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Reaction of (Phenylenedioxy)trihalophosphoranes with Arylacetylenes:
VI.[1] Regiochemistry of the Reaction of 2,2,2-Trihalo-5-methylbenzo[*d*][1,3,2]dioxaphospholes with Arylacetylenes

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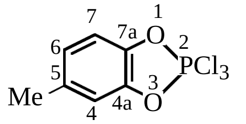
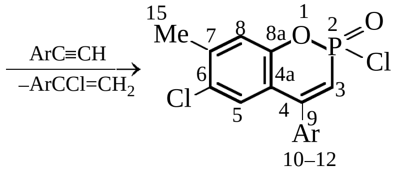
Abstract—NMR and IR spectroscopy and X-ray diffraction were used to show that the reaction of 2,2,2-trichloro- and 2,2,2-tribromo-5-methylbenzo[*d*][1,3,2]dioxaphospholes with *para*-substituted arylacetylenes proceeds with regioselective formation of 4-aryl-2-halo-7-methyl-2- oxobenzo[*e*][1,2]oxaphosphorines. With the trichlorophosphole, selective chlorination of the phenylene fragment in the *para* position to the endocyclic oxygen atom occurs. With the tribromophosphole, 6-bromo- and unsubstituted benzo[*e*][1,2]oxaphosphorines are formed as major products. The molecular and supramolecular structure of some of the obtained oxaphosphorines was studied by X-ray diffraction.

We recently showed [2] that the reaction of 2,2,2-trichlorobenzo[*d*][1,3,2]dioxaphosphole (**I**) with arylacetylenes unexpectedly provides 4-aryl-2,6-dichlorobenzo[*e*][1,2λ^5]oxaphosphorine 2-oxides. This mechanistically rather complex reaction involves facile formation of the phosphoryl group and carbon–phosphorus bond, *ipso* substitution of the oxygen atom, and regioselective chlorination of the phenylene substituent in the *para* position to the oxygen atom of the foming benzo[*e*][1,2]oxaphosphorine ring. Introduction of one, two, or four halogen atoms in the *o*-phenylene fragment of starting phosphole **I** does not alter the reaction pathway [3–5], but the regioselective chlorination of the benzo fragment to form 4-aryl-2,6,7-trihalobenzo[*e*][1,2]oxaphosphorines takes place only if it bears only one halogen substituent.

In this work we present the results of investigation of the effect of the electron-donor methyl substituent in the phenylene fragment of 2,2,2-trichloro- and 2,2,2-tribromo-5-methylbenzo[*d*][1,3,2]dioxophospholes (**II**, **III**) on the synthetic result of their reaction with arylacetylenes. It was found that the reaction of compound **II** with arylacetylenes proceeds with a high degree of regioselectivity and leads mainly (or exclusively) to a phosphonate product. The product gives a singlet at 17–18 ppm in the ^{31}P–{^{1}H} NMR spectrum, that convents into a doublet ($^2J_{PCH}$ 23–24 Hz) in the proton-coupled spectrum. The ^{1}H NMR spectrum diplays a downfield (δ 6.28–6.34 ppm) doublet with the same constant, belonging to the P–CH=C(Ar) proton. Considering the mass and ^{13}C NMR spectral data (see below) we identified the product as benzophosphorine **IV**.



II



IV

Ar = Ph (**a**), 4-Cl–C_6H_4 (**b**), 4-Me–C_6H_4 (**c**).

The structure of the obtained compounds was confirmed by electron impact mass spectrometry, using the example of compound **IVb**. The mass spec-

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[1] For communication V, see [1].

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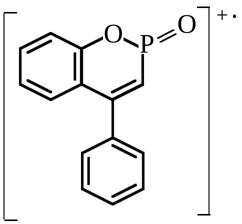
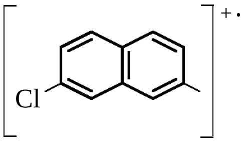
trum of the latter contains ion peaks at *m/z* 358, 360, and 362, that relate to the molecular ion ($M^{+\cdot}$) with the formula $C_{15}H_{10}Cl_3O_2P$. The intensity ratio of these peaks is 1.0 : 0.97 : 0.32 and agrees with the intensity ratio of the isotope peaks for the $M^{+\cdot}$ ion of **IVb**, calculated from its empirical formula. The first stage of fragmentation of compound **IVb** under electron impact involves elimination of the chlorine atom from the phosphorinane phosphorus atom. This process gives rise to an *m/z* 323 ion. The latter easily loses an HCl molecule to form an *m/z* 287 ion. The loss of hydrogen chloride evidently proceeds from the chlorine-substituted benzo fragment. An intense peak at *m/z* 241 belongs to ion **A** of the composition $C_{14}H_{10}O_2P$, which lacks all the three chlorine atoms and the methyl group.


A


B

The base peak in the mass spectrum is at *m/z* 176. It can be evidently assigned to chloronaphthalene ion **B** resulting from complex rearrangements. This ion is evidently formed from the *m/z* 287 ion via cleavage of the C–O and C–C bonds in the phosphorinane ring, accompanied by rearrangement of the aromatic substituent in the 4 position. Such processes forming of polyphenyl ions and involving rearrangement of aromatic rings under electron impact are also characteristic of organophosphorus compounds with several aromatic substituents [6]. Other fragment ions at low *m/z* values in the mass spectrum of compound **IVb** are likely to be formed by consecutive fragmentation of the above-mentioned ions.

Hence, the chlorination attendant in the formation of benzophosphorines probably involves the phenylene fragment of the molecule. The fact that the chlorine atom is present just in this fragment is proved by the ^1H NMR spectra. Hence, the aromatic resonance region contains, together with two complex multiplees of phenyl protons, two singlets related to the tetrasubstituted phenylene ring (see Experimental). Therewith, the lack of any signal splitting is unambiguous evidence for a *para* position of the corresponding protons. In this case, it is evident that the methyl group and the chlorine atom locate *para* to the carbon and oxygen atoms of the annelated phosphorine heteroring.

To establish mutual location of the chlorine atom and the methyl group, i.e. regiochemistry of the *ipso* substitution of the oxygen atom, we performed a more detailed structural study of the benzophosphorines obtained by means of ^{13}C NMR spectroscopy, using the example of compound **IVa** (see Table 1).

Table 1. ^{13}C–{^1H} NMR spectral data (100.6 MHz, $CDCl_3$) for benzophosphorines **IV, V, VII–XII, XV**, and **XVI** (parenthesized is the shape of the signal in the ^{13}C NMR spectrum), δ_C, ppm (*J*, Hz)

Atom	**IVa** (25°C, $CDCl_3$)	**Vc**^{a} (40°C, DMSO-d_6)	**VIIb**^{b} (50°C, DMSO-d_6)	**VIIc**^{c} (50°C, DMSO-d_6)
C^3	114.02 d (d.d) (154.6, PC^3; 171.4, HC^3)	115.19 d (d.d) (169.0, PC^3; 163.5, HC^3)	117.09 d (d.d) (155.4, PC^3; 162.5, HC^3)	116.10 d (d.d) (156.4, PC^3; 161.6, HC^3) 151.30 s (m)
C^4	155.49 d (m) (2.0, PC^3C^4)	150.24 d (m) (1.8, PC^3C^4)	149.94 d (m) (1.5, PC^3C^4)	151.30 s (m)
C^{4a}	120.32 d (br.d.d.d) (17.9, HC^3CC^{4a}; 7.7, PC^3CC^{4a}; 5.9, HC^8CC^{4a})	121.03 d (br.d.d.d) (16.4, PC^3CC^{4a}; 8.4, HC^3CC^{4a}; 6.0, HC^8CC^{4a})	120.21 d (br.d.d.d) (17.7, PC^3CC^{4a}; 8.9, HC^3CC^{4a}; 6.1, HC^8CC^{4a})	120.55 d (m) (17.8, PC^3CC^{4a})
C^5	129.27 d (br.d) (1.6, $POCCC^5$; 166.8, HC^5)	HC^8CC^{4a}) 127.37 d (br.d) (1.0, $POCCC^5$; 164.7, HC^5)	HC^8CC^{4a}) 128.72 s (d) (164.7, HC^5)	127.51 s (d) (163.9, HC^5)
C^6	130.37 d (m) (1.5, $POCCCC^6$; 10.1, HC^8CC^6; 5.0, H^3CCC^6; 5.0, HC^5C^6)	126.93 d (br.d. q) (1.1, $POCCCC^6$; 10.2, HC^8CC^6; 5.5,H^3CCC^6; 4.5, HC^5C^6)	127.15 s (d.q.d) (10.6, HC^8CC^6; 6.6, $H^3CC^7C^6$; 4.6, HC^5C^6)	127.04 s (m)
C^7	141.10 s (d.q) (6.3, HC^5CC^7; 6.3, H^3CC^7)	138.26 s (d.q) (6.3–6.4, HC^5CC^7; 6.3–6.4, H^3CC^7)	138.81 s (q.d) (6.3, H^3CC^7; 6.3, HC^5CC^7)	138.64 s (q. d) (6.2, HC^5CC^7; 6.2, H^3CC^7)

Table 1. (Contd.)

Atom	**IVa** (25°C, CDCl$_3$)	**Vc**^{a} (40°C, DMSO-d_6)	**VIIb**^{b} (50°C, DMSO-d_6)	**VIIc**^{c} (50°C, DMSO-d_6)
C^{8}	121.53 d (d.d.q.d) (8.1, POCC^{8}; 164.6, HC^{8}; 5.0, HC^{15}CC^{8}; 1.2, HC^{5}CCC^{8})	121.17 d (d.d.q) (164.0, HC^{8}; 7.1, POCC^{8}; 5.2–5.3, H^{3}CCC^{8})	121.58 d (d.d.q) (163.1, HC^{8}; 6.6, POCC^{8}; 4.7–4.8, H^{3}CC^{7}C^{8})	121.57 d (d.d.q) (161.6, HC^{8}; 6.9–7.0, POCC^{8}; 5.5, H^{3}CCC^{8})
C^{8a}	149.10 d (d.d.d) (10.1, POC^{8a}; 10.1, HC^{5}CC^{8a}; 4.4, HC^{8}C^{8a})	149.44 d (d.d.d) (9.2, HC^{5}CC^{8a}; 7.2, POC8^{a}; 4.0, HC^{8}C^{8a})	149.85 d (d.d.d) (9.3–9.5, HC^{5}CC^{8a}; 7.8, POC^{8a}; 3.8, HC^{8}C^{8a})	149.95 d (d.d.d) (9.2–9.3, HC^{5}CC^{8a}; 7.7, POC8^{a}; 3.7, HC^{8}C^{8a})
C^{9}	136.60 d (br.d.t.d) (20.6, PCCC^{9}; 7.1, HC^{11}CC^{9}; 6.0, HC^{3}CC^{9})	134.72 d (d.t.d) (18.5, PCCC^{9}; 7.5, HC^{11}CC^{9}; 6.2, HC^{3}CC^{9})	136.68 d (br.d.t.d) (17.8, PCCC^{9}; 7.3–7.5, HC^{11}CC^{9}; 6.3, HC^{3}CC^{9})	135.05 d (br.d.t.d) (17.8, PCCC^{9}; 7.8, HC^{11}CC^{9}; 6.5, HC^{3}CC^{9})
C^{10}	128.03 s (br.d.m) (162.0, HC^{10}; 5.7–6.1, HCCC^{10})	127.61 s (d.d) (160.0, HC^{10}; 6.1, HCCC^{10})	128.73 s (d.d) (168.3, HC^{10}; 5.3, HCCC^{10})	127.99 s (d.d) (159.1, HC^{10}; 6.6,HCCC^{10})
C^{11}	128.74 s (d. m) (163.0, HC^{11}; 6.4–6.7, H^{3}CCC^{11})	128.86 s (d.d.q) (160.0, HC^{11}; 6.1, HCCC^{11}; 5.0, H^{3}CCC^{11})	130.00 s (br.d.d) (164.6, HC^{11}; 7.1, HCCC^{11})	129.25 s (d.d. q) (159.0, HC^{11}; 6.2, HCCC^{11}; 5.1, H^{3}CCC^{11})
C^{12}	129.75 s (d.t) (161.9, HC^{12}; 7.1, HC^{10}CC^{12})	138.13 s (t.q) (6.7, HC^{10}CC^{12}; 6.3, H^{3}CC^{12})	133.70 s (t.t) (11.0, HC^{10}CC^{12}; 3.2–3.3, HC^{11}C^{12})	138.47 s (q.t) (6.4, H^{3}CC^{12}; 6.4, HC^{10}CC^{12})
CH$_3$C^{7}	19.97 s (q.d) (128.7, HC; 4.7, HC^{8}CC)	18.87 s (br.q.d) (128.6, HC; 4.7, HC^{8}C^{7}C)	19.27 s (q. d) (128.4, HC^{13}; 4.5, HC^{8}C^{7}C)	19.31 s (q.d) (128.8, HC; 4.8, HC^{8}CC)

