Reactions of phenylenedioxytrihalophosphoranes with arylacetylenes

5.* Regiochemistry of the reaction of 2,2,2-trichloro-5-chlorocarbonylbenzo[*d*]-1,3,2-dioxaphosphole with phenylacetylene. Synthesis and three-dimensional structures of 6-alkylaminocarbonyl-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinine derivatives

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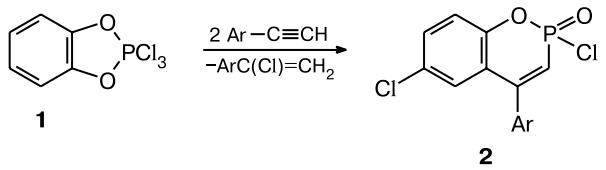
2,2,2-Trichloro-5-chlorocarbonylbenzo[*d*]-1,3,2-dioxaphosphole was prepared for the first time by the reaction of protocatechuic acid with phosphorus pentachloride or trichloride followed by chlorination. According to the results of NMR spectroscopy, the reaction of this phosphole with phenylacetylene gave rise to 2,5-dichloro- and 2,8-dichloro-6-chlorocarbonyl-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinines as the major products. The molecular and supramolecular structures of their stable derivatives, *viz.*, 2-*tert*-butylamino-6-*tert*-butylaminocarbonyl-5-chloro-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinine and isopropylammonium 8-chloro-6-isopropylaminocarbonyl-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinin-2-oate, respectively, were established by X-ray diffraction analysis.

Key words: phenylacetylene, phosphorus(v) chlorides, 1,3,2-dioxaphospholes, regiochemistry of the reaction, benzophosphorinines, chlorination, *ipso*-substitution of oxygen.

P,*P*,*P*-Trihalobenzo[*d*]-1,3,2-dioxaphospholes are typical representatives of derivatives containing the pentacoordinated phosphorus atom, *viz.*, phosphoranes, which can readily react with compounds containing C=O, C=C, or C=N double bonds to yield products in which the coordination number of the phosphorus atom can remain unchanged, increase, or decrease.[2] If the reaction gives rise to the phosphoryl group, these transformations can be assigned to nonclassical Arbuzov reactions.[2] Arylacetylenes react with *P*,*P*,*P*-trihalobenzo[*d*]-1,3,2-dioxaphospholes in an unusual way. Earlier, we have demonstrated[3] that the reactions of *P*,*P*,*P*-trichlorobenzo[*d*]-1,3,2-dioxaphosphole (**1**) with arylacetylenes afforded benzo[*e*]-1,2-oxaphosphorinine derivatives (**2**), which are phosphorus-containing analogs of the natural heterocyclic compound coumarin (Scheme 1). Under mild conditions, the latter reaction involves the *ipso*-substitution of the O atom, the formation of the P—C and P=O bonds, and regioselective chlorination of the phenylene fragment at the *para* position with respect to the endocyclic O atom of the oxaphosphorinine heterocycle.

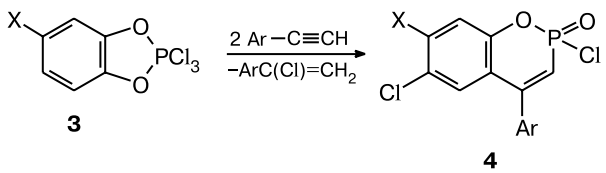
Scheme 1



1 **2**

In the presence of a halogen atom in the benzo fragment of the starting phosphole **3**, the second halogen atom is introduced at the *ortho* position with respect to the first halogen atom and at the *para* position with respect to the O atom of the annelated O,P heterocycle (Scheme 2, compound **4**).[4]

Scheme 2



3 **4**

X = Cl, Br

* For Part 4, see Ref. 1.

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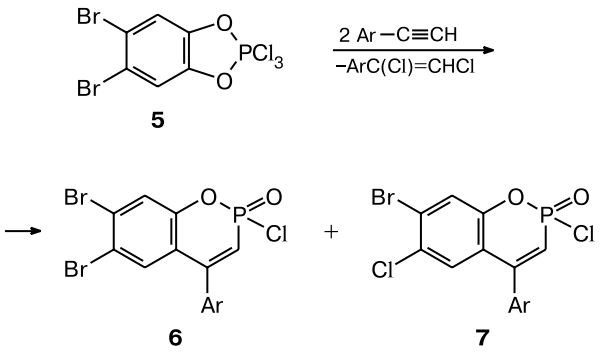
If positions 5 and 6 in benzophosphole (**5**) are occupied by Br atoms, the insertion of the third halogen (chlorine) atom does not take place, and the reaction produces compound **6** (the reaction proceeds with elimination of the chlorine molecule) (Scheme 3). However, this reaction is also accompanied by partial *ipso*-substitution with the replacement of the bromine atom by the chlorine atom (compound **7**).[5]

