
P(1)-C(12)-C(13)	118.3(3)	O(3) - C(3) - C(2)	121.1(3)
P(1) - C(18) - C(19)	123.3(3)	C(2) - C(3) - C(4)	121.6(3)
P(1) - C(12) - C(17)	124.1(3)	C(4) - C(5) - C(6)	121.9(4)
P(1)-C(18)-C(23)	118.0(3)	C(5)-C(6)-C(11)	119.8(4)

Molecule 5 consists of 1,3,2-dioxaborinane fused with naphthalene. The phosphoryl and amino groups have pseudoaxial orientation and are cis-located relative to the heterocycle plane (see Fig. 1). The O atom of the phosphoryl group lies under the heterocycle plane. The P, B, and N atoms have tetrahedral coordination (the angles vary within 106.7(2)-112.9(2)°, 101.3(3)-113.6(3)°, and 102.4(2)-115.9(2)°, respectively). The B-N distance is 1.619(5) Å; the B(1)-O(2) [1.442(5) Å] and B(1)-O(3) [1.490(5) Å] distances differ somewhat, which correlates with the different O(2)-C(1) [1.414(4) Å] and O(3)-C(3) [1.356(4) Å] bond lengths. The six-membered BOCCCO ring is planar to within 0.18 Å and forms an angle of 22.9° with the plane of the naphthalene fragment. The C(1), C(2), and O(3) atoms are coplanar to within 0.005 Å. No stacking-type intra- or intermolecular interactions were found. However, we should note the formation of an intermolecular hydrogen bond, $N(1) - H(1) \cdot \cdot \cdot O(1)$ [the N-H distance is 0.93(4) Å, H-O is 1.96(4) Å, N···O is 2.863(3) Å, the N-H-O angle is 164(2)°]. These bonds assemble the molecules into centrosymmetrical dimers (see Fig. 2).

According to one method, novel 1,3,2-dioxaborinanes containing an exocyclic P atom can be obtained by changing the borylating agent. Previously,⁶ an alkyl diphenylborate has been used for this purpose; the use of boric acid as the reagent resulted in 2-[(2-hydroxy-1-naphthyl)(diphenylphosphinoyl)methoxy]-4-diphenyl-phosphinoyl-4H-1,3-dioxa-2-boraphenanthrene (6) (Scheme 3), whose molecule contains one B atom for two P atoms. As noted above, compounds that contain a tetracoordinated B atom and a P-C-O-B moiety readily undergo oxidation; therefore, this procedure gave only the corresponding phosphine oxide.

The ³¹P spectra of compound **6** contain one signal at δP 28.28, which indicates that the phosphoryl groups in the molecule are equivalent due to bicyclo-monocyclo tautomerism.² The IR spectrum of the crystalline borate **6** contains a broad band with a maximum at 3056 cm⁻¹, which corresponds to the vibrations of the bound phenolic hydroxyl group, whereas the intense band of B^{III}—O bond vibrations in the region of 1340—1360 cm⁻¹ is not observed. This allowed us to assume that compound **6** has a spiro-bicyclic structure due to the formation of an O—B intramolecular coordination bond.

Treatment of compound **6** with triethylamine gives complex 7, whose ³¹P NMR spectra also contain only one signal at δ P 30.33. The IR spectrum of the crystal-line complex 7 does not contain absorption bands of the

Scheme 3



N⁺—H bond (2500–2700 cm⁻¹), of hydroxyl groups (3200–3400 cm⁻¹), or of the B^{III}—O fragment (~1350 cm⁻¹). On the other hand, the IR spectra of solutions of compound 7 contain absorption bands of the N⁺—H bond (2476 and 2730 cm⁻¹) and of hydroxyl groups (3340 and 3660 cm⁻¹). Probably, crystalline compound 7 exists as a complex, whereas in solution it exists in equilibrium with the ionic form due to ion-complex tautomerism.² The absence of absorption of the characteristic groups in the crystalline state has been previously observed for a complex of triethylamine with (α -diphenyl-boryloxy-2-hydroxybenzyl)(α ,2-dihydroxybenzyl)phenyl-phosphine, whose IR spectra did not show the presence of the three hydroxyl groups.⁷

Compound 8, which contains two dioxaborinane rings at one P atom, was obtained according to Scheme 4.