Atom	**VIIIa**^{d} (50°C, DMSO-d_6)	**VIIc**^{e} (50°C, DMSO-d_6)	**IX** (25°C, CDCl$_3$)	**X** (25°C, CDCl$_3$)
C^{3}	123.49 d (d.d) (163.6, PC^{3}; 156.9, HC^{3})	123.61 d (d.d) (163.8, PC^{3}; 155.7, HC^{3})	114.89 d (d.d) (142.6, PC^{3}; 171.7, HC^{3})	116.18 d (d.d) (142.0, PC^{3}; 171.7, HC^{3})
C^{4}	144.67 d (m)	144.42 s (m)	155.80 d (m) (2.0, PC^{3}C^{4})	154.47 d (m) (1.7, PC^{3}C^{4})
C^{4a}	122.83 d (m) (15.3, PC^{3}CC^{4a}; 9.2, HC^{3}CC^{4a}; 5.9, HC8CC4^{a})	123.11 d (d.d.d) (15.3, PC^{3}CC^{4a}; 8.7, HC^{3}CC^{4a}; 6.1, HC8CC4^{a})	118.54 d (br.d.d.d) (18.0, PC^{3}CC^{4a}; 7.8–7.9, HC^{3}CC^{4a}; 5.4–5.6, HC8CC4^{a})	120.49 d (br.d.d.d) (18.1, PC^{3}CC^{4a}; 7.8–7.9, HC^{3}CC^{4a}; 5.4–5.6, HC8CC4^{a})
C^{5}	126.75 s (d) (164.1, HC^{5})	126.85 s (d) (162.9, HC^{5})	129.40 d (br.d) (162.5, HC^{5}; 1.6, POCCC^{5})	132.48 d (br.d) (168.0, HC^{5}; 1.4, POCCC^{5})
C^{6}	125.04 s (m) (10.5, HC^{8}CC^{6}; 5.1, H^{3}CC^{7}C^{6}; 5.0, HC^{5}C^{6})	124.97 s (d.d.q) (10.5, HC^{8}CC^{6}; 5.0, H^{3}CC^{7}C^{6}; 5.0, HC^{5}C^{6})	125.70 d (d.m) (1.6, POCCCC^{6}; 162.4, HC^{6}; 6.1, HC^{8}CC^{6}; 5.0, H^{3}CCC^{6})	120.24 d (m) (1.7, POCCCC^{6}; 10.1, HC^{8}CC^{6}; 4.7–5.0, HC^{5}C^{6}; 5.0–6.0, H^{3}CCC^{6})
C^{7}	136.40 s (q.d) (6.1, H^{3}CC^{7}; 6.1, HC^{5}CC^{7})	136.25 s (q.d) (6.2, HC^{5}CC^{7}; 6.2, H^{3}CCC^{7})	143.61 s (d.q) (8.7, HC^{5}CC^{7}; 6.1, H^{3}CC^{7})	143.01 s (d.q) (6.4, HC^{5}CC^{7}; 6.4, H^{3}CC^{7})
C^{8}	121.41 d (d.d.q) (161.4, HC^{8}; 5.5, POCC^{8}; 4.3, H^{3}CC^{7}C^{8})	121.49 d (d.d.q) (161.5, HC^{8}; 5.4, POCC^{8}; 5.4–5.5, H^{3}CCC^{8})	128.49 s (d. m) (162.3, HC^{11}; 6.6–6.7, HCCC^{11})	121.41 d (d.m) (8.1, POCC^{8}; 5.1–5.2, H^{3}CCC^{8}; 1.1, HC^{5}CCC^{8})
C^{8a}	151.79 d (m) (7.1, POC8^{a}; 3.3, HC^{8}C^{8a})	152.03 d (d.d.d) (9.1, HC^{5}CC^{8a}; 6.9, POC^{8a}; 3.7–3.8, HC^{8}C^{8a})	119.79 d (d.m) (162.4, HC^{8}; 8.0, POCC^{8}; 6.3–6.5, H^{3}CCC^{8}; 1.1, HC^{5}CCC^{8})	149.64 d (d.d.d) (10.5, POC^{8a}; 10.5, HC^{5}CC^{8a}; 4.3, HC^{8}C^{8a}) 5.0–5.5, HC^{3}CC^{9})
C^{9}	139.47 d (d.t.d) (16.7, PCCC^{9}; 7.6, HC^{11}CC^{9}; 5.5, HC^{3}CC^{9})	136.76 d (d.t.d) (16.2, PCCC^{9}; 7.7, HC^{11}CC^{9}; 6.5, HC^{3}CC^{9})	150.62 d (m) (10.6, POC^{8a}; 10.6, HC^{5}CC^{8a}; 4.3, HC^{8}C^{8a})	136.20 d (m) (20.9, PCCC^{9}; 7.4, HC^{11}CC^{9};
C^{10}	127.98 s (br.d.d.d) (160.7, HC^{10}; 6.9, HCCC^{10}; 6.9–7.1, HC^{12}CC^{10})	127.98 s (d.d) (159.0, HC^{10}; 6.6, HCCC^{10})	136.91 d (m) (20.9, PCCC^{9}; 7.6, HC^{11}CC^{9}; 5.0–5.5, HC^{3}CC^{9})	127.98 s (br.d. m) (161.7, HC^{10}; 7.5, HCCC^{10}; 6.2–6.6, H^{12}CCC^{10})

Table 1. (Contd.)

Atom	**VIIIa**[d] (50°C, DMSO-d_6)	**VIIc**[e] (50°C, DMSO-d_6)	**IX** (25°C, CDCl$_3$)	**X** (25°C, CDCl$_3$)
C^{11}	128.40 s (br.d.d) (162.3, HC^{11}; 7.8, HCCC^{11})	129.06 s (d.d.q) (158.3, HC^{11}; 6.0, HCCC^{11}; 5.4, H^{3}CCC^{11})	128.08 s (br.d. m) (161.7, HC^{10}; 7.5, HCCC^{10}; 6.2–6.6, H^{12}CCC^{10})	128.74 s (d.m) (162.2, HC^{11}; 6.7, HCCC^{11})
C^{12}	127.89 s (d.t) (160.3, HC^{10}; 8.0, HC^{10}CC^{12})	137.33 s (q.d) (6.4, H^{3}CC^{12}; 6.4, HC^{10}CC^{12})	129.47 s (d.t) (161.8, HC^{12}; 7.8, HC^{10}CC^{12})	129.82 s (d.t) (161.5, HC^{12}; 7.0, HC^{10}CC^{12})
*C*H$_3$C^7	19.06 s (q.d.d) (128.2, HC; 4.0, HC^{8}C^{7}C; 1.1, HC^{5}C^{6}C^{7}C)	19.20 s (q.d) (128.2, HC; 4.8, HC^{8}CC)	21.18 s (q.d.d) (127.5, HC; 4.4, HC^{6}CC; 4.4, HC^{8}CC)	22.89 s (q.d) (128.9, HC; 4.5, HC^{8}CC)

Atom	**XI** (25°C, CDCl$_3$)	**XII** (50°C, CDCl$_3$)	**XV**[f] (50°C, DMSO-d_6)	**XVIc**[g] (50°C, DMSO-d_6)
C^3	116.03 d (d.d) (142.1, PC^3; 171.2, HC^3)	116.36 d (d.d) (141.9, PC^3; 171.0–173.0, HC^3)	117.02 d (d.d) (155.8, PC^3; 161.7, HC^3)	118.47 d (d.d) (155.0, PC^3; 162.1, HC^3)
C^4	155.82 d (m) (1.8, PC^{3}C^4)	154.76 d (m) (1.6, PC^{3}C^4)	151.40 d (m) (2.0, PC^{3}C^4)	150.08 d (m) (1.6, PC^{3}C^4)
C^{4a}	120.80 d (m) (17.8, PC^{3}CC^{4a})	120.85 d (m) (17.9, PC^{3}CC^{4a})	119.14 d (m) (15.5, PC^{3}CC^{4a})	121.53 d (m) (16.0, PC^{3}CC^{4a}; 7.4–7.5, HC^{3}CC^{4a}; 6.0–7.0, HC^{8}CC^{4a}
C^5	129.73 d (d.m) (162.0–164.0, HC5; 1.6, POCCC^5)	129.67 d (m) (1.3, POCCC^5)	128.30 d (br.d) (161.0–162.0, HC^5; 1.2, POCCC^5)	131.17 br.s (br.d) (165.7, HC^5)
C^6	134.54 d (m) (1.5, POCCCC^6; 6.3–6.6, H^{3}CCC^6)	134.52 d (m) (1.3, POCCCC^6; 6.0–6.5, HC^{8}CC^6; 5.0, H^{2}CC^6)	123.81 s (d.m) (161.3, HC^3; 6.7, HC^{8}CC^6; 4.7–5.0, H^{3}CC^{7}C^6)	117.33 d (m) (10.7, HC^{8}CC^6; 4.8, H^{3}CC^{7}C^6; 4.3–4.5, HC^{5}C^6; 1.0, POCCCC^6)
C^7	132.90 s (d.d.q) (161.2, HC^7; 7.7, HC^{5}CC^7; 4.8, H^{3}CCC^7)	132.64 s (d.m) (161.2, CH^7; 7.7, HC^{5}CC^7; 6.4, H^{2}CCC^7)	141.54 s (d.q.d) (9.0, HC^{5}CC^7; 5.5–5.7, H^{3}CC^7; 0.7, HCC)	140.74 s (q.d) (6.4, HC^{5}CC^7; 6.4, H^{3}CC^7)
C^8	119.18 d (d.d) (165.0, HC^8; 8.0, POCC^8)	119.61 d (d.d) (164.7, HC^8; 8.0, POCC^8)	119.66 d (d.m) (160.0, HC^8; 6.9–7.1, HC^{6}CC^8; 8.0, POCC^8; 5.2, H^{3}CC^{7}C^8)	121.73 d (d.m) (163.6, HC^8; 6.8, POCC^8; 5.7–5.8, H^{3}CCC^8)
C^{8a}	149.84 d (m) (10.8, POC^{8a}; 10.5, HC^{5}CC^{8a}; 10.3, HC^{7}CC^{8a}; 3.5–4.0, HC^{8}C^{8a})	150.13 d (m) (10.8, POC^{8a})	151.63 d (m) (9.0–10.0, HC^{5}CC^{8a}; 8.0, POC^{8a}; 3.8–4.0, HC^{8}C^{8a})	150.81 d (br.d.d.d) (10.2, HC^{5}CC^{8a}; 7.9, POC^{8a}; 4.2, HC^{8}C^{8a})
C^9	136.42 d (m) (20.8, PCCC^9)	136.22 d (m) (20.7, PCCC^9; 6.5–7.0, HC^{11}CC^9; 5.0–5.5, HC^{3}CC^9)	139.77 d (m) (17.9, PCCC^9; 6.8–7.2, HC^{11}CC^9; 6.5, HC^{3}CC^9)	138.62 d (m) (17.6, PCCC^9; 6.8–7.2, HC^{11}CC^9; 6.5, HC^{3}CC^9)
C^{10}	128.09 s (br.d. m) (161.6, HC^{10}; 7.4, HCCC^{10}; 6.3–6.7, H^{12}CCC^{10})	–	128.28 s (br.d.m) (160.1, HC^{10}; 6.8–7.0, HCCC^{10}; 5.9–6.3, HCCC^{10})	128.24 s (br.d.m) (160.5, HC^{10}; 6.8–7.0, HCCC^{10}; 5.9–6.3, HCCC^{10})
C^{11}	128.54 s (d.m) (162.0, HC^{11}; 6.5–6.7, HCCC^{11})	–	128.68 s (br.d.d) (162.0, HC^{11}; 7.2–7.4, HCCC^{11})	128.88 s (br.d.d) (161.3, HC^{11}; 7.4, HCCC^{11})
C^{12}	129.50 s (d.t) (161.3, HC^{12}; 7.2, HC^{10}CC^{12})	–	128.97 s (d.t) (161.3, HC^{12}; 7.4, HC^{10}CC^{12})	128.63 s (d.t) (160.9, HC^{12}; 7.3, HC^{10}CC^{12})

Table 1. (Contd.)

Atom	**XI** (25°C, $CDCl_3$)	**XII** (50°C, $CDCl_3$)	**XV**[f] (50°C, DMSO-d_6)	**XVIc**[g] (50°C, DMSO-d_6)
CH_3C^7	20.54 s (q.d.d) (127.0, HC; 4.5, HC^6CC; 4.4, HC^7CC)	$BrCH_2$, 31.65 s (t.d.d) (154.0, HC; 5.1, HC^7CC; 5.1, HC^5CC)	20.69 s (q.d.d) (127.1, HC^{13}; 4.6, HC^8CC; 4.3, HC^6CC),	22.18 s (q. d) (128.6, HC; 4.8, HC^8CC)
NCH	–	–	51.22 d (m) (1.9, PNC)	51.41 d (m) (1.8, PNC)
$(CH_3)_3$	–	–	31.36 s (q.m) (125.9, HC; 4.8, PNCC; 2.4, HCCH)	31.56 s (q.m) (125.9, HC; 4.8, PNCC; 2.4, HCCH)

[a] CH_3C^{12}, 20.27 s (q.t) (126.4, HC; 4.3, $HC^{11}C^{12}C$). [b] NCH, 42.74 br.s (br.d.m) (135.8–136.1, HC; 3.9–4.0, HCC). $(CH_3)_2$, 25.01 d (q.m) (125.4, HC; 5.7, PNCC), 24.81 d (q.m) (126.6, HC; 5.1, PNCC). [c] CH_3C^{12}, 20.69 s (q.t) (126.4, HC; 4.9–5.0, $HC^{11}C^{12}C$). NCH, 43.24 d (d.m) (138.7, HC; 1.4, PNC). $(CH_3)_2$, 24.83 d (q.m) (125.3, HC; 4.6, PNCC), 25.03 d (q.m) (125.2, HC; 6.1, PNCC). [d] NCH_2, 42.48 s (br.t) (143.5, HC). OCH_2, 63.02 s (br.t.m) (145.5, HC; 2.4–2.5, HCOC; 2.4–2.5, HCC). [e] CH_3C^{12}, 20.69 s (q.t) (126.4, HC; 4.9–5.0, $HC^{11}C^{12}C$). NCH, 42.76 br.s (br.d.m) (145.5, HC). $(CH_3)_2$, 20.24 br.s (br.q) (127.1, HC). [f] NCH, 51.22 d (m) (1.9, PNC). $(CH_3)_3$, 31.36 s (q.m) (125.9, HC; 4.8, PNCC; 2.4, HCCH). [g] NCH, 51.41 d (m) (1.8, PNC).

As seen from Table 1, the spectrum contains six signals of carbon atoms bound with hydrogen and six signals of carbon atoms bearing no protons. Taking into account the pair equivalence of the C^{10} and C^{11} atoms of the phenyl substituent, we can conclude that the chlorine atom locates in the phenylene fragment. The multiplicity of the C^{4a} and C^{8a} signals (d.d.d) is consistent with the presence of substituents in the 6 and 7 positions. Of C^8 and C^5, the first atom is shielded stronger because of the strong *ortho* effect of oxygen; moreover, the C^8 signal appears as a doublet due to coupling with phosphorus with a noticeable $^2J_{POCC}$ constant (8.1 Hz). In the proton-coupled spectrum, the C^8 signal is a complex multiplet whose shape is determined by coupling of C^8 with H^8 ($^1J_{HC}$ 164.6 Hz), H^5 ($^4J_{HCCC}$ 1.2 Hz), and methyl protons ($^3J_{HCCC}$ 5.2 Hz). Such a multiplet structure is possible only if the methyl group is *ortho* to C^8. From that it follows that the reaction involves selective migration of the chlorine atom into the *para* position to the endocyclic oxygen atom of the phosphorinane heteroring. This process is analogous to chlorine migration in the reaction of unsubstituted trichlorobenzophosphole **I** with arylacetylenes [2]. The *ipso* substitution of the oxygen atom, too, regioselectively proceeds *para* to the methyl group. This result resembles that of the reaction of 5-chloro- or 5-bromo-2,2,2-trichlorobenzo[*d*][1,3,2]dioxaphospholes with arylacetylenes [4].

The above conclusions were completely confirmed by a single-crystal X-ray diffraction study of compound **IVa**. The resulting coordinates, selected bond lengths, and bond and torsion angles are listed in Tables 2 and 3. Figure 1 gives a general view of the molecule.