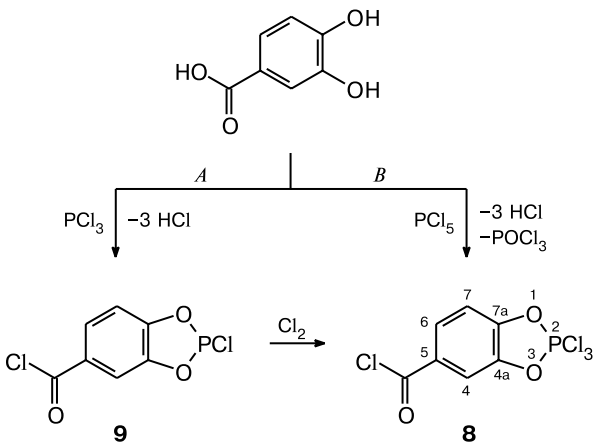
Scheme 3



Results and Discussion

The aim of the present study was to examine the possibility of extending the above-described reaction to more complex benzophosphole derivatives containing a residue of the natural compound, *viz.*, protocatechuic acid. To prepare 2,2,2-trichloro-5-chlorocarbonylbenzo[*d*]-1,3,2-dioxaphosphole (**8**), we investigated the following two approaches (Scheme 4): phosphorylation of protocatechuic acid with phosphorus trichloride to form derivative **9** followed by chlorination (path *A*) and phosphorylation directly with phosphorus pentachloride (path *B*). Both approaches appeared to be efficient and gave rise to product **8** in moderate yields. The reactions were accompanied by chlorination of the carboxy group to form the chlorocarbonyl group. Since the molecule cannot contain simultaneously the free carboxy group and the phosphorane fragment with three P—Cl bonds,[6] the reaction was carried out in the presence of a two-fold excess of PCl_3 or PCl_5.

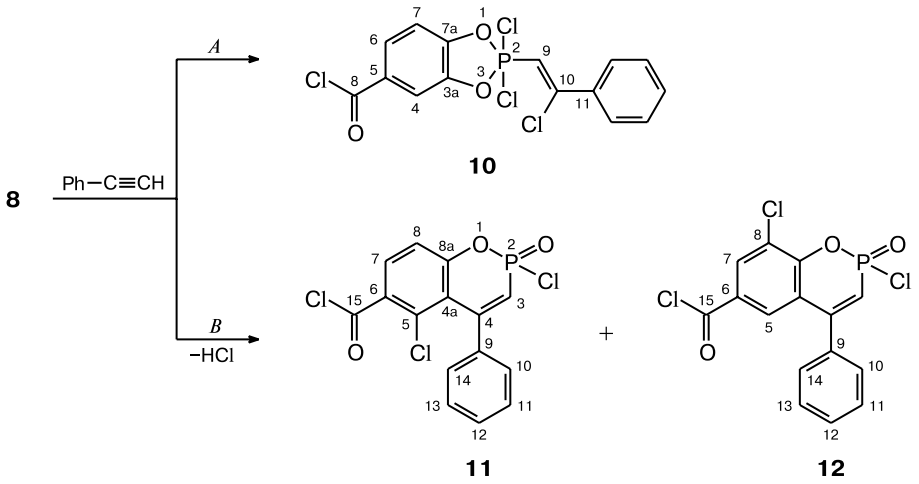
Scheme 4



Trichlorophosphole **8** is thermally stable and can be distilled *in vacuo*. The EI mass spectrum of benzophosphole **8** shows the molecular ion peak $[M]^{\bullet+}$ at *m/z* 306. The precisely measured mass of the $[M]^{\bullet+}$ ion (305.8577) agrees well with the ion mass (305.8574) calculated from the elemental composition $C_7H_3Cl_4O_3P$. The first step of the fragmentation of molecule **8** under electron impact involves the detachment of the Cl atom from the phosphorus atom. This process is responsible for the presence of the ion peak $[M - Cl]^{\bullet+}$ at *m/z* 271 with the highest intensity. The peak at *m/z* 201 belongs, apparently, to the ion obtained as a result of loss of three Cl atoms detached from the P atom. The structure of benzophosphole **8** was confirmed also by ^{13}C NMR spectroscopy (see the Experimental section). The signals of the C atoms of the benzo fragment were interpreted taking into account the *para* and *ortho* effects of deshielding of the chlorocarbonyl substituent. The C(4) and C(7) atoms are easily distinguishable from the C(4a) and C(7a) atoms also based on the multiplicities of the corresponding signals (for the C(4a) and C(7) atoms, the multiplets have a smaller number of lines).