Scheme 4



The molecule of compound 8 incorporates two asymmetric C atoms; for this reason, it exists as a diastereomeric mixture. The ³¹P spectra contain two signals at δP 12.27 and 10.37, whose ratio is 1 : 2. The downfield shift of the signals should be noted. A comparison of the positions of the signals of phosphines 8, 2 (δP 7.3), and 1 $(\delta P \ 10)^3$ allowed us to assume that intramolecular dispersion interaction exists in compound 8. like in the two latter compounds. However, dissolution of compound 8 in pyridine gives a mixture of products characterized by ³¹P NMR chemical shifts of -23.89, -27.61, -36.43, and -40.23 ppm and ${}^{1}J_{P,H}$ of 211.3, 224.8, 207.5, and 211.9 Hz, respectively. The ¹H NMR spectra of phosphine 8 in acetone- d_6 contain a signal of the aldehyde proton at δ 10.04, which indicates that the compound undergoes hydrolytic decomposition to a significant extent. A similar ready hydrolysis has been

observed previously³ for 1,3,2-dioxaborinane 1. Compound 8 is readily oxidized in solution to give oxide 9.

Thus, there are intramolecular dispersion interactions in fused 4-phosphino-1,3,2-dioxaborinanes containing a tricoordinated P atom. The reactivity of these 1,3,2-dioxaborinanes is somewhat similar to that of the anomalously stable dioxaboraphosphorinanes: of B,P-compounds belonging to both types, the compounds with similar coordination of the P and B atoms display the highest stability.

Experimental

 31 P NMR spectra were recorded on Bruker MSL-400 (161 MHz) and YaMR-KGU-4 (10.2 MHz) spectrometers. 11 H NMR spectra were obtained on Bruker MSL-400 (400 MHz) and Bruker WM-250 (250 MHz) spectrometers. IR spectra of suspensions in vaseline oil and of solutions were recorded on a Specord M-80 spectrophotometer. Mass spectra (EI) of compound 2 were recorded on an MKh-1310 mass spectrometer controlled by an SM-4 computer; the energy of ionizing electrons was 70 eV, and the current of the electron collector was 70 μ A. The compounds were introduced directly into the ion source at 100 °C. Exact measurement of ion masses was performed automatically based on reference peaks of perfluorokerosene.*

2-Phenyl-4-diphenylphosphinoyl-4H-1,3-dioxa-2-boraphenanthrene (2). Diisobutyl phenylborate (1.66 g, 7.09 mmol) and diphenylphosphine (1.32 g, 7.1 mmol) were added to a solution of 2-hydroxy-1-naphthaldehyde (1.22 g, 7.09 mmol) in benzene (5 mL). After 3 h, the reaction mixture was concentrated *in vacuo*, and the resulting crystals were filtered off and washed with acetonitrile to give compound **2** (2.24 g, 70 %). Recrystallization from an acetonitrile—DMF mixture (3 : 1) gave a sample for analysis, m.p. 192–196 °C. Found (%): C, 77.68; H, 4.76; P, 7.39. C₂₉H₂₂BO₂P. Calculated (%): C, 78.38; H, 4.96; P, 6.98. IR, v/cm⁻¹: 1350 (B^{III}–O). ³¹P NMR (C₆H₆), δ : 7.3.

A complex of 2-phenyl-4-diphenylphosphinoyl-4H-1,3-dioxa-2-boraphenanthrene with pyridine (3). Compound 2 (0.2 g, 0.45 mmol) was dissolved in pyridine (0.5 mL). Immediately after dissolution, the ³¹P NMR spectrum of the reaction mixture contained one signal at δP 2. The white crystals that precipitated on standing were filtered off and washed with acetonitrile. The filtrate was concentrated; the crystals that precipitated were washed with acetonitrile and combined with the first portion to give 0.1 g (43 %) of compound 3. Recrystallization from pyridine gave a sample for analysis, m.p. 195 °C (decomp.). Found (%): C, 76.29; H, 4.68; N, 3.09; P, 5.78. C₃₄H₂₇BNO₃P. Calculated (%): C, 75.69; H, 5.01; N, 2.59; P, 5.75. IR, v/cm⁻¹: 1185 (P=O). ³¹P NMR (C₆H₆), δ : 27.3.