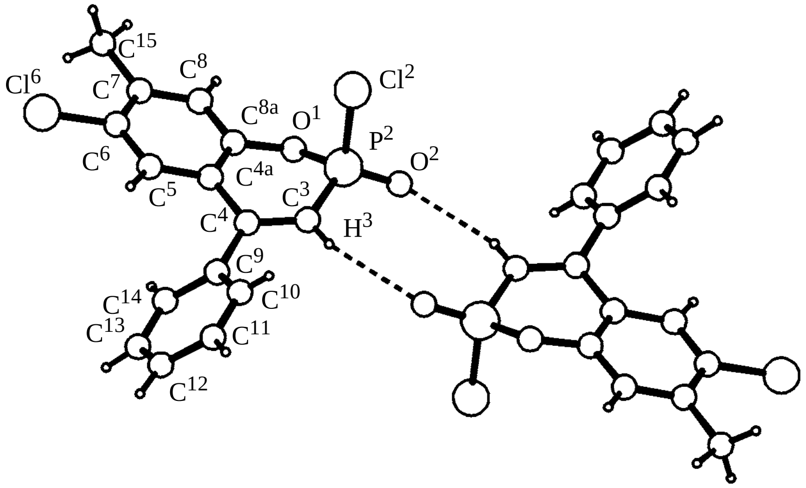


Fig. 1. Molecular geometry of compound **IVa** in crystal and scheme of dimer formation by intermolecular C–H···O hydrogen bonds (shown by dashed lines).

Table 2. Atomic coordinates in molecule **IVa**, equivalent isotropic thermal parameters of non-hydrogen atoms $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j) B(i, j)$ (Å^2) and thermal parameters of hydrogen atoms B_{iso} (Å^2)

Atom	*x*	*y*	*z*	*B* or B_{iso}
Cl^2	1.46891(8)	0.42542(8)	–0.13773(8)	2.33(2)
Cl^6	0.74055(8)	0.71543(8)	–0.30376(8)	2.31(2)
P^2	1.43291(8)	0.23435(8)	–0.16522(8)	1.68(2)
O^1	1.3855(2)	0.3024(2)	–0.3134(2)	1.71(4)
O^2	1.5846(2)	0.1152(2)	–0.1862(2)	2.31(5)
C^3	1.2483(3)	0.1864(3)	–0.0226(3)	1.67(6)
C^4	1.0982(3)	0.2513(3)	–0.0383(3)	1.33(6)
C^{4a}	1.0886(3)	0.3753(3)	–0.1753(3)	1.32(6)
C^5	0.9378(3)	0.4775(3)	–0.1794(3)	1.56(6)
C^6	0.9325(3)	0.5909(3)	–0.3092(3)	1.59(6)
C^7	1.0712(3)	0.6097(3)	–0.4390(3)	1.61(6)
C^{8a}	1.2271(3)	0.3977(3)	–0.3050(3)	1.46(6)
C^8	1.2206(3)	0.5096(3)	–0.4344(3)	1.63(6)
C^9	0.9441(3)	0.1987(3)	0.0764(3)	1.40(6)
C^{10}	0.9187(3)	0.1608(3)	0.2290(3)	1.86(7)
C^{11}	0.7774(3)	0.1113(3)	0.3374(3)	2.40(8)
C^{12}	0.6569(3)	0.0943(3)	0.2935(3)	2.27(7)
C^{13}	0.6809(3)	0.1275(3)	0.1430(3)	1.86(7)
C^{14}	0.8231(3)	0.1791(3)	0.0345(3)	1.69(7)
C^{15}	1.0627(3)	0.7388(3)	–0.5771(3)	2.05(7)
H^3	1.259(2)	0.118(2)	0.049(2)	0.1(4)
H^8	1.310(3)	0.517(3)	–0.515(3)	1.5(5)
H^5	0.839(3)	0.475(2)	–0.097(3)	1.4(5)
H^{10}	0.987(3)	0.173(2)	0.252(3)	1.6(6)
H^{11}	0.751(3)	0.087(3)	0.442(3)	3.2(7)
H^{12}	0.555(3)	0.068(3)	0.365(3)	1.8(6)
H^{13}	0.607(3)	0.107(3)	0.112(3)	3.2(7)
H^{14}	0.847(3)	0.203(2)	–0.073(2)	1.5(5)
H^{151}	1.169(3)	0.734(3)	–0.651(3)	2.9(7)
H^{152}	1.038(3)	0.841(3)	–0.560(3)	3.2(7)
H^{153}	0.987(3)	0.735(3)	–0.618(3)	3.8(7)

The phosphorine heteroring in molecule **IVa** contains two planar fragments $O^1C^{8a}C^{4a}C^4$ and $P^2C^3C^4C^{4a}$, which form a dihedral angle of 15.8(3)° with each other. The C^3 and P^2 atoms of the heteroring deviate from the $O^1C^{8a}C^4C^{4a}$ plane by –0.375(3) and –0.739(1)Å, i.e. these atoms are located on the same side of the plane. From the second planar fragment ($P^2C^3C^5C^{4a}$), the heteroring O^1 and C^{8a} atoms, too, deviate to the same side by different distances (–0.543(2) and –0.286(2)Å, The fact that two of the six atoms deviate to the same side but by different distances suggests that the conformation of the phosphorine ring is distorted *bath*. The O^2 and Cl^2 atoms of the exocyclic substituents deviate from the $O^1C^{8a}C^{4a}C^4$ plane by –0.419(2) and –2.6864(7) Å and from the $P^2C^3C^4C^{4a}$ plane, by 0.674(2) and –1.8942(7) Å, respectively. These deviate point to an axial location of the chlorine atom and to an equatorial location of the phosphoryl oxygen atom. The P–Cl bond length in this molecule is 2.024(1) Å, which is slightly larger than in 2,5,6,7,8-pentachloro-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**IVd**) [2.018(1) Å] we studied previously [5]. Since compounds **IVa** and **IVd** have the same substituents in the heteroring, it is expedient to compare their other geometric parameters. The P=O bond lengths are equal within the experimental error: 1.451(2) and 1.456(3) Å in **IVa** and **IVd**, respectively. The endocyclic bonds at the phosphorus atom in this molecule appreciably differ from each other: the O^1–P^2 bond in **IVa** (1.589(2)Å) is shorter than **IVd** [1.597(3) Å]. The same relates to the P^2–C^3 bond lengths: 1.742(2) Å in **IVa** vs. 1.750(4) Å in **IVd**. Such bond length redistribution provides evidence showing that the hyperconjugation of the lone electron pair of the endocyclic oxygen atom with the antibonding orbital of the P–Cl bond (the anomeric effect) in **IVa** is stronger than in **IVd**. These difference in bond angles on phosphorus, too, is also consistent with these interactions: The endocyclic $O^1P^2C^3$ angle in molecule **IVa** [103.9(1)°]

Table 3. Selected bond angles φ (deg), bond lengths *d* (Å), and torsion angles τ (deg) in molecule **IVa**

Angle	φ	Angle	φ	Angle	φ
$Cl^2P^2O^1$	101.93(8)	$P^2C^3H^3$	116(1)	$O^1C^{8a}C^8$	115.7(2)
$Cl^2P^2O^2$	110.9(1)	$C^4C^3H^3$	123(1)	$C^{4a}C^{8a}C^8$	123.3(2)
$Cl^2P^2C^3$	107.9(1)	$C^3C^4C^{4a}$	119.2(2)	$C^{8a}C^8C^7$	120.6(2)
$O^1P^2O^2$	112.0(1)	$C^3C^4C^9$	121.2(2)	$C^9C^{14}C^{13}$	120.6(3)
$O^1P^2C^3$	103.9(1)	$C^4C^{4a}C^{8a}$	122.2(2)	$C^8C^7C^6$	116.8(2)
$O^2P^2C^3$	118.7(1)	$C^4C^{4a}C^5$	121.6(2)	$C^8C^7C^{15}$	121.5(2)
$P^2O^1C^{8a}$	119.3(2)	$C^{8a}C^{4a}C^5$	116.1(2)	$Cl^6C^6C^8$	119.7(2)
$P^2C^3C^4$	121.5(2)	$O^1C^{8a}C^{4a}$	121.1(2)	$Cl^6C^6C^5$	117.4(2)

Table 3. (Contd.)

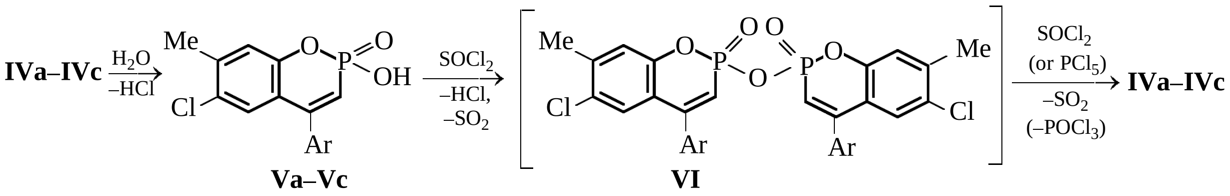
Bond	d	Bond	d	Bond	d
Cl^{2}–P^{2}	2.024(1)	C^{4}–C^{4a}	1.485(3)	C^{9}–C^{10}	1.384(4)
Cl^{6}–C^{6}	1.743(2)	C^{4}–C^{9}	1.478(3)	C^{9}–C^{14}	1.395(5)
P^{2}–O^{1}	1.589(2)	C^{4a}–C^{8a}	1.379(3)	C^{10}–C^{11}	1.369(3)
P^{2}–O^{2}	1.451(2)	C^{4a}–C^{5}	1.400(3)	C^{11}–C^{12}	1.392(5)
P^{2}–C^{3}	1.742(2)	C^{8a}–C^{8}	1.377(3)	C^{12}–C^{13}	1.369(4)
O^{1}–C^{8a}	1.407(3)	C^{8}–C^{7}	1.384(3)	C^{13}–C^{14}	1.382(3)
C^{3}–C^{4}	1.347(4)	C^{7}–C^{6}	1.378(3)	C^{5}–H^{5}	0.93(2)
C^{3}–H^{3}	0.80(2)	C^{6}–C^{5}	1.383(3)	C^{7}–C^{15}	1.513(3)
Angle	τ	Angle	τ	Angle	τ
Cl^{2}P^{2}O^{1}C^{8a}	–72.9(2)	O^{2}P^{2}C^{3}H^{3}	28(2)	C^{3}C^{4}C^{4a}C^{5}	–161.0(3)
O^{2}P^{2}O^{1}C^{8a}	168.5(2)	P^{2}O^{1}C^{8a}C^{4a}	–32.5(3)	C^{9}C^{4}C^{4a}C^{8a}	–160.2(2)
C^{3}P^{2}O^{1}C^{8a}	39.2(2)	P^{2}O^{1}C^{8a}C^{8}	149.2(2)	C^{9}C^{4}C^{4a}C^{5}	20.4(4)
Cl^{2}P^{2}C^{3}C^{4}	86.4(2)	P^{2}C^{3}C^{4}C^{4a}	–4.7(3)	C^{3}C^{4}C^{9}C^{10}	39.1(4)
Cl^{2}P^{2}C^{3}H^{3}	–99(1)	P^{2}C^{3}C^{4}C^{9}	173.8(2)	C^{3}C^{4}C^{9}C^{14}	–138.0(3)
O^{1}P^{2}C^{3}C^{4}	–21.2(2)	H^{3}C^{3}C^{4}C^{4a}	–179(2)	C^{4a}C^{4}C^{9}C^{10}	–142.3(2)
O^{1}P^{2}C^{3}H^{3}	153(1)	H^{3}C^{3}C^{4a}C^{8a}	–1(2)	C^{4a}C^{4}C^{9}C^{14}	40.6(3)
O^{2}P^{2}C^{3}C^{4}	–146.4(2)	C^{3}C^{4}C^{4a}C^{8a}	18.3(4)	C^{4}C^{4a}C^{8a}O^{1}	0.3(4)

is increased compared with the respective angle in **IVd** [101.8(1)°], whereas the exocyclic O^{1}P^{2}Cl^{2} angle is decreased [101.93(8)° in **IVa** against 103.6(1)° in **IVd**]. The differences in the O^{1}–C^{8a} [1.407(3) and 1.382(5)Å], C^{3}=C^{4} [1.347(4) and 1.358(5) Å], and C^{4}–C^{4a} [1.485(3) and 1.474(5)Å] in **IVa** and **IVd** are also worthy of mention. The shortening of these bonds in **IVd** compared with **IVa** is evidently connected with the electron-acceptor perchloro effect of the condensed aromatic fragment. Probably, the attenuated anomeric effect in molecule **IVd**, too, is caused by the same electron-acceptor effect. The *ortho*-chlorine substituents in the benzo fragment of structure **IVd** may also be responsible for the above-described structural differences in the molecules in question. It is this effect that explains the noticeable increase of the C^{4}C^{4a}C^{5} angle [124.8(3)°] in **IVd** as compared with **IVa** [121.6(2)°]. Therewith, a short intramolecular Cl^{5}-C^{11} contact is observed [3.000(3) Å; sum of van der Waals radii 3.45Å]. The opposite O^{1}C^{8a}C^{8} angle is much decreased in both molecules [115.7(2)° in **IVa** and 116.2(3)° **IVa**]. The phenyl substituent is strrongly turned about the C^{3}=C^{4} double bond [the C^{3}C^{4}C^{9}C^{10} torsion angle is 39.1(4)°], which unfavors conjugation of these two fragments.

Such location of the phenyl substituent occurs to be favorable for π–π contacts with the same fragment of a neighboring molecule, with the distance between the ring centers of 4.85(1)Å and the dihedral angle of 0°. At the same time, the benzo fragment of the molecule, too, takes part in such interactions with the benzo fragments of molecules bound with it by the center of symmetry and translations by +1 and –1 along the 0z axis, with the shortest distance between the ring centers of 4.61(1)Å and the dihedral angle of 0°; as a result, inclined stacks of molecules bound by such contacts are formed. Contacts of the π–H type are also observed in the crystal, as well as multiple Cl···H contacts with distances spanning the range 2.91–3.69 Å. The most significant effect on the molecular packing is produced by a C–H···O intermolecular contact o between H^{3} and O$^{2'}$ (1 –x, –y, 2 – z), with the following parameters: d(H^{3}···O^{2}) 2.51(2) Å and C^{3}–H^{3}···O^{2} angle 155.0(2)°; this leads to formation of centrosymmetric dimers (Fig. 1). In whole, the intermolecular contacts present in the crystal give rise to a 3D supramolecular structure and a sufficiently tight molecular packing (packing coefficient 69.2%).

Hydrolysis of benzophosphorines **IV** under mild conditions gave hydroxyphosphorines **V** with preserved heterocyclic structure.