The reaction of benzophosphole **8** with phenylacetylene proceeded readily in a solution in CH_2Cl_2 at 20 °C (Scheme 5). After 4 h, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows three singlets at δ_{P1} 16.0, δ_{P2} 16.1, and δ_{P3} –14.7 in a ratio of 5 (δ_{P1} and δ_{P2}) : 1 (δ_{P3}). In the ^{31}P NMR spectrum, all three singlets turn into doublets with the constants $^2J_{P,CH}$ = 24—25 Hz (δ_{P1} and δ_{P2}) and 37.5 Hz (δ_{P3}). Since the signals at δ_{P1} and δ_{P2} are close together, it is impossible to determine the ratio between them from the ^{31}P or $^{31}P\{^1H\}$ NMR spectra. However, we succeeded in determining this ratio from the ^1H NMR spectrum (400 MHz), in which the integral intensity ratio of the signals at δ 6.49 and 6.57 appearing as doublets with similar constants ($^2J_{P,CH}$ = 24.2 and 25.6 Hz) is 1 : 2. The doublet at low field (δ 7.36) with the constant $^2J_{P,CH}$ = 37.6 Hz belongs to a compound characterized by δ_{P3}. Taking into account the chemical shifts of the protons, it can be concluded that the reaction afforded three compounds containing the P—CH=C fragment. Based on the chemical shifts δ_{P1}, δ_{P2}, and δ_{P3}, the first two signals can be assigned to compounds bearing the phosphoryl group and the third signal can be assigned to a derivative containing the pentacoordinated P atom. According to the $^{13}C\{^1H\}$ and ^{13}C NMR spectroscopic data (Table 1) for the reaction mixture, which was kept *in vacuo* at 0.05 Torr to remove volatile impurities at a temperature of no higher

Scheme 5



than 20 °C, these compounds are benzophosphole **10** (δ_{P3}) and isomeric benzooxaphosphorinines **11** and **12** (δ_{P2} and δ_{P1}). Therefore, the reaction of benzophosphole **8** with phenylacetylene follows two pathways, *viz.*, the classical electrophilic addition at the double bond (see Scheme 5, path *A*) and the path *B* involving the formation of benzooxaphosphorinines **11** and **12**.

To establish the structures of these compounds, we recorded the ^{13}C NMR spectra of the reaction mixture before heating and after its heating *in vacuo* at 150 °C. This allowed us to more reliably assign the key signals to phosphorane **10**, because this compound is thermally unstable and undergoes ambiguous disproportionation processes, which are, apparently, analogous to the transformations of 2,2-dichloro-2-(2-phenylethen-1-yl)benzo[*d*]-1,3,2-dioxaphosphole.[7] Because of a small amount of compound **10**, we failed to unambiguously interpret these processes. The signals corresponding to this compound disappear after heating, which is reflected in the spectrum. The high-field regions of the ^{13}C NMR spectrum

Table 1. Parameters of the $^{13}C\{^1H\}$ and ^{13}C NMR spectra of compounds **11** and **12** in $CDCl_3$