The reaction of compound 2 with 1,2-naphthoquinone. 1,2-Naphthoquinone (0.18 g, 1.1 mmol) was added to a solution of compound 2 (0.5 g, 1.1 mmol) in benzene (3 mL). After some time, an unidentified precipitate (m.p. >250 °C) was separated, and the filtrate was concentrated *in vacuo*. The resulting crystals were filtered off and washed with acetonitrile to give 0.19 g (37 %) of 2-phenyl-4-diphenylphosphoryl-4H-

1,3-dioxa-2-boraphenanthrene (**4**), m.p. 215–218 °C. Found (%): C, 74.85; H, 4.97; P, 7.21. $C_{29}H_{22}BO_3P$. Calculated (%): C, 75.65; H, 4.78; P, 6.73. IR, v/cm⁻¹: 1360 (B¹¹¹–O); 1190 (P=O). ³¹P NMR (C₆H₆), δ : 27.3.

The reaction of compound 2 with 2,3-di(*N*-butylimino)butane. A solution of 2,3-di(*N*-butylimino)butane (0.2 g, 1.04 mmol) in benzene (3 mL) was added to compound 2 (0.48 g, 1.04 mmol). After 3 h, the reaction mixture was concentrated *in vacuo*, and the precipitate was crystallized from acetonitrile to give 0.15 g (27 %) of a 2-phenyl-4diphenylphosphinoyl-4*H*-1,3-dioxa-2-boraphenanthrene butylamine complex (5). Recrystallization from acetonitrile gave a sample for analysis, m.p. 130–136 °C (decomp.). Found (%): C, 74.25; H, 6.77; N, 3.02; P, 5.98. C₃₃H₃₃BNO₃P. Calculated (%): C, 74.30; H, 6.19; N, 2.63; P, 5.82. IR, v/cm⁻¹: 3196 (N-H); 1154 (P=O). ¹H NMR (acetone-d₆), δ : 0.63–1.71 (m, 7 H, CH₂CH₂CH₃); 3.58–3.82 (m, 2 H, NCH₂); 6.75–8.50 (m, 22 H, CH, ArH). ³¹P NMR (C₆H₆), δ : 33.02.

2-[(2-Hydroxy-1-naphthyl)(diphenylphosphinoyl)methoxy]-4-diphenylphosphinoyl-4*H*-1,3-dioxa-2-boraphenanthrene (6). A mixture of diphenylphosphine (0.94 g, 5.0 mmol), 2-hydroxy-1-naphthaldehyde (0.86 g, 5.0 mmol), and boric acid (0.31 g, 5.0 mmol) in benzene (20 mL) was refluxed with a Dean–Stark trap until water evolution ceased. The unreacted boric acid was filtered off, the filtrate was concentrated *in vacuo*, and the residue was crystallized from ether to give 1.12 g (59 %) of compound **6**. Recrystallization from DMF gave a sample for analysis, m.p. 200–205 °C. Found (%): C, 72.21; H, 4.76; P, 8.15. C₄₆H₃₅BO₆P₂. Calculated (%): C, 73.01; H, 4.63; P, 8.20. IR, v/cm⁻¹: 3056 br (O–H); 1166 (P=O). ³¹P NMR (C₆H₆), δ : 28.28.