The structure of compounds **V** was established by means of ^{1}H, ^{13}C, ^{31}P NMR and IR spectroscopy (see Experimental). The cyclic structure of the products was confirmed by X-ray diffraction on an example of benzophosphorine **Vc**. The atomic coordinates and



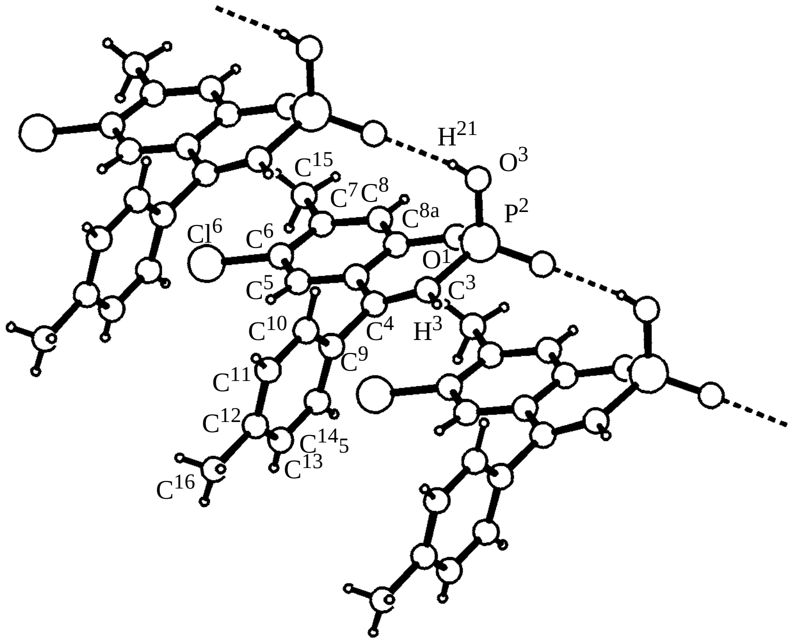


Fig. 2. Molecular geometry of compound **Vc** in crystal and scheme of dimer formation by intermolecular C–H···O hydrogen bonds (shown by dashed lines).

selected geometric parameters of the latter (bond lenghts, bond and torsion angles) are listed in Tables 4 and 5. The molecular geometry and scheme of hydrogen bonds in the crystal are shown in Fig. 2.

Like in above-described case, the heteroring in compound **Vc** has two planar fragments, $O^1C^{8a}C^{4a}C^4$ and $P^2C^3C^4C^{4a}$, that form a dihedral angle of 9.9(6)° with each other. The heteroring C^3 and P^2 atoms deviate from the $O^1C^{8a}C^{4a}C^4$ plane by 0.232(3) and 0.4751(8)Å, respectively, i.e. to the same side of the plane. From the second planar fragment ($P^2C^3C^4C^{4a}$), the O^1 and C^{8a} atoms, too, deviate to the same side (by –0.407(2) and –0.174(3)Å, respectively). The fact that the above-mentioned atoms deviate to the same side but by different distances suggests a distorted *boat* conformation of the phosphorinane ring. The O^2 and O^3 atoms of the exocyclic substituents deviate by –0.279(2) and 1.956(2)Å from the $P^2C^3C^4C^{4a}$ plane and by –0.947(2) and 1.394(2) Å from the $P^2C^3C^4C^{4a}$ plane, respectively. Such deviations of the O^3 and O^2 atoms point to an axial position of the hydroxy group and an equatorial position of the phosphoryl oxygen, which completely agrees with published data for analogous structures studied [2, 4, 5]. The principal geometric parameters of the heteroring in these compounds are almost the same. The 4-phenylmethyl and $P^2C^3C^4C^{54a}$ planes are almost orthogonal to each other. The torsion angle between them is –65.3(5)°.

Analysis of intermolecular interactions in the crystal of compound **Vc**, carried out by means of the PLATON program [6], shows that here, unlike the above-described compound **IVa**, there are no short contacts, except for the classical hydrogen bond between the hydroxyl proton and $O^{2'}$ $(-1 + x, y, z)$, with the parameters: $d(H^{31}\cdots O^{2'})$ 1.88(2) Å and $O^3–H^3\cdots O^{2'}$ angle 170(3)°. Each molecule is involved into two such hydrogen bonds (as a donor and as an acceptor), which results in formation of supramolecular structures having the shape of infinite chains of the hydrogen-bonded molecules, running along the 0*x* crystallographic axis (Fig. 2).

Treatment of phosphonic acids **V** with thionyl chloride or phosphorus pentachloride permits to pre-

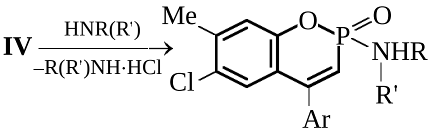
Table 4. Atomic coordinates in molecule **Vc**, equivalent isotropic thermal parameters of non-hydrogen atoms $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j) B(i, j)$ (Å^2) and thermal parameters of hydrogen atoms B_{iso} (Å^2)

Atom	*x*	*y*	*z*	*B* or B_{iso}
Cl^1	0.6711(2)	–0.14710(7)	0.55663(7)	5.73(2)
P^2	–0.0402(2)	–0.31378(7)	0.21336(6)	3.96(2)
O^1	0.0008(5)	–0.3542(2)	0.3364(2)	4.50(5)
O^2	–0.3169(4)	–0.3430(2)	0.1968(2)	5.84(6)
O^3	0.1967(4)	–0.3750(2)	0.1592(2)	4.79(5)
C^3	0.0053(7)	–0.1711(3)	0.1774(2)	4.41(8)
C^4	0.1138(7)	–0.1215(2)	0.2377(2)	3.82(7)
C^{4a}	0.2145(6)	–0.1890(2)	0.3404(2)	3.47(7)
C^5	0.3736(7)	–0.1454(2)	0.3965(2)	3.81(7)
C^6	0.4710(7)	–0.2086(2)	0.4918(2)	3.92(7)
C^7	0.4112(7)	–0.3204(2)	0.5366(2)	4.08(8)
C^8	0.2540(7)	–0.3643(2)	0.4810(2)	4.10(8)
C^{8a}	0.1599(6)	–0.3009(2)	0.3855(2)	3.67(7)
C^9	0.1431(7)	0.0019(2)	0.2010(2)	4.00(8)
C^{10}	0.321(1)	0.0487(3)	0.1160(3)	7.8(1)
C^{11}	0.341(1)	0.1636(3)	0.0803(3)	9.0(1)
C^{12}	0.1852(9)	0.2351(3)	0.1246(3)	5.8(1)
C^{13}	0.012(1)	0.1868(3)	0.2106(3)	8.3(1)
C^{14}	–0.0102(9)	0.0711(3)	0.2533(3)	6.9(1)
C^{15}	0.5146(8)	–0.3915(3)	0.6414(3)	5.56(9)
C^{16}	0.205(1)	0.3621(3)	0.0839(3)	9.2(1)
H^3	–0.047(5)	–0.133(2)	0.119(2)	2.5(5)
H^5	0.422(4)	–0.077(2)	0.369(1)	2.3(5)
H^8	0.220(5)	–0.433(2)	0.510(2)	3.2(5)
H^{10}	0.428(7)	–0.001(2)	0.085(2)	7.6(9)
H^{11}	0.444(6)	0.185(2)	0.028(2)	6.1(8)
H^{13}	–0.071(5)	0.216(2)	0.247(2)	4.1(6)
H^{14}	–0.14(1)	0.038(3)	0.323(3)	13(1)
H^{31}	0.328(5)	–0.370(2)	0.165(2)	2.5(5)
H^{151}	0.436(8)	–0.355(3)	0.696(3)	11(1)
H^{152}	0.462(8)	–0.459(3)	0.654(2)	8.5(9)
H^{153}	0.683(8)	–0.392(3)	0.640(2)	9(1)
H^{161}	0.111(8)	0.395(3)	0.131(3)	11(1)
H^{162}	0.214(9)	0.382(3)	0.025(3)	11(1)
H^{163}	0.35(1)	0.376(4)	0.099(4)	18(2)

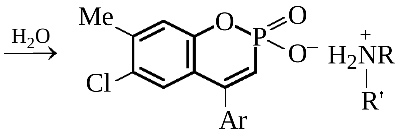
pare starting chlorophosphorines **IV**. Unlike phosphorus pentachloride, thionyl chloride fairly slowly reacts with compounds **V**. In the course of the reaction we could detect a pyrophosphonate intermediate **VI**. This compound becomes a single product if the ratio of the starting components is 1 : 1. In the ^{31}P NMR spectrum, this product gives a broadened doublet at 2.0 to –1.0 ppm ($^2J_{PCH}$ 17.0–18.1 Hz). It is interesting to note that pyrophosphonate **VI** is rather inert to thionyl chloride and slowly transforms to chlorophosphonate **IV**. On treatment with phosphorus pentachloride, complete and rather fast conversion to final reaction product **IV** occurs.

By treatment of chlorophosphorines **IV** with amines we obtained corresponding amides **VIIa, VIIb**, and **VIIc**. In their ^{31}P and $^{31}P–\{^1H\}$ NMR spectra, the signals of starting benzophosphorines **IV** are shifted upfield to δ_P 8.0–10.0 ppm and acquire a characteristic multiplicity (d.d) due to additional coupling through three bonds with the amido proton ($^3J_{PCH}$ 10.0–11.0 Hz) (compounds **IVb** and **IVc**). In the ^{13}C NMR spectra of the amides, all coupling constants with phosphorus (except for the direct one) are characteristically decreased by 1–3 Hz; therewith, the long-range constants for C^5 and C^6 disappear. Note that the methyl carbon atoms of the amide fragment are nonequivalent. For example, in the spectrum of compound **VIIb** they appear as upfield doublets of equal intensity (δ_C 24.91 and 24.72 ppm, $^3J_{PNCC}$ 5.7 and 5.0 Hz, respectively).

Morpholide **VIIa** proved to be the least resistant to hydrolysis. It converts to salt **VIIIa** just when washed with water during isolation. Amidophosphonates **VIIb** and **VIIc** are more stable, but on treatment with water in DMSO they yield salts **VIII**. Therewith, their phosphorus signals are shifted even more upfield (δ_P 2.0 to –1.0 ppm).



VII



VIIIa–VIIIc

R + R' = $O(C_2CH_2)_2N$, Ar = Ph (**VIIa, VIIIa**); R = $CH(CH_3)_2$, R' = H, Ar = 5-Cl–C_6H_4 (**VIIb**), 4-Me–C_6H_4 (**VIIc, VIIIc**).

Noticeable changes in the ^{13}C NMR spectra are observed in going from amides to corresponding salts. Figures 3 and 4 shows fragments of the $^{13}C–\{^1H\}$ NMR spectra of amide **VIIb** and ammonium salt **VIIIa**. As seen from these figures and Table 1, the phosphorine ring in these salts remains unchanged (as judged from the $^2J_{POC^{8a}}$, $^3J_{POCC^8}$, and $^3J_{PCCC^{4a}}$ constants). The transfer to the salt form causes a strong downfield shift ($\Delta\delta_C$ 6–7 ppm). At the same time, a

Table 5. Selected bond angles φ (deg), bond lenghts *d* (Å), and torsion angles τ (deg) in molecule **Vc**

Angle	φ	Angle	φ	Angle	φ
$O^1P^2O^2$	109.6(1)	$C^4C^3H^3$	120(2)	$C^6C^7C^{15}$	122.1(3)
$O^1P^2O^3$	107.4(1)	$C^3C^4C^{4a}$	120.2(3)	$C^8C^7C^{15}$	121.0(3)
$O^1P^2C^3$	103.0(1)	$C^3C^4C^9$	120.6(3)	$C^7C^8C^{8a}$	121.6(3)
$O^2P^2O^3$	109.6(1)	$C^{4a}C^4C^9$	119.2(3)	$O^1C^{8a}C^{4a}$	121.2(2)
$O^2P^2C^3$	115.7(1)	$C^4C^{4a}C^5$	122.2(3)	$O^1C^{8a}C^8$	116.6(3)
$O^3P^2C^3$	111.0(1)	$C^4C^{4a}C^{8a}$	121.9(3)	$C^{4a}C^{8a}C^8$	122.2(3)
$P^2O^1C^{8a}$	124.4(2)	$C^5C^{4a}C^{8a}$	115.9(2)	$C^4C^9C^{10}$	121.3(3)
$P^2O^3H^{31}$	119(2)	$C^{4a}C^5C^6$	122.3(3)	$C^4C^9C^{14}$	120.8(3)
$P^2C^3C^4$	124.1(2)	$C^5C^6C^7$	121.0(3)	$C^{10}C^9C^{14}$	117.9(3)
$P^2C^3H^3$	116(2)	$C^6C^7C^8$	116.9(3)	$C^9C^{10}C^{11}$	121.1(4)
Bond	*d*	Bond	*d*	Bond	*d*
$Cl^1–C^6$	1.736(4)	$C^3–H^3$	0.83(2)	$C^7–C^{15}$	1.514(4)
$P^2–O^1$	1.591(2)	$C^4–C^{4a}$	1.475(4)	$C^8–C^{8a}$	1.375(4)
$P^2–O^2$	1.461(2)	$C^4–C^9$	1.491(4)	$C^9–C^{10}$	1.346(5)
$P^2–O^3$	1.525(2)	$C^{4a}–C^5$	1.382(5)	$C^9–C^{14}$	1.370(5)
$P^2–C^3$	1.736(3)	$C^{4a}–C^{8a}$	1.387(4)	$C^{10}–C^{11}$	1.382(5)
$O^1–C^{8a}$	1.396(4)	$C^5–C^6$	1.377(4)	$C^{11}–C^{12}$	1.331(6)
$O^3–H^{31}$	0.64(2)	$C^6–C^7$	1.393(4)	$C^{12}–C^{13}$	1.346(5)
$C^3–C^4$	1.334(5)	$C^7–C^8$	1.372(5)	$C^{13}–C^{14}$	1.398(5)
Angle	τ	Angle	τ	Angle	τ
$O^2P^2O^1C^{8a}$	–149.5(2)	$O^1P^2C^3H^3$	–166(2)	$P^2O^1C^{8a}C^8$	–158.7(2)
$O^3P^2O^1C^{8a}$	91.4(2)	$O^2P^2C^3C^4$	133.1(3)	$P^2C^3C^4C^{4a}$	2.4(4)
$C^3P^2O^1C^{8a}$	–25.8(3)	$O^2P^2C^3H^3$	–46(2)	$C^3C^4C^{4a}C^{8a}$	–10.5(5)
$O^1P^2O^3H^{31}$	–56(2)	$O^3P^2C^3C^4$	–101.1(3)	$C^3C^4C^9C^{10}$	–65.3(5)
$O^2P^2O^3H^{31}$	–175(2)	$O^3P^2C^3H^3$	80(2)	$C^3C^4C^9C^{14}$	115.0(4)
$C^3P^2O^3H^{31}$	55(2)	$P^2O^1C^{8a}C^{4a}$	22.4(4)	$C^{4a}C^4C^9C^{10}$	112.9(4)
$O^1P^2C^3C^4$	13.5(3)	$P^2C^3C^4C^9$	–179.5(2)	$C^{4a}C^4C^9C^{14}$	–66.8(4)

noticeable downfield shift of the C^{8a} signal ($\Delta\delta_C$ 1.0–1.2 ppm) and an upfield shift of the C^6 atom ($\Delta\delta_C$ ca. 2 ppm) are observed. It is interesting to note that the acids themselves can form sodium salts on treatment with aqueous sodium hydrocarbonate. For example, benzophosphorine **Vb** was treated with aqueous sodium hydrocarbonate to obtain, after crystallization from water, sodium 6-chloro-7-methyl-4-(4-methylphenyl)-2-oxobenzo[*e*][1,2λ^5]oxaphosphorin-2-olate **VIIId**.