Atom	δ (*J*/Hz)	
	11	**12**
C(3)	120.66 (d [dd], $J_{P,C(3)}$ = 157.2, $J_{H,C(3)}$ =172.6) {120.46 (d)}	116.16 (d [dd], $J_{P,C(3)}$ = 153.2, $J_{H,C(3)}$ = 171.8)
C(4)	154.94 (s [m]) {155.03 (s)}	154.93 (s [m])
C(4a)	122.79 (d [dddd], $J_{P,C(4a)}$ = 18.7, $J_{H(3),C(4a)}$ = 9.0, $J_{H(8),C(4a)}$ = 4.9—5.0, $J_{H(7),C(4a)}$ = 1.6) {122.75 (d)}	123.02 (d [dd], $J_{P,C(4a)}$ = 18.2, $J_{H(3),C(4a)}$ = 8.6)
C(5)	133.43 (d [br.d], $J_{H(7),C(5)}$ = 8.0, $J_{P,C(5)}$ = 1.1) {133.26 (d)}	130.92 (s [dd], $J_{H,C(5)}$ = 169.9, $J_{H(7),C(5)}$ = 6.6)
C(6)	133.40 (d [br.d], $J_{H(8),C(6)}$ = 10.3, $J_{P,C(6)}$ = 2.4) {133.50 (d)}	129.67 (s [br.s])
C(7)	133.95 (s [d], $J_{H,C(7)}$ = 169.2) {134.34 (s)}	134.31 (s [dd], $J_{H,C(7)}$ = 171.8, $J_{H(5),C(7)}$ = 6.9—7.0)
C(8)	118.68 (d [dd], $J_{H,C(8)}$ = 171.3, $J_{P,C(8)}$ = 7.4) {118.73 (d)}	125.95 (d [br.d], $J_{P,C(8)}$ = 7.7)
C(8a)	153.99 (d [ddd], $J_{H(7),C(8a)}$ = 12.2, $J_{P,C(8a)}$ = 10.2, $J_{H(8),C(8a)}$ = 3.8) {159.99 (d)}	151.88 (d [ddd], $J_{P,C(8a)}$ = 9.4, $J_{H(7),C(8a)}$ = 9.1, $J_{H(5),C(8a)}$ = 9.1)
C(9)	138.50 (d [br.dtd], $J_{P,C(9)}$ = 19.6, $J_{H(11),C(9)}$ = 8.1, $J_{H(3),C(9)}$ = 6.9) {138.55 (d)}	135.80 (d [dtd], $J_{P,C(9)}$ = 20.4, $J_{H(11),C(9)}$ = 7.1, $J_{H(3),C(9)}$ = 6.6)
C(10), C(14)	126.46 (s [ddd], $J_{H,C(10)}$ = 160.6, $J_{H(12),C(10)}$ = $J_{H(14),C(10)}$ = 6.8—7.0) {126.45 (s)}	128.07 (s [br.ddd], $J_{H,C(10)}$ = 160.4, $J_{H(12),C(10)}$ = $J_{H(14),C(10)}$ = 6.7—6.9)
C(11), C(13)	128.89 (s [br.dm], $J_{H,C(11)}$ = 161.6, $J_{H(13),C(11)}$ = 5.0—6.5) {128.88 (s)}	129.04 (s [dd], $J_{H,C(11)}$ = 163.4, $J_{H(13),C(11)}$ = 6.7)
C(12)	129.68 (s [dt], $J_{H,C(12)}$ = 161.6, $J_{H(10),C(12)}$ = $J_{H(14),C(12)}$ = 7.5) {129.66 (s)}	130.35 (s [dt], $J_{H,C(12)}$ = 161.0, $J_{H(10),C(12)}$ = $J_{H(14),C(12)}$ = 7.3)
C(15)	164.07 (s [d], $J_{H(7),C(15)}$ = 5.1) {164.15 (s)}	165.44 (s [dd], $J_{H(5),C(15)}$ = $J_{H(7),C(15)}$ = 5.3)

Note. Here and in Table 2, the types of the signals in the ^{13}C NMR spectrum are given in brackets, the chemical shifts and the types of the signal in the ^{13}C NMR spectrum of a pure sample of **11** are given in braces.

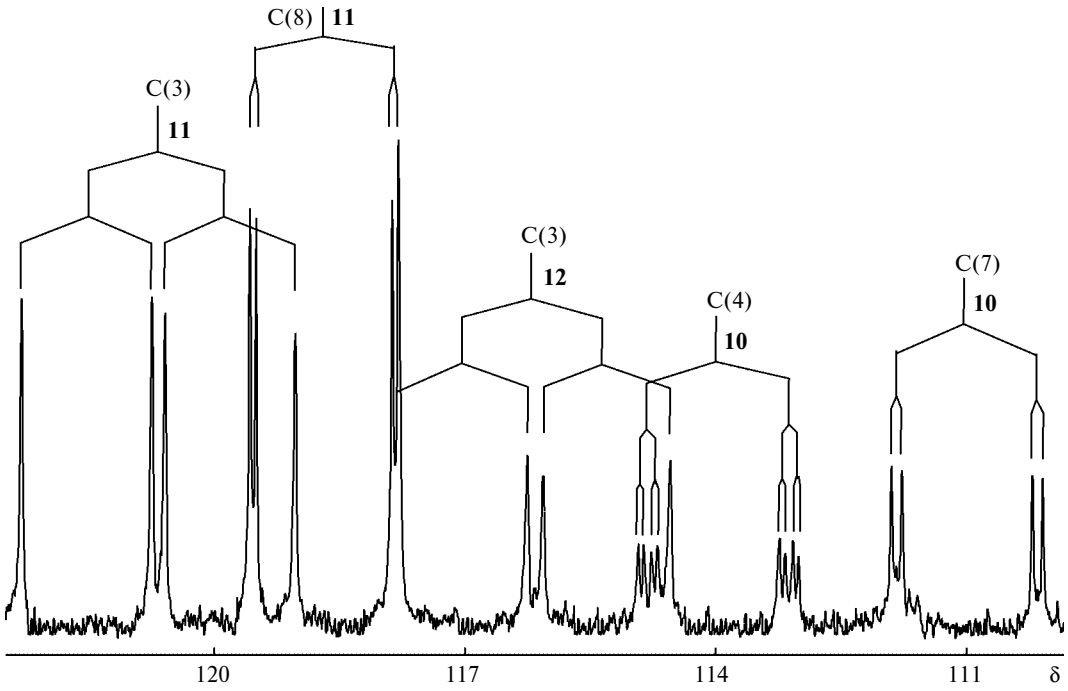


Fig. 1. Fragment of the high-field region of the ^{13}C NMR spectrum of a mixture of compounds **10—12** prepared by the reaction of benzophosphole **8** with phenylacetylene (before heating).