A complex of 2-[(2-hydroxy-1-naphthyl)(diphenylphosphinoyl)methoxy]-4-diphenylphosphinoyl-4H-1,3-dioxa-2-boraphenanthrene with triethylamine (7). Triethylamine (0.16 g, 1.6 mmol) was added to a suspension of compound 6 (0.4 g, 0.53 mmol) in benzene (3 mL) to give a solution that crystallized after several hours; the crystals that precipitated were filtered off and washed with acetonitrile to give 0.22 g (48 %) of compound 7, m.p. 184–190 °C. Found (%): C, 72.11; H, 6.24; N, 1.95; P, 6.98. $C_{52}H_{50}BNO_6P_2$. Calculated (%): C, 72.81; H, 5.83; N, 1.63; P, 7.23. IR, ν/cm^{-1} : (in vaseline oil): 1160 (P=O); (in CHCl₃): 3660, 3340 br (O-H); 2730, 2476 (N⁺-H); 1168 (P=O). ¹H NMR (DMSO-d₆), δ : 1.83 (t, 9 H, CH₃, ${}^{3}J_{H,H} = 7$ Hz); 2.96 (q, 6 H, NCH₂, ${}^{3}J_{H,H} = 7$ Hz); 6.73–8.33 (m, 34 H, CH, ArH). ³¹P NMR (DMSO), δ : 30.33.

Bis(benzo[d]-2-phenyl-1,3,2-dioxaborinane-4-yl)phenylphosphine (8). A solution of diisobutyl phenylborate (6.35 g, 27 mmol) and salicylic aldehyde (3.28 g, 27 mmol) in benzene (10 mL) was added to phenylphosphine (1.48 g, 13.5 mmol). After the exothermic reaction ceased, the solvent was removed *in vacuo*, and the precipitate was crystallized from ether. The resulting crystals of bis(benzo[d]-2-phenyl-1,3,2-dioxaborinan-4-yl)phenylphosphine oxide (9) were filtered off and washed with acetonitrile gave a sample for analysis, m.p. 207–212 °C. Found (%): C, 71.26; H, 4.73; P, 5.88. $C_{32}H_{25}B_{2}O_{5}P$. Calculated (%): C, 70.85; H, 4.61; P, 5.72. IR, v/cm⁻¹: 1340 (B^{III}–O); 1180 (P=O). ³¹P NMR (C₆H₆), 8: 31

When the filtrate was cooled to 0 °C, crystals precipitated (a mixture of compounds 8 and 9), which were filtered off and washed with acetonitrile; yield 2.26 g. The filtrate was concentrated, and the residue was crystallized from acetonitrile to give 2 g (28 %) of compound 8, m.p. 126-129 °C. Found (%): C, 73.07; H, 5.14; P, 6.14. C₃₂H₂₅B₂O₄P. Calculated

^{*} The mass spectra were obtained by R. Z. Musin (Ph.D. (Chem.)).

(%): C, 73.00; H, 4.75; P, 5.89. IR, v/cm^{-1} : 1330 (B^{III}-O). ³¹P NMR (C₆H₆), δ : 10.37 and 12.27.

A monocrystal of C₃₃H₃₃BNO₃P, which was obtained from acetone-d₆ as a colorless transparent prism measuring 0.3×0.3×0.4 mm, was studied at 173 K on a Siemens P3/PC four-circle automated diffractometer (Mo-Ka irradiation, graphite monochromator, $\theta/2\theta$ -scanning). The crystals are triclinic, a = 9.797(3) Å, b = 11.938(4) Å, c = 12.513(3) Å, $\alpha =$ 86.8(2)°, $\beta = 83.3(2)°$, $\gamma = 89.51(2)°$, space group P1, V =1453.0(7) Å³, z = 2, M = 533.4, $d_{calc} = 1.219$ g cm⁻³, μ (Mo-K α) 0.129 mm⁻¹, F(000) = 564. The intensities of 4620 independent reflections were measured in the range $2^{\circ} < 2\theta < 46^{\circ}$. The structure was solved by the direct method using SHELXTL PLUS programs on an IBM PC/AT-386 computer and refined by the full-matrix least-squares method in the anisotropic approximation for the nonhydrogen atoms. The H atoms were refined in the isotropic approximation to R =0.0614, $R_{\rm w} = 0.0661$ (the refinement used 2991 reflections with $I \geq 3\sigma(I)$.

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