Tribromophosphorane **III** reacts with phenylacetylene not so unambiguously as chlorine-containing derivative **II**. The reaction yields a mixture of 2-bromo-7-methyl-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**IX**), 2,6-dibromo-7-methyl-4-phenylbenzo[*e*][1,2λ^5]oxophosphorine 2-oxide (**X**), 2-bromo-6-methyl-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**XI**), and 2-bromo-6-(bromomethyl)-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**XII**) in an 88 : 45 : 22 : 9 ratio.

Figure 5 shows the upfield and downfield fragments of the $^{13}C–\{^1H\}$ NMR spectrum of the reaction mixture of tribromophosphorane **III** with phenylacetylene, obtained after removal of volatile admixtures in a vacuum. The signals of all the four compounds are well resolved, have different intensities, and do not overlap, which allows one to interpret the ^{13}C NMR spectra in sufficient detail and to make conclusions about the structure of the compounds. The major reaction products, compounds **IX** and **X**, gradually crystallize from chloroform in a 2 : 3 ratio. According to the ^1H NMR (see Experimental) and ^{13}C NMR (Table 2) spectral data, they can be considered as 7-methyl-substituted benzophosphorines, one of which contains a bromine atom in the phenylene

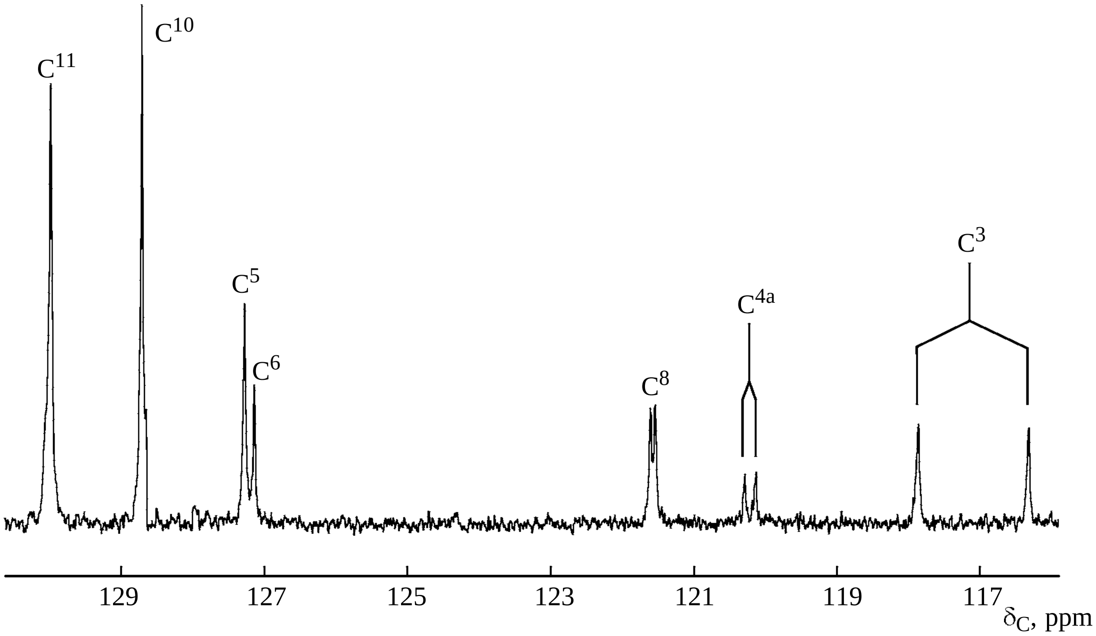


Fig. 3. Fragment of the $^{13}C-\{^1H\}$ NMR spectrum of benzophosphorine **VIIb**.

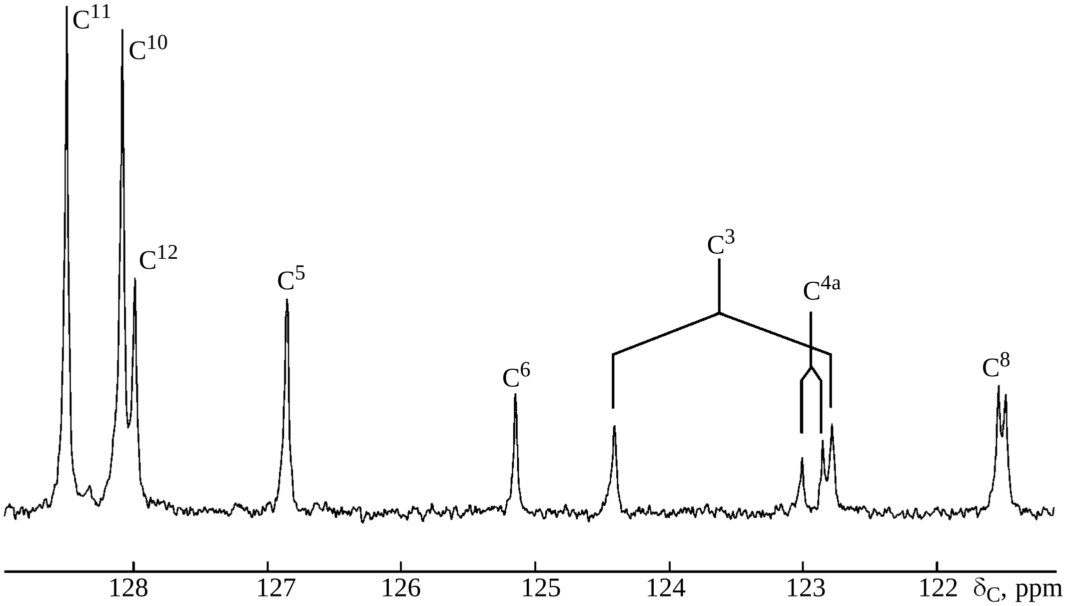
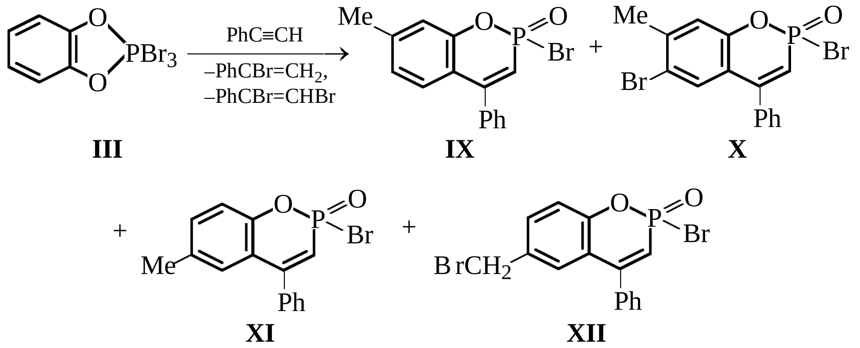


Fig. 4. Fragment of the $^{13}C-\{^1H\}$ NMR spectrum of salt **VIIIa**.

fragment, probably in the 6 position of the benzophosphorine system. The signal of the carbon atom bound with bromine appears in an upfield region (due to the shielding heavy atom effect and the *para* effect of oxygen), and has a multiplicity characteristic of the proposed surrounding (Table 1). Further evidence for the 6 position of the bromine atom comes from the multiplicity of the C^8 and C^{4a} signals that correspondingly contain a smaller number of lines. Note that the direct $^1J_{PC^3}$ constants of bromophosphorines **IX**–**XII** are invariably lower by 12.5 Hz than those of chlorophosphorines **IV**, whereas the $^1J_{HC^3}$ constants of these two groups of compounds are equal to each other, which agrees with the results in [2].

Analysis of the ^1H and ^{13}C NMR spectra shows that the two minor benzophosphorines are 6-methyl- and 6-bromomethyl-substituted derivatives **XI** and **XII**.



This conclusion was based primarily of the multiplicities of the C^8 signals (d.d) split by coupling with H^8 ($^1J_{HC}$) and phosphorus ($^2J_{POCC}$) and appearing in characteristic upfield regions (Fig. 5). If there would be no substituent in the 6 position, the C^8 signal would has been additionally split into a doublet by coupling with H^6, as it is observed for compound **IX**. The bromomethyl group in benzophosphorine **XII** gives a characteristic upfield triplet of triplets (31.65 ppm).

Hydrolysis of the mixture of compounds **IX** and **X** gives hydroxyphosphorines **XIII** and **XIV** which crystallize as a 1:4 mixture from dioxane and cannot be separated by recrystallization. The ^{1}H NMR spectrum of this mixture (250 MHz, DMSO-d_6) contains two doublets near 6.16 ($^2J_{PCH}$ 17.8 Hz) and 6.28 ppm ($^2J_{PCH}$ 17.8 Hz), characteristic of the P–CH=C proton.

Treatment of the mixture of benzophosphorines **IX** and **X** with *tert*-butylamine gave a 2:3 mixture of *tert*-

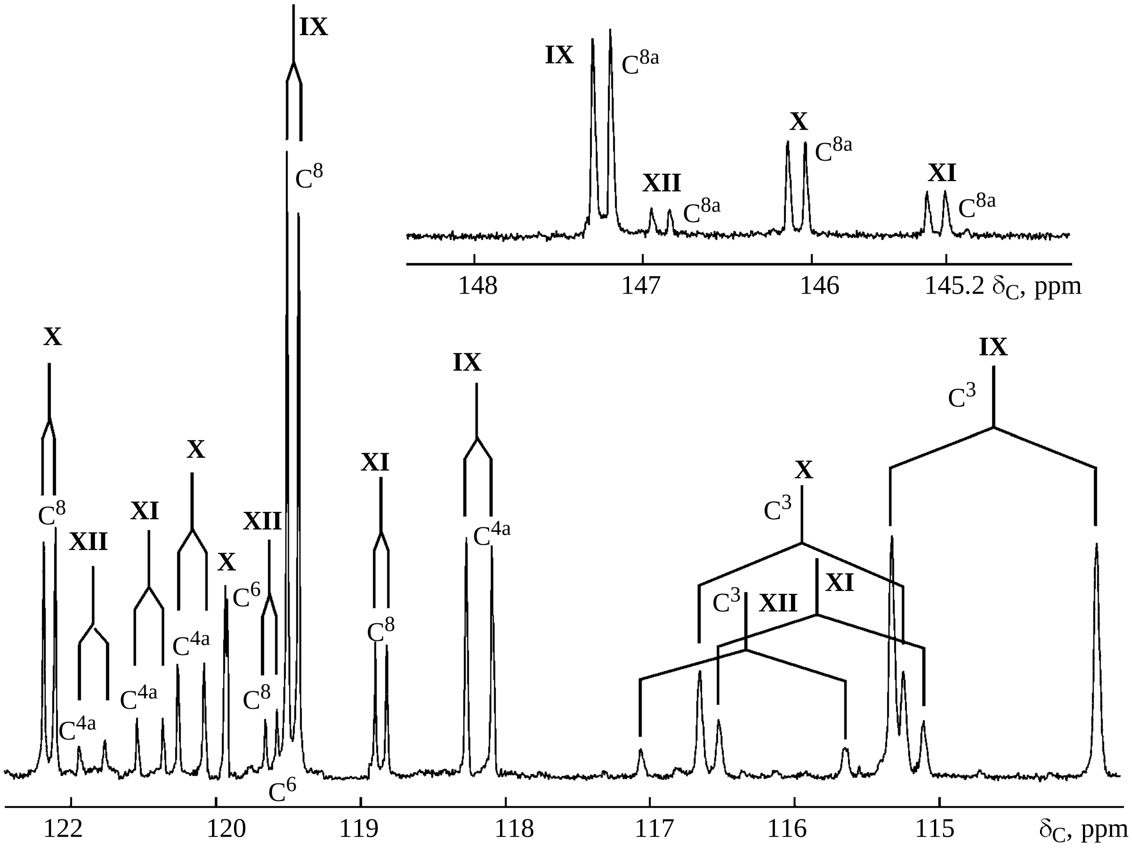
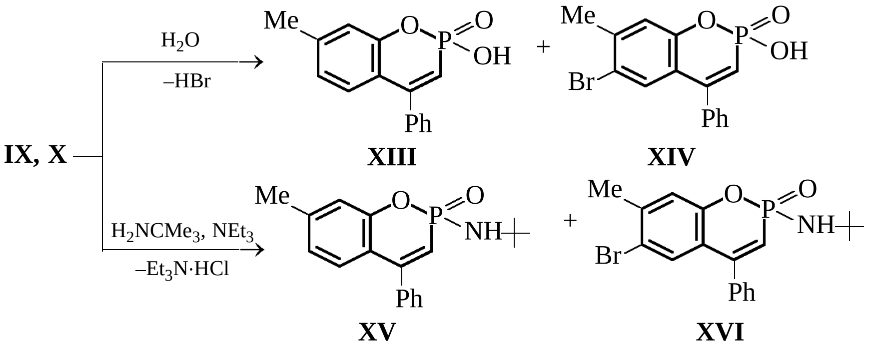


Fig. 5. Fragments of the $^{13}C–\{^1H\}$ NMR spectrum of the reaction mixture of tribromobenzophosphole **III** with phenylacetylene after removal of volatile admixtures.



butylamides **XV** and **XVI**, obtained as a crystalline precipitate. The structure of the products was confirmed by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy (see Experimental and Table 1). Unlike acids **XIII** and **XIV**, the mixture of amides **XV** and **XVI** could be separated by recrystallization to isolate the major product, benzophosphorine **XVI**. Its structure was confirmed by X-ray diffraction. Table 6 lists the atomic coordinates in molecule **XVI** and Table 7, its selected geometric parameters (bond lengths and bond and torsion angles). Figure 6 presents a general view of molecule **XVI** in crystal.