has signals of the C(4) (δ 113.97) and C(7) (δ 111.0) atoms (Fig. 1) of phosphorane **10** with the multiplicities characteristic of the trisubstituted benzene ring (ddd ($^1J_{H,C(4)}$ = 168.7 Hz, $^3J_{P,C(4)}$ = 16.4 Hz, $^3J_{H(6),C(4)}$ = 6.8 Hz) and dd ($^1J_{H,C(7)}$ = 169.2 Hz, $^3J_{P,C(7)}$ = 12.5 Hz)). On the whole, these multiplicities are analogous to those observed for the corresponding signals of the starting phosphole **8**. Figure 2 presents fragments of the low-field region of the $^{13}C\{^1H\}$ NMR spectrum (see Fig. 2, *a*) and the ^{13}C NMR spectra (see Fig. 2, *b—d*) of a mixtures of the resulting compounds (**10—12**). As can be seen from Fig. 2, the signals of the C atoms of the corresponding compounds are well-resolved, which facilitates their interpretation. The signal of the C(8) atom of the chlorocarbonyl substituent in compound **10** is observed at low field (δ 166.19, ddd, $^3J_{H(6),C(8)}$ = $^3J_{H(4),C(8)}$ = 5.3 Hz, $^4J_{H(7),C(8)}$ = 1.0 Hz). This region of the spectrum shows also the resonances of the C(7a) atom (δ 150.31, ddd, $^3J_{H(6),C(7a)}$ = 11.1 Hz, $^3J_{H(4),C(7a)}$ = 5.7 Hz, $^2J_{H(7),C(7a)}$ = 2.7 Hz, $^2J_{P,C(7a)}$ = 0 Hz) and the C(4a) atom (δ 142.48, ddd, $^3J_{H(7),C(4a)}$ = 5.7 Hz, $^2J_{H(4),C(4a)}$ = 3.3 Hz, $^4J_{H(6),C(4a)}$ = 1.2 Hz, $^2J_{P,C(4a)}$ = 0 Hz). The C(10) and C(11) atoms come into resonance at δ 142.47 (m, $^2J_{P,C(10)}$ = 9.5 Hz) and δ 134.96 (m, $^3J_{P,C(11)}$ = 23.6 Hz), respectively. It should be noted that the value of the constant $^3J_{P,C(11)}$ is indicative of the *trans* arrangement of the phosphorane fragment and the Ph substituent, *i.e.*, of the *E* configuration of the substituted ethene. The resonance of the C(9) atom is observed at δ 128.76. The multiplicity (dd) and constants ($^1J_{P,C(9)}$ = 202.0 Hz and $^1J_{H,C(9)}$ = 168.8 Hz) of this resonance are consistent with those observed for the chemically similar compound, *viz.*, 2,2-dichloro-2-(2-phenylethen-1-yl)benzo[*d*]-1,3,2-dioxaphosphole.[7] The assignment of all other C atoms is unreliable because of overlapping of the signals of oxaphosphorinines **11** and **12**.

The EI mass spectrum measured directly for the reaction mixture consisting of compounds **11** and **12** has only one molecular ion peak $[M]^{\bullet+}$. Its precisely measured mass is 371.9281, which is in good agreement with the value calculated from the elemental composition $C_{15}H_8Cl_3O_3P$, *i.e.*, both compounds, apparently, contain the Cl atom in the benzo fragment. The first step of fragmentation of both compounds under electron impact involves detachment of the Cl atom from the phosphorus atom giving rise to a peak at *m/z* 337 $[M - Cl]^{\bullet+}$, which has the maximum height in the mass spectrum. The cleavage of the P—O and P—C bonds in the phosphorinine ring results in an ion with *m/z* 274. This process is accompanied by migration of one H atom to the neutral fragment to form an ion with *m/z* 273. For the above-mentioned ions, the relative intensities of the peaks associated with the presence of isotopes correspond to those calculated from the molecular formulas of the ions. The presence of other fragmentation ions with small *m/z* (see the Experimental section) is, apparently, attributed to further successive fragmentation of these ions under electron impact. Therefore, the mass spectra show clear evidence for