The heterocyclic skeleton in benzophosphorine **XVI** contains two planar fragments, $O^1C^{8a}C^{4a}C^4$ and $C^{4a}C^4C^3P^2$, which form a dihedral angle of 9.90(8)° with each other. The C^3 and P^2 atoms deviate from the $O^1C^{8a}C^{4a}C^4$ plane by 0.150(9) and 0.458(2) Å, that is to the same side of it. From the other planar fragment $C^{4a}C^4C^3P^2$, the heteroring O^1 and C^{8a} deviate by –0.4353 and –0.2681 Å, respectively, that is to the same side but by different distances. These data suggest that here, too, the phosphorine heteroring has a distorted *boat* conformation. The O^2 and N^2 atoms of the exocyclic substituents deviate from the

Table 6. Atomic coordinates in molecule **XVI**, equivalent isotropic thermal parameters of non-hydrogen atoms $B = 4/3 \sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i,\ j)$ (Å^2) and thermal parameters of hydrogen atoms B_{iso}(Å^2)

Atom	*x*	*y*	*z*	*B* or B_{iso}	Atom	*x*	*y*	*z*	*B* or B_{iso}
Br^6	0.0291(3)	1.0253(2)	0.8020(3)	0.1015(11)	C^{18}	0.580(2)	0.3140(18)	0.5708(17)	0.069(7)
P^2	0.3768(4)	0.2404(3)	0.8944(3)	0.0198(10)	C^{19}	0.547(2)	0.086(2)	0.5769(18)	0.083(9)
O^1	0.4177(9)	0.3843(8)	0.8669(9)	0.021(3)	H^2	0.57230	0.03975	0.86111	0.01(2)
O^2	0.3410(9)	0.1658(8)	1.0473(8)	0.027(2)	H^3	0.19259	0.24616	0.80132	0.04(4)
N^2	0.5280(11)	0.1313(10)	0.7999(10)	0.027(2)	H^5	–0.00801	0.75407	0.80568	0.0311
C^3	0.2224(12)	0.3139(12)	0.8228(13)	0.022(4)	H^8	0.45338	0.59395	0.88681	0.0311
C^4	0.1442(13)	0.4629(12)	0.7951(11)	0.019(4)	H^{10}	0.05932	0.67808	0.57998	0.0305
C^{4a}	0.1823(13)	0.5692(12)	0.8232(11)	0.018(3)	H^{11}	–0.14984	0.74328	0.49967	0.0413
C^5	0.0874(14)	0.7220(12)	0.8175(13)	0.026(3)	H^{12}	–0.30126	0.61698	0.59231	0.0358
C^6	0.1366(18)	0.8227(14)	0.8295(14)	0.042(5)	H^{13}	–0.27934	0.42260	0.79307	0.0447
C^7	0.2738(14)	0.7816(12)	0.8594(12)	0.019(4)	H^{14}	–0.07592	0.36276	0.88065	0.0303
C^8	0.3606(15)	0.6284(12)	0.8687(13)	0.026(3)	H^{15a}	0.42227	0.83489	0.89396	0.0847
C^{8a}	0.3183(13)	0.5311(12)	0.8534(11)	0.018(3)	H^{15b}	0.25339	0.93001	0.95834	0.0847
C^9	0.0076(14)	0.5093(15)	0.7444(14)	0.030(3)	H^{15c}	0.33019	0.96325	0.79358	0.0847
C^{10}	–0.0084(15)	0.6275(12)	0.6241(12)	0.026(4)	H^{17a}	0.79483	–0.02602	0.66888	0.1212
C^{11}	–0.1328(17)	0.6636(14)	0.5756(14)	0.034(5)	H^{17b}	0.81323	0.12225	0.65665	0.1212
C^{12}	–0.2240(14)	0.5907(16)	0.6322(14)	0.030(3)	H^{17c}	0.82171	0.08196	0.52035	0.1212
C^{13}	–0.2120(14)	0.4736(17)	0.7510(14)	0.038(5)	H^{18a}	0.47360	0.36446	0.58269	0.1040
C^{14}	–0.0891(14)	0.4395(14)	0.8017(13)	0.026(4)	H^{18b}	0.63302	0.31893	0.47104	0.1040
C^{15}	0.324(2)	0.8866(16)	0.8779(18)	0.056(6)	H^{18c}	0.61525	0.36041	0.61035	0.1040
C^{16}	0.6102(14)	0.1529(12)	0.6470(12)	0.025(4)	H^{19a}	0.44036	0.13827	0.59221	0.1242
C^{17}	0.774(2)	0.076(2)	0.621(2)	0.081(7)	H^{19b}	0.56611	–0.01708	0.61974	0.1242
					H^{19c}	0.59728	0.09684	0.47638	0.1242

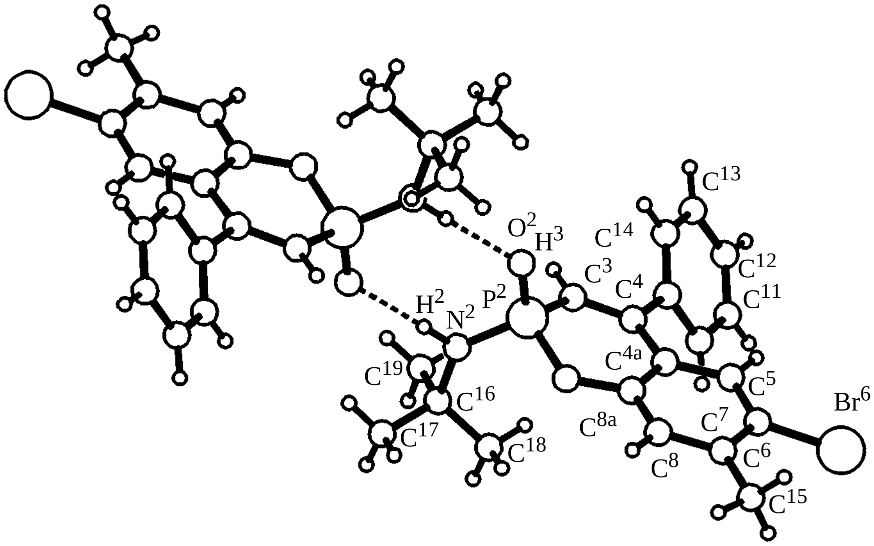


Fig. 6. Molecular geometry of compound **XVI** in crystal and scheme of dimer formation by intermolecular N–H···O hydrogen bonds (shown by dashed lines).

$O^1C^{8a}C^{4a}C^4$ plane by 1.854(6) and –0.586(6)Å and from the $C^{4a}C^4C^3P^2$ plane by –1.317(6) and –1.202(6) Å, respectively. It is readily seen from these deviations that the *tert*-butylamino group is equatorial, while the phosphoryl group is axial. Previously we studied the structure of an analogous compound, 6-chloro-2-morpholino-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**XVII**) [3], in which the morpholine substituent is also equatorial. The principal geometric parameters of molecules **XVI** and **XVII** are similar, except for the $P^2=O^2$ bond that is slightly longer in **XVI** [1.485(6) Å] compared with **XVII** [1.43(1) Å]. This difference may be explained by the involvement of the phosphoryl group of compound

Table 7. Selected bond angles φ (deg), bond lengths *d* (Å), and torsion angles τ (deg) in molecule **XVI**

Angle	φ	Angle	φ	Angle	φ
$O^1P^2O^2$	113.1(5)	$C^{16}N^2H^2$	117.4(5)	$N^2C^{16}C^{17}$	112(1)
$O^1P^2N^2$	104.1(6)	$P^2C^3C^4$	121(1)	$N^2C^{16}C^{18}$	114(1)
$O^1P^2C^3$	102.5(5)	$P^2C^3H^3$	119.4	$N^2C^{16}C^{19}$	105(1)
$O^2P^2N^2$	110.9(5)	$C^4C^3H^3$	119.1	$C^{17}C^{16}C^{18}$	109(1)
$O^2P^2C^3$	113.4(6)	$C^3C^4C^4a$	122(1)	$C^{17}C^{16}C^{19}$	110(1)
$N^2P^2C^3$	112.2(6)	$C^4C^4aC^5$	123(1)	$Br^6C^6C^5$	123(1)
$P^2O^1C^8a$	126.1(9)	$C^4C^4aC^8a$	122(1)	$Br^6C^6C^7$	114(1)
$P^2N^2C^{16}$	132.0(8)	$C^5C^4aC^8a$	115(1)	$O^1C^{8a}C^{4a}$	120(1)
$P^2N^2H^2$	110.8(8)	$C^4aC^5C^6$	120(1)	$O^1C^{8a}C^8$	116(1)
Bond	***d***	**Bond**	***d***	**Bond**	***d***
$Br^6–C^6$	1.85(1)	$C^3–H^3$	0.98	$C^8–C^8a$	1.32(2)
$P^2–O^1$	1.609(9)	$C^4–C^{4a}$	1.45(2)	$C^9–C^{10}$	1.42(2)
$P^2–O^2$	1.487(8)	$C^4–C^9$	1.51(2)	$C^9–C^{14}$	1.31(2)
$P^2–N^2$	1.63(1)	$C^{4a}–C^5$	1.43(2)	$C^{10}–C^{11}$	1.41(2)
$P^2–C^3$	1.77(1)	$C^{4a}–C^{8a}$	1.41(2)	$C^{11}–C^{12}$	1.29(2)
$O^1–C^8a$	1.39(1)	$C^5–C^6$	1.39(2)	$C^{12}–C^{13}$	1.40(2)
$N^2–C^{16}$	1.47(1)	$C^6–C^7$	1.41(3)	$C^{13}–C^{14}$	1.41(2)
$N^2–H^2$	0.9681	$C^7–C^8$	1.42(2)	$C^{16}–C^{17}$	1.46(3)
$C^3–C^4$	1.36(2)	$C^7–C^{15}$	1.47(2)	$C^{16}–C^{18}$	1.52(2)

Table 7. (Contd.)

Angle	τ	Angle	τ	Angle	τ
$O^2P^2O^1C^{8a}$	–97(1)	$O^2P^2C^3C^4$	106(1)	$H^2N^2C^{16}C^{18}$	–154
$N^2P^2O^1C^{8a}$	142.8(9)	$O^2P^2C^3H^3$	–75	$H^2N^2C^{16}C^{19}$	90
$C^3P^2O^1C^{8a}$	26(1)	$N^2P^2C^3C^4$	–127(1)	$P^2C^3C^4C^{4a}$	0(2)
$O^1P^2N^2C^{16}$	–57(1)	$N^2P^2C^3H^3$	–52.4(9)	$P^2C^3C^4C^9$	–175.6(9)
$O^2P^2N^2C^{16}$	–179(1)	$P^2O^1C^{8a}C^{4a}$	–18(1)	$C^3C^4C^{4a}C^{8a}$	13(2)
$O^2P^2N^2H^2$	–4	$P^2O^1C^{8a}C^8$	162.8(9)	$C^9C^4C^{4a}C^{8a}$	–172(1)
$C^3P^2N^2C^{16}$	53(1)	$P^2N^2C^{16}C^{17}$	145(1)	$C^3C^4C^9C^{10}$	–133(1)
$C^3P^2N^2H^2$	–132	$P^2N^2C^{16}C^{18}$	20(2)	$C^3C^4C^9C^{14}$	42.8(2)
$O^1P^2C^3C^4$	–16(1)	$P^2N^2C^{16}C^{19}$	–96(1)	$C^{4a}C^4C^9C^{10}$	52(2)
$O^1P^2C^3H^3$	–163	$H^2N^2C^{16}C^{17}$	–29	$C^{4a}C^4C^9C^{14}$	–132(1)

XVI in an intermolecular hydrogen bond N–H···O^2 (Fig. 6). The plane of the 4-Ph substituent forms a fairly large torsion angle with the plane of the C^3=C^4 bond [–45(1)°], which makes conjugation between them hardly possible. The phosphoryl group and the N^2–C^{16} bond are *trans* to each other [the $O^2P^2N^2C^{16}$ torsion angle is 180.0(1)°], which is the most favorable for the bulky *tert*-butyl substituent. The sum of bond angles at the nitrogen atom ($P^2N^2C^{16}$, $P^2N^2H^2$, and $H^2N^2C^{16}$) is 359.8(3)°, what means that this atom has a planar trigonal configuiration.

Intermolecular interactions in the crystal of compound **XVI** are more diverse than in the above-described crystal of compound **Vc**. The interaction of the H^2 atom of the amino group with the $O^{2''}$ atom (1 – *x*, –*y*, 2 – *z*) of the phosphoryl group [*d*(H^2···$O^{2''}$) 1.95(2) Å, N^2H^2···O^2 angle 188(1)°] forms molecular dimers (Fig. 6). The participation of bromine atoms in C–H···Br contacts [*d*(Br^6···$H^{17B''}$) 2.79(2) Å, Br^6···$H^{17B'''}$–$C^{6'''}$ angle 115(1)°] results in binding of the molecular dimers in two perpendicular directions to form a lamellar supramolecular structure (Fig. 7a). Such lamellar super structures are bound to each other by π–π interactions of the phenyl rings of molecules relates to each other as –*x*, 1 – *y*, 1 – *z*, with the distance between the ring centers of 3.91 Å and the dihedral angle of 0°.

Inspite of the presence of the bulky *tert*-butyl substituents, a fairly tight crystal packing of molecules **XVI** is achieved (packing coefficient 69.1%) (Fig. 7b). Note that in this crystal there are separate regions with mainly hydrophilic and mainly hydrophobic properties. Previously we showed [3] that molecular associates formed due to this effect can be of different type depending on the relative volumes of the hydrophilic and hydrophobic parts of the molecules, like microphase separation in polymeric systems. In the latter case, such separation gives rise to lamellar structures whose type differs from the type of the supramolecular structure formed by intermolecular interactions (3D net). Contrary to that, in the crystal of compound **Vc** the type of the supramolecular structure formed intermolecular hydrogen bonds (infinite chain of molecules) coincides by its morphologic type with superstuctures formed as a result of separation of hydrophilic and hydrophobic regions, even though the crystal packing here is not very tight (65.8%). These regions represent cylindrical hydrophilic associates in a hydrophobic matrix (Fig. 8). A more detailed analysis of this effect and classification of the resulting structures for condensed phosphorus-containing heterocycles will be given elsewhere.

EXPERIMENTAL

The ^{1}H, ^{13}C, ^{13}C–{^{1}H}, ^{31}P, and ^{31}P–{^{1}H} NMR spectra were recorded on Bruker WM-250 (250 MHz, ^{1}H), Bruker MSL-400 (162.0 MHz, ^{31}P; 100.6 MHz, ^{13}C), and Bruker CXP-100 (36.48 MHz, ^{31}P) spectrometers in DMSO-*d*$_6$ and $CDCl_3$ against of residual proton signals or carbon signals of solvents or against external H_3PO_4. All the spectra were recorded at 25°C, unless otherwise stated. The IR spectra were obtained for suspensions in Vaseline on UR-20 and Bruker Vector-22 instruments. The electron impact mass spectra were measured on a Finnigan-MAT TRACE MS instrument at an ionizing energy of 70 eV and an ion source temperature of 200°C. Direct inlet of samples into the ion source was used, the inlet probe was programmed from 35 to 150°C with a step of 35 deg/min. The mass spectral data were treated by means of the XCALIBUR program.

Conditions of the X-ray diffraction experiments are listed in Table 8.