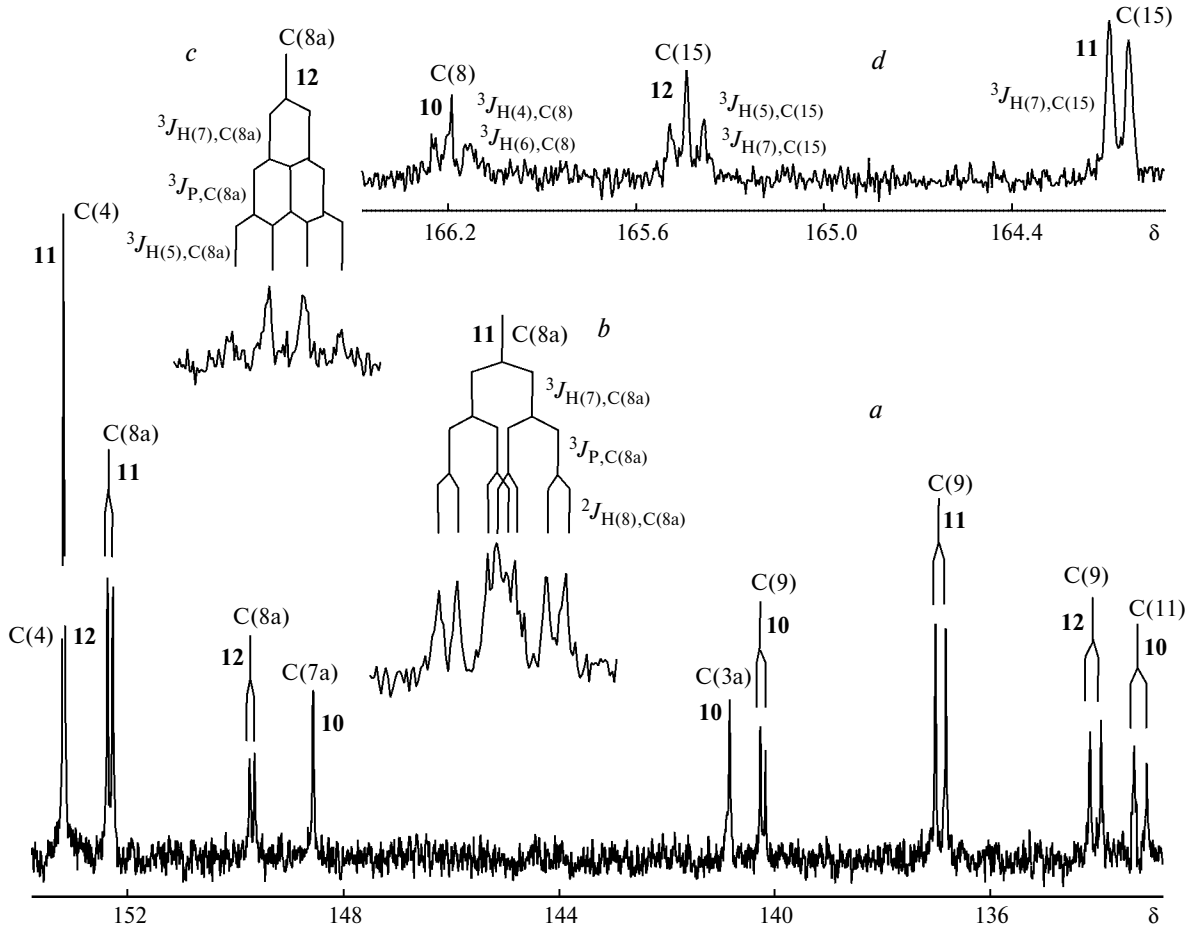


Fig. 2. Fragments of the low-field region of the $^{13}C\{^1H\}$ NMR spectrum (*a*) and the ^{13}C NMR spectra (*b*—*d*) of a mixture of compounds **10**—**12** prepared by the reaction of benzophosphole **8** with phenylacetylene (before heating).

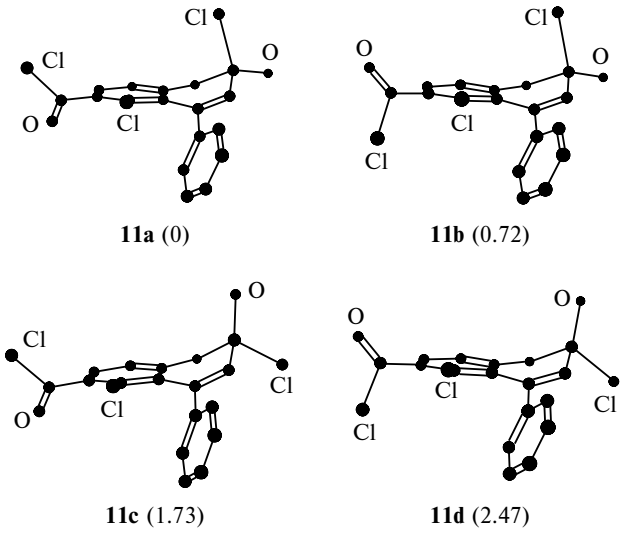
the formation of two benzooxaphosphorinines containing three Cl atoms.

The ^{13}C NMR spectroscopic data (see Table 1) unambiguously demonstrate that the Cl atom is introduced into the phenylene fragment (rather than into the phenyl substituent) at position 4 of the heterocycle. The presence of the only doublet of doublets at high field (δ_C 118.75) indicates that the C(8) atom in the major isomer (compound **11**) bears the proton, whereas this atom in the minor isomer (compound **12**) is bound to the Cl atom. The multiplicity of the signal of C(8) (see Fig. 1) is evidence for the presence of the substituent at position 6 (*i.e.*, the constant $^3J_{H(6),C(8)}$ is absent). The fact that the signal of the C(8a) atom in both compounds **11** and **12** appears at lower field compared to those in benzooxaphosphorinines **2**, **4**, **6**, and **7** [3—5] is indicative of the presence of the chlorocarbonyl substituent in the *para* position with respect to the C(8a) atom. The difference in the multiplicity of the signals of the C(15) atoms in isomers **11** and **12** at low field (see Fig. 2, *d*) is very informative. In the spectrum of isomer **12**, this signal appears as a doublet of doublets, which is evidence that the C(5) and C(7) atoms bear H atoms (for the aromatic nuclei, the vicinal constant $^3J_{H,C}$ is larger than the geminal constant[7]). By contrast, the spectrum of isomer **11** shows this signal as a doublet, which indicates that the Cl atom is bound to either the C(5) or C(7) atom. In the spectra of compounds **2**, **4**, **6**, and **7**, the resonance of the analogous C(7) atom bearing the Cl atom is observed at rather low field (δ 136—138),[3,4] whereas the signal of the C(5)(Cl) atom in the spectra of 4-aryl-2,5,6,7,8-pentachloro-2-oxobenzo[*e*]-1,2-oxaphosphorinines is present in the region of δ 131—132 due to shielding by the aryl substituent at position 4.[8,9] It should be noted that both the multiplicities and the constants $^3J_{H,C}$, $^3J_{P,C}$, and $^2J_{H,C}$ of the signals of the C(4a) atom (see Fig. 2, *b*, *c*) are also consistent with the structures of 1,2,3,4- and 1,2,4,6-tetrasubstituted benzenes **11** and **12**, respectively. Taking into account these data, it can be concluded that the Cl atom in major isomer **11** is attached to the C(5) atom. The question as to the position of the Cl atom in the phenylene ring can also be solved by ^1H NMR spectroscopy. If the Cl atom is located at position 5, the H(7) and H(8) protons would appear as either an AX or AB spin system.

Actually, the ^{1}H NMR spectrum (250 MHz) of the reaction mixture shows signals corresponding to the resonance of an AMX system (δ 8.11 (dd, H(7), $^3J_{H(7),H(8)}$ = 8.8 Hz, $^5J_{P,H(7)}$ = 1.6 Hz); δ 7.42 (dd, H(8), $^3J_{H(7),H(8)}$ = 8.8 Hz, $^4J_{P,H(8)}$ = 0.8 Hz)). This spectrum has also signals belonging to the protons of the benzo fragment of compound **12** (at δ 7.95 (br.d, H(5), $^4J_{H(7),H(5)}$ = 2.2 Hz); 8.30 (dd, H(7), $^4J_{H(7),H(5)}$ = 2.2 Hz, $^5J_{P,H(7)}$ = 1.8 Hz)), which confirm the presence of the H atoms at the C(5) and C(7) atoms.

Because of the complexity of the spectra associated with the presence of three compounds in the reaction mixture, we also calculated the chemical shifts of the compounds under study by quantum-chemical methods. The modern calculation methods can be successfully used for complex organic compounds containing C, H, N, and O atoms (see, for example, the studies[10–18]). In the present investigation, we calculated the ^{1}H and ^{13}C chemical shifts of benzooxaphosphorinines **11** and **12** by the GIAO B3LYP/6-31G(d) method for geometries optimized at the HF/6-31G level of theory. To our knowledge, this approach has not previously been used for systems containing the P atom in the ring and several polar substituents. A complication of the electronic structures of compounds, which is associated with the introduction of heavy atoms, such as P and Cl, as well as with the conformational inhomogeneity, makes calculations more difficult.[19] The preliminary results of these calculations are given below. The detailed data will be published elsewhere. The absolute values of shielding were calculated and the chemical shifts were assigned relative to the signal of Me_4Si calculated under the identical conditions.