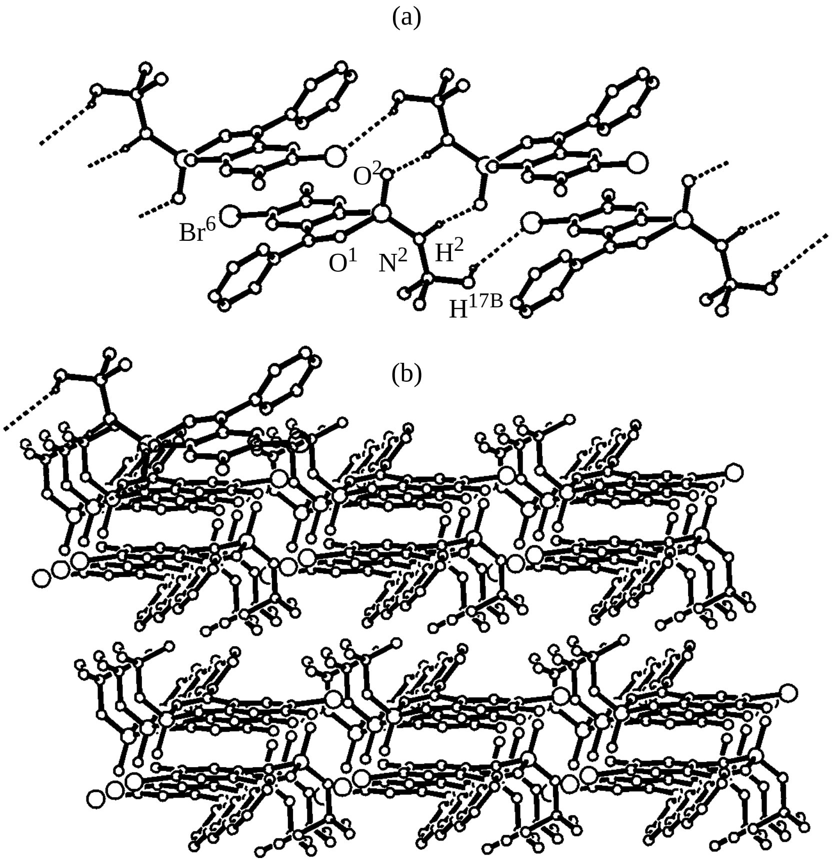


Fig. 7. (a) Formation of lamellar structures by intermolecular contacts in the crystal of compound **XVI** (shown by dashed lines) and (b) crystal packing.

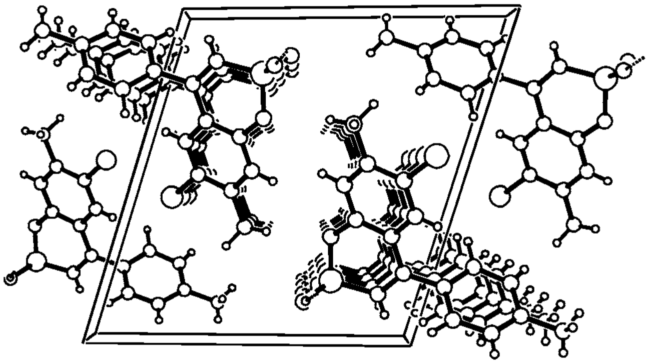


Fig. 8. Crystal packing of molecules **Vc**.

2,2,2-Trichloro-5-methylbenzo[*d*][1,3,2]dioxaphosphole (II). To a solution of 39.4 g of PCl_5 in 143.7 ml of benzene, 19.47 g of a crystalline 4-methylbenzene-1,2-diol was added in portions with stirring. Strong foaming and HCl evolution were observed. Benzene was distilled off, and the residue was distilled in a vacuum. The major fraction of phosphorane **II**, a yellow liquid crystallizing at room temperature, was collected at 95–100°C (0.8 mm Hg), yield 20.2 g (49.6%). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz) (parenthesized are signal shapes in the ^{13}C–{^{1}H} NMR spectrum): 142.84 d.d.d (d) (C^{3a}, $^3J_{HC^7CC^{3a}}$ 7.1, $^2J_{HC^4C^{3a}}$ 3.6, $^2J_{POC^{3a}}$ 0.8); 111.32 d.d.q.d. (d) (C^4, $^3J_{POCCC^4}$ 17.6, $^3J_{HC^6CC_4}$ 7.7, $^3J_{HCCC^4}$ 5.1, $^4J_{HC^7CCC^4}$ 1.4); 133.81 d.q. (s) (C^5, $^3J_{HHC^6CC^5}$ 7.8, $^4J_{HCCC}$ 6.1); 123.51 d.d.q.d. (s) (C^6, $^1J_{HC^6}$ 161.4, $^3J_{HC^4CC^6}$ 7.0, $^3J_{HCCC^6}$ 5.1, $^2J_{HC^7C^6}$ 1.1); 110.43 d.d. (d) (C^7, $^1J_{HC^7}$ 166.7, $^3J_{POCC^7}$ 17.7); 140.40 m (d) (C^{7a}, $^2J_{POC^{7a}}$ 0.8); 21.21 q.d.d. (d) CH_3, $^1J_{HC}$ 127.2, $^3J_{HO^4CC}$ 4.7, $^3J_{HCO^6CC}$ 4.7). ^{31}P–{^{1}H} NMR spectrum (36.48 MHz, CH_2Cl_2): δ_P –27.26 ppm.

2,2,2-Tribromo-5-methylbenzo[*d*][1,3,2]dioxaphosphole (III). *a*. A mixture of 20 g of 4-methylbenzene-1,2-diol, 17.5 ml of PBr_3, and 5–6 drops of water was heated with stirring over the course of 30–40 min at 90°C. Strong HBr evolution was observed. Vacuum distillation gave 30.44 g (81%) of compound **III** as a colorless liquid with bp 70–75°C (0.8 mm Hg). ^{31}P–{^{1}H} NMR spectrum (CH_2Cl_2): δ_P 189.0 ppm.

Table 8. Crystal parameters of compounds **IVa, Vc**, and **XVI** and conditions of X-ray diffraction experiments[a]

Parameter	**IVa**[b]	**Vc**[b]	**XVI**[c]
Color, habitus	Colorless, prysmatic		
Syngony	Triclinic		
Space group	*P*-1		
Unit cell parameters[d]	*a* 8.011(1), *b* 9.122(2) *c* 9.342(1) Å α 77.7(6)° α 73.10(3)° γ 69.9(6)°	*a* 4.642(1), *b* 12.546(4) *c* 13.334(3) Å α 70.1(4)° β 66.4(6)° γ 83.56(2)°	*a* 10.253(2), *b* 10.236(2) *c* 10.399(5) Å β 83.02(2)° β 67.04(1)° γ 64.05(1)°
V, Å^3	701.9(3)	747(1)	844.5(2)
Z	2	2	2
Molecular weight	325.13	320.72	403.24
d_{calc}, g cm^{-3}	1.538	1.426	1.514
Absorption coefficient, cm^{-1}	5.709	3.643	23.986
F(000)	332	332	410
Radiation (λ, Å)	MoK_α, λ 0.71073		
θ range	$2.12 < \theta < 27.4$		
Scan angle	$0.68 + 0.4\tan\theta$		
Standard reflections	Two control by orientation and three control by intensity every 200 reflections		
Index range	$-9 < h < 8$, $-10 < k < 9$, $-10 < l < 0$	$-5 < h < 0$, $-13 < k < 12$, $-13 < l < 13$	$-12 < h < 11$, $-12 < k < 11$, $-12 < l < 9$
Reflections measured	1866	1904	4911
Number of observed reflections with $I > 3\sigma(I)$	1436	1428	1211
Absorption corrections	Not used		Empirical
Location and and refinement of hydrogen atoms	Located by difference synthesis, refined isotropically		
Final values of divergence factors	*R* 0.031, R_W 0.037	*R* 0.035, R_W 0.048	*R* 0.0979, R_W 0.2212
Fitting parameter	1.363	1.732	1.176
Δ/σ	0.00	0.01	0.006
Number of refined parameters	225	246	196
Number of unique reflections	1433	1496	2870

[a] Enraft–Nonius CAD-4 diffractometer; ω/2θ scanning, scan rate 1–16.4 deg min^{-1} by θ; no correction for the intensity decay of control reflections was applied; MolEN program, AlphaStation 200 computer [8]. [b] Direct method of structure solution, SIR program [9]; full-matrix least-squares refinement; minimized function $-\Sigma w(|Fo| - |Fc|)^2$; no extinction correction was applied; weight scheme $4F_0^2/[\sigma(I)^2 + (0.04F_0^2)]^2$. Analysis of intermolecular contacts, including hydrogen bonds in crystals, was carried out by the PLATON program [7]. [c] Direct method of structure solution, SIR program [9]; refinement by the SHELX program [10].
[d] Standard deviations are given in parentheses.

b. To a solution of 11 g of 2-bromo-5-methylbenzo[*d*][1,3,2]dioxaphosphole in 20 ml of CH_2Cl_2, 2.4 ml of bromine was added dropwise with stirring under argon. Phosphorane **III** was quantitatively formed. It was further used without isolation as a solution in methylene chloride. ^{31}P–{^{1}H} NMR spectrum (36.48 MHz, CH_2Cl_3): δ_P –190 ppm.

Reaction of phosphole II with phenylacetylene. To a solution of 7.9 g of phosphorane **II** in 5 ml of methylene chloride, a solution of 6.2 g of phenylacetylene in 2 ml of methylene chloride was added dropwise at 10–15°C under argon. The reaction mixture was left to stand for a day. Therewith, crystals of 2,6-dichloro-7-methyl-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**IVa**) (yield 70%) formed. The residual solution was carefully decanted, and the crystals were washed with cold (–30°C) methylene chloride and dried in a vacuum (0.8 mm Hg), mp 140–145°C. ^{31}P NMR spectrum (162.0 MHz, CH_2Cl_2), δ_P, ppm: 17.4 d.d ($^2J_{PCH}$ 26.3 Hz). Found, %: C 55.73; H 3.92; P 9.11. $C_{15}H_{11}Cl_2O_2P$. Calculated, %: C 55.38; H 3.78;P 8.88. The solvent, excess phenylacetylene, and chlorostyrenes were removed in a vacuum, and the residue was hydrolyzed in acetone to obtain crystals of 6-chloro-2-hydroxy-7-methyl4-phenyl-6-benzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**Va**), yield 2.45 g, mp 235–240°C. IR spectrum, ν, cm^{-1}: 416, 485, 462, 541, 595, 675, 698, 729, 758, 813, 834, 876, 882, 1012, 1036, 1074, 1129, 1167, 1193, 1207, 1248 sh., 1255, 1338, 1377, 1443, 14.84, 1594, 1600, 2298 v.br (P–OH), 2551 v.br, 3060. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 40°C), δ, ppm (*J*, Hz): 2.36 s (CH$_3$, 3H), 6.31 d (H^3, 1H, $^2J_{PCH}$ 17.5); 7.00 s (H^8, 1H), 7.34 s (H^5, 1H), 7.38 m and 7.52 m (C_6H_5, 5H). ^{31}P NMR spectrum (163.0 MHz, DMSO-d_6), δ_P, ppm: 3.7 d ($^2J_{PCH}$ 17.5 Hz). Found, %: C 58.95; H 3.78, P 9.88. $C_{15}H_{12}ClO_3P$. Calculated, %: C 58.73; H 3.92; P 10.11.

Reaction of trichlorophosphole II with 4-chlorophenylacetylene. To a solution of 11.3 g of phosphorane **II** in 10 ml of methylene chloride, 9.0 g of 4-chlorophenylacetylene in 10 ml of methylene chloride was gradually added under argon at 10–15°C. After 2 h, the solvent and chlorostyrene were removed from the reaction mixture in a vacuum, and the residue was crystallized from CCl$_4$ to isolate 7.6 g (49%) of 2,6-dichloro-4-(4-chlorophenyl)-7-methylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**IVb**), mp 145–147°C. ^{31}P NMR spectrum (162.0 MHz, CDCl$_3$), δ_P, ppm: 16.2 d ($^2J_{PCH}$ 23.6 Hz). ^{1}H NMR spectrum (250 MHz, CDCl$_3$), δ, ppm (*J*, Hz): 2.44 s (CH$_3$, 3H), 6.28 d (H^3, 1H, $^2J_{PCH}$ 26.3), 7.15 s (H^8, 1H), 7.21 s (H^5, 1H), 7.31 m and 7.48 m (H^{10}, H^{11}, 4H, *AA'BB'* spectrum, $^3J_{AB} = {}^3J_{A'B'}$ 8.7). Mass spectrum, *m/z* (I_{rel} %) (peaks of ions containing the most abundant isotope are given): 363 (1.6), 362 (7.8), 3.61 (4.4), 3.60 (24.0), 361 (5.9), 358 (24.9) [$M^{+\cdot}$]; 323 (43.1), 287 (34.9), 241 (41.1), 176 (100.0), 105 (44.4), 77 (51.8),] 47 (69.2), 36 (37.8), 35 (10.7). The filtrate containing about 7 g of chlorophosphorine **IVb** was hydrolyzed with excess of water in dioxane (20 ml). A precipitate formed after two days and was washed with ether and dried to give 4.0 g (60.2%) of 6-chloro-4-(4-chlorophenyl)-2-hydroxy-7-methylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**Vb**), mp 238–242°C. IR spectrum, ν, cm^{-1}: 414, 451, 519, 543, 565, 617, 714, 737, 804, 824, 849, 871, 887, 923, 1015, 1037, 1093, 1129, 1166, 1182, 1250–1253, 1337, 1398, 1482, 1510, 1600, 2284– 2254 v.br, 2600–2500 v.br, 3678, 3843. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 50°C), δ, ppm (*J*, Hz): 2.37 s (CH$_3$, 3H), 6.31 d (H^3, 1H, $^2\mathrm{J}_{PCH}$ 17.6), 7.00 s (H^8, 1H), 7.32 s (H^5, 1H), 7.41 m and 7.57 m (H^{10}, H^{11}, 4H, *AA'BB'* spectrum, $^3J_{AB} = {}^3J_{A'B'}$ 8.7). ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6), δ_P, ppm: 3.2 d ($^2J_{PCH}$ 7.0 Hz). Found, %: C 52.84; H 2.97; Cl 20.47. $C_{15}H_{11}Cl_2O_3P$. Calculated, %: C 52.79; H 3.23; Cl 20.82.

Reaction of phosphorane II with 4-methylphenylacetylene was carried out by the above procedure using 8.1 g of phosphorane **II** in 6 ml of methylene chloride and 6.55 g of 4-methylphenylacetylene in 4 ml of methylene chloride. The reaction mixture was kept in a vacuum (0.8 mm Hg) to remove the solvent, excess acetylene, and chlorostyrene. The resulting viscous glassy material containing, according to the ^{31}P NMR spectrum (162.0 MHz, CH$_2$Cl$_3$), 77% of 2,6-dichloro-7-methyl-4-(4-methylphenyl)-benzo[*e*]-[1,2λ^5]oxaphosphorine 2-oxide (**IVc**) (δ_P 17.4 ppm, $^2J_{PCH}$ 24.6 Hz) was dissolved in 50 ml of dioxane and hydrolyzed with excess water. After 1–2 h, a precipitate formed and was filtered off, washed with ether, and dried to give 5.49 g (55%) of 6-chloro-2-hydroxy-7-methyl-4-(4-methylphenyl)benzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**Vc**), mp 245–247°C. IR spectrum, ν, cm^{-1}: 445, 461, 515, 525, 545, 579, 638, 667, 736, 746, 800, 820, 847, 883, 922, 1010, 1036, 1129, 1166, 1191, 1203, 1215, 1242, 1255, 1337, 1510, 1541, 1594, 1613, 2324–2300 v.br (P–OH), 2588–2520 v.br (P–OH). ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 50°C) δ, ppm (*J*, Hz): 2.48 s and 2.50 s (CH$_3$, 6H), 6.34 d (H^3, 1H, $^2J_{PCH}$ 17.7), 7.15 s and 7.38 s (H^5 and H^8, 2H), 7.39–7.42 m (H^{10}, H^{11}, 4H, *AA'BB'* spectrum, $^3J_{AB} = {}^3J_{A'B'}$ 8.2). ^{31}P NMR spectrum (162.0 MHz, DMF), δ_P, ppm: 3.4 d ($^2J_{PCH}$ 17.7 Hz). Found, %: C 58.54; H 4.33; P 9.87. $C_{16}H_{14}ClO_3P$. Calculated, %: C 59.91; H 4.37; P 9.67.

2,6-Dichloro-4-(4-chlorophenyl)-2-(isopropylamino)-7-methylbenzo[*e*][1,2]oxaphosphorine (VIIb). A mixture of 2.8 g of phosphonic acid **Vb** and 2.6 g of phosphorus pentachloride suspended in 12 ml of benzene was heated for 3 h at 80°C. The solvent and phosphorus oxychloride were then removed by distillation, and the solid residue was diluted with 30 ml of benzene. The resulting solution was treated with excess isopropylamine (1.6 ml) and kept for 1–2 h at 20°C. A precipitate formed and was filtered off, the filtrate was washed with 10% sodium carbonate and water and dried over sodium sulfate. After 7–9 days, a white precipitate formed and was filtered off, washed with diethyl ether and dried in a vacuum (12 mm Hg) to give 2.79 g (89%) of oxaphosphorine **VIIb**, mp 184–165°C. IR spectrum, ν, cm^{-1}: 447, 471, 524, 578, 614, 675, 710, 735, 754, 807, 846, 869, 917, 1016, 1037, 1072, 1093, 1130, 1166, 1213, 1235, 1336, 1399, 1442, 1535, 1562, 1597, 3178. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 40°C), δ, ppm (*J*, Hz): 1.11 d and 1.17 d [6H, (CH$_3$)$_2$, $^3J_{HCCH}$ 6.5], 2.38 s (3H, CH$_3$), 3.32 m (1H, CH), 5.43 d.d (1H, NH, $^2J_{HNH}$ 10.4, $^3J_{HCNH}$ 10.4), 6.21 d (1H, H^3, $^2J_{PCH}$ 17.2), 7.02 s (1H, H^8), 7.35 s (1H, H^5), 7.43 m and 7.59 m (4H, H^{10}, H^{11}, *AA'BB'*spectrum, $^3J_{AB} = {}^3J_{A'B'}$ 8.5). ^{31}P NMR spectrum (162.2 MHz, DMSO-d_6), δ_P, ppm: 9.7 d.d ($^2J_{PCH}$ 17.2, $^3J_{PNCH}$ 10.4 Hz). Found, %: C 56.59; H 4.58; N 3.86. $C_{18}H_{18}Cl_2NO_2P$. Calculated, %: C 56.54; H 4.71; N 3.66.

6-Chloro-2-(isopropylamino)-7-methyl-4-(4-methylphenyl)benzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (VIIc). A mixture of 3.1 g of phosphonic acid **Vc**, 15 ml of benzene, and 3 g of phosphorus pentachloride was heated under reflux for 3 h until the precipitate of compound **Vc** dissolved completely. The reaction mixture was kept in a vacuum to remove volatile admixtures, and the solid residue was dissolved in 20 of benzene, treated with 1.8 ml of isopropylamine, and stirred for 3 h. The precipitate was filtered off and washed with 10% sodium carbonate and water. During washing a white precipitate insoluble in water and benzene formed and was filtered off, washed with ether, and dried in a vacuum (12 mm Hg) to give 3.0 g (87%) of oxaphosphorine **VIIc**, mp 168–189°C. IR spectrum, ν, cm^{-1}: 472, 525, 636, 732, 797, 811, 832, 845, 861, 916, 1020, 1070, 1130, 1165, 1217, 1235, 1337, 1443, 1509, 1535, 1567, 1589, 1610, 3185. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 40°C), δ, ppm (*J*, Hz): 1.10 d and 1.11d [6H, $(CH_3)_2$, $^3J_{HCCH}$ 6.5], 2.38 s (3H, C^7CH_3) and (3H, $C^{12}CH_3$), 5.40 d.d (1H, NH, $^2J_{PNH}$ 10.8, $^3J_{HCNH}$ 9.7), 6.12 d (1H, H^3, $^2J_{OCH}$ 17.8), 7.07 s (1H, H^5), 7.31 m (4H, H^{10}, H^{11}, *AA'BB'* spectrum, $^3J_{AB} = {}^3J_{A'B'} = 8.3$). ^{31}P NMR spectrum (162 MHz, DMSO-d_6), δ_P, ppm: 10.1 d.d ($^2J_{PCH}$ 17.7, $^2J_{PNH}$ 10.8 Hz). Found, %: C 62.54; H 5.78; N 3.69. $C_{19}H_{21}ClNO_2P$. Calculated, %: C 63.07; H 5.81; N 3.87.

Morpholinium 6-chloro-7-methyl-2-oxo-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorin-2-olate (VIIIa). To a solution of 4 g of benzophosphorine **IVa** in 15 ml of methylene chloride, 1.2 g of morpholine and 2 ml of triethylamine were added. After stirring for 2 h, the reaction mixture was washed with water, the organic layer was dried over $MgSO_4$, and the solvent was evaporated. The residue was treated with ether to obtain a white precipitate that was filtered off, dried, and crystallized from acetone to obtain 4.2 g (87%) of benzophosphorine **VIIIa**, mp 192–193°C. IR spectrum, ν, cm^{-1}: 2720, 2651, 2559, 2467, 2348, 2293, 2238 (NH_2^+), 1636, 1592, 1572, 1535, 1338, 1223, 1182, 1164, 1130, 1106, 1073, 1045, 1019, 984, 922, 912, 874, 835, 804, 755, 728, 700, 677, 655, 600, 539, 517, 475, 456, 427. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 50°C), δ, ppm (*J*, Hz): 2.32 s (3H, CH_3), 3.05 m (4H, NCH_2, $^3J_{HCCH}$ 4.7), 3.89 m (4H, OCH_2, $^3J_{HCCH}$ 4.7), 6.10 d (1H, H^3, $^2J_{PCH}$ 16.5) 6.88 s and 7.09 s (2H, H^5 and H^8), 7.31 m and 7.46 m (5H, C_6H_5, 5H). ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, DMF): δ_P –1.0 ppm. ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6), δ_P, ppm: –1.7 d ($^2J_{PCH}$ 16.5 Hz). Found,%: C 57.47; H 5.44; Cl 9.28; N 3.51; P 7.74. $C_{19}H_{21}ClNO_4P$. Calculated,%: C 57.94, H 5.34, Cl 9.02, N 3.56, P 7.88.

Isopropylammonium 6-chloro-7-methyl-4-(4-methylphenyl)-2-oxobenzo[*e*][1,2λ^5]oxaphosphorin-2-olate (VIIIc). To a mixture of 1.0 g of hydroxyphosphorine **Vc** in 20 ml of anhydrous ether, 0.3 ml of isoproipylamine was added. Phosphorine **Vc** dissolved. After 2–4 h, salt **VIIIc** precipitated and was filtered off, washed with ether, and dried in a vacuum (12 mm Hg) to give 1.0 g (85%) of ammonium salt **VIIIc**, mp 199°C. IR spectrum, ν, cm^{-1}: 2743, 2558, 1631, 1812, 1590, 1532, 1509, 1484, 1334, 1245, 1229, 1196, 1168, 1131, 1074, 1018, 964, 914, 894, 877, 832, 799, 732, 666, 640, 584, 546, 527, 475. 464, 434, 421. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 50°C), δ, ppm (*J*, Hz): 1.15 d [6H, $(CH_3)_3$, $^3J_{HCCH}$ 6.5], 2.31 s (3H, C^7CH_3, 3H) and 2.36 s (3H, $C^{12}CH_3$), 5.99 d (1H, H^3, $^2J_{PCH}$ 16.1), 6.68 s (1H, H^8), 6.98 s (1H, H^5), 7.18 m and 7,41 m (4H, H^{10}, H^{11}, *AA'BB'* spectrum, $^3J_{AB} = {}^3J_{A'B'}$ 8.3). ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6), δ_P, ppm: –1.4 d ($^2J_{PCH}$ 16.2 Hz). Found, %: C 60.12; H 6.21; N 3.77. $C_{19}H_{23}ClNO_3P$. Calculated, %: C 60.08; H 6.07; N 3.69.

Sodium 6-chloro-7-methyl-4-(4-methylphenyl)-2-oxobenzo[*e*][1,2λ^5]oxaphosphorin-2-olate (VIIId). Benzophosphorine **Vc**, 1 g, was treated with an excess of 10% sodium carbonate. Dissolution of the precipitate was observed. The reaction mixture was left to stand for 1.5–2 days. Salt **VIIId** precipitated as fine crystals, yield 1.0 g (95%), mp > 350°C. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 50°C), δ, ppm (*J*, Hz): 2.29 s and 2.35 s, (6H, CH_3), 5.97 d (1H, H^3, $^2J_{PCH}$ 16.0); 6.86 s (1H, H^8), 6.96 s (1H, H^5), 7.156 m (4H, H^{11}, *AA'* part of the *AA'BB'* spectrum, $^3J_{AB} = {}^3J_{A'B'}$ 8.2, 2H), 7.246 m (4H, H^{10}, *BB'* part of the *AA'BB'* spectrum, $^3J_{AB} = {}^3J_{A'B'}$ 8.2, 2H). ^{31}P NMR spectrum (36.48 MHz, DMSO-d_6), δ_P, ppm: –1.0 d ($^2J_{PCH}$ 16.0 Hz). ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6), δ_P, ppm: –1.4 d ($^2J_{PCH}$ 16.2 Hz). Found, %: C 56.12; H 3.91; P 9.11. $C_{16}H_{13}ClNaO_3P$. Calculated, %: C 56.06; H 3.80; P 9.05.

Reaction of tribromophosphorane III with phenylacetylene. To 18.5 g of a freshly prepared tribromophosphorane **III** in 20 ml of CH_2Cl_2, a solution of 9.6 g of phenylacetylene in 10 ml of CH_2Cl_2 was added dropwise with stirring at 0°C. After 5 days, methylene chloride was distilled off, and excess acetylene and bromostyrenes were removed in a vacuum (0.8 mm Hg). The glassy residue was a mixture of 2-bromo-7-methyl-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**IX**), 2,6-dibromo-7-methyl-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**X**), 2-bromo-6-methyl-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**XI**), and 2-bromo-6-(bromomethyl)-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**XII**) in an 88 : 45 : 22 : 9 ratio. ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$), δ_P, ppm: 8.0 (**IX**), 6.8 (**X**), 7.8 (**XI**), and 6.6 (**XII**). ^{1}H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 2.39 s (CH_3), 6.23 d [H^3, $^2J_{PCH}$ 26.5 (**IX**)]; 2.43 s (CH_3), 6.28 d [H^3, $^2J_{PCH}$ 26.1 (**X**)]; 2.24 s (CH_3), 6.27 d [H^3, $^3J_{PCH}$ 26.3 (**XI**)]; 4.36 br.s (CH_2Br), 6.33 d [H^2, $^2J_{PCH}$ 26.2 (**XII**)]. The residue was treated with a little $CHCl_3$ and kept at 0–10°C for two weeks. Crystals formed and, after decantation of the solvent, were washed with cold (–30°C) CCl_4 and dried in a vacuum (0.8 mm Hg) to obtain a mixture of 2-bromo-7-methyl-4-phenylbenzo-[*e*][1,2-oxazaphosphorine 2-oxide **IX** and 2.6-dibromo-7-methyl-2-oxo-4-phenylbenzo[*e*][1,2λ^5]oxazaphosphorine in a 2 : 3 ratio was obtained (^{1}H and ^{31}P NMR data). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 6.26 d (H^3, $^2J_{PCH}$ 28.0), 7.13 s and 7.32 s [H^5 and H^8, **IX**, 6.15 d [H^3, $^3J_{PCH}$ 28.7 **X**. The mixture of phosphorines **IX** and **X** was dissolved in 40 ml of methylene chloride and treated with excess *tert*-butylamine. The reaction mixture was washed with water, and the organic layer was evaporated to obtain a crystalline precipitate of a mixture of 2-(*tert*-butylamino)-7-methyl-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**XV**) and 6-bromo-2-(*tert*-butylamino)-7-methyl-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**XVI**) in a 40 : 60 ratio. ^{31}P–{^{1}H} NMR spectrum (36.48 MHz, DMF): δ_P, ppm: 9.23 (**XV**), 9.52 (**XVI**). The precipitate was subjected to fractional crystallization from DMSO with a small admixture of DMF to obtain 0.2 g of benzophosphorine **XVI**, mp 185–186°C (from acetone). Found, %: C 56.29; H 5.51; Br 19.27; N 3.39; P 7.81. $C_{19}H_{21}Br \cdot NO_2P$. Calculated,%: C 56.18; H 5.17; Br 19.70, N 3.44; P 7.63.

A mixture of benzophosphorines **IX** and **X**, 3.5 g, was dissolved in 20 ml of dioxane and treated with 0.7 ml of water. After 3-4 days, a 1 : 3 mixture of 2-hydroxy-7-methyl-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide (**XIII**) and 6-bromo-2-hydroxy-7-methyl-4-phenylbenzo[*e*][1,2λ^5]oxaphosphorine 2-oxide precipitated and was filtered off, washed with ether, and crystallized from dioxane. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 50°C), δ, ppm (*J*, Hz): compound**XIV**: 6.28 d ($^2J_{PCH}$ 17.8), 7.17 s and 7.34 s (H^4, H^8), 7.39 m and 7.52 m (C_6H_5), 2.39 s (CH_3); compound **XIII**: 6.16 d ($^2J_{PCH}$ 17.8), 2.36 s (CH_3). ^{31}P NMR spectrum (162.0 MHz, DMSO), δ_P, ppm: 3.2 d ($^2J_{PCH}$ 17.8) (**XIV**) and 3.3 d ($^2J_{PCH}$ 17.8) (**XIII**).

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