For compound **11**, the geometry optimization revealed four forms (Fig. 3) corresponding to the energy minima.



11a (0) **11b** (0.72)

11c (1.73) **11d** (2.47)

Fig. 3. Main forms of compound **11** (the relative energies in kcal mol^{-1} (HF/6-31G) are given in parentheses).

Two forms differ in the orientation of the substituents at the asymmetric P atom (axial and equatorial orientations). For each of these forms, two conformers can occur due to rotation of the substituent about the C(6)—CO bond. Each form is presented in Fig. 3 by one of enantiomers. Below, we consider in detail only two most stable conformations, *viz.*, **11a** and **11b**.

In all four forms, the conformation of the heterocyclic fragment can be described as a boat with the P(2) and C(3) atoms deviating from the plane of the fragment. The presence of the bulky groups (ClC(O), Cl, or Ph) leads to a substantial distortion of the geometry of the aromatic fragment from the usual planar structure. The selected calculated dihedral angles describing the conformation of the heterocycle and the chlorocarbonyl substituent for major conformer **11a** are as follows:

Cl—C(15)—C(6)—C(7) 142.0°,
Cl(5)—C(5)—C(4a)—C(4) −166.6°,
C(5)—C(4a)—C(4)—C(3) 25.7°,
P(2)—C(3)—C(4)—C(4a) −5.3°,
C(4)—C(3)—P(2)—O(1) −22.0°,
C(3)—P(2)—O(1)—C(8a) 38.3°,
P(2)—O(1)—C(8a)—C(4a) −26.1°,
O(1)—C(8a)—C(4a)—C(4) 10.0°,
O(1)—C(8a)—C(4a)—C(5) −7.7° .

On the whole, the calculated chemical shifts for the above-given conformers of compound **11** correlate well with the experimental data (except for two points), and the dependence is nearly linear (Fig. 4, *a*, *b*). The theoretical values of the ^{13}C chemical shifts are somewhat underestimated, which is typical of this method. This effect has been observed earlier[11] for compounds containing C, H, O, and N atoms and is, apparently, associated with either limitations of the method used for calculations of chemical shifts or with the fact that the experimental data are obtained in solutions, whereas calculations are carried out for the gas phase. The exceptions are the chemical shifts of the C(4) and C(3) atoms, for which deviations are as high as 13—14 and 6 ppm, respectively.

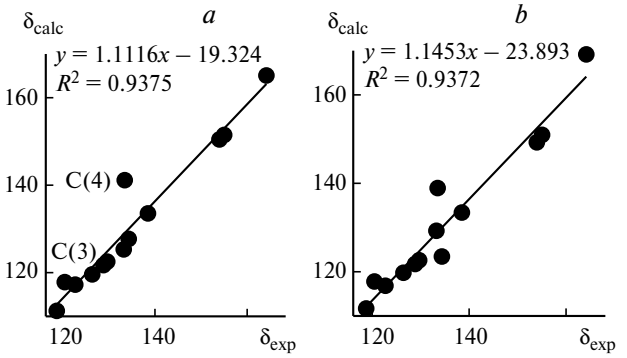


Fig. 4. Correlation between the calculated and experimental chemical shifts of the C atoms in major conformers **11a** (*a*) and **11b** (*b*).

It is quite possible that this discrepancy results from either a not-too-"good" optimized geometry determined within the framework of the method used (which is not sufficiently correct to describe Period III elements, such as P and Cl), or limitations of the model used for calculations of the chemical shifts.

A comparison of the experimental chemical shifts with the calculated data on four conformers shows that the best agreement is observed for the conformer with the minimum energy. According to the results of calculations, the orientation of the substituent at the P atom has the most pronounced effect on the chemical shift of the C(3) atom and, to some extent, on that of the C(4) atom. The change in the orientation of the substituent at the C(6) atom has also a predictable effect on the chemical shifts of the C(7), C(5), and C(15) atoms, *i.e.*, the chemical shifts δ_C can serve as a spectroscopic test for the identification of fine conformational details of such structures.

Rotational isomerism about the C(6)—C(15) bond has an appreciable effect on the chemical shifts of the vicinal protons of the aromatic fragment. Thus, the difference between the chemical shifts calculated for the conformer with the *cis* orientation of the Cl atoms has a minimum value (0.19 ppm), whereas this difference for the conformers with the *trans* orientation of these atoms may be as large as 0.84 ppm, which is close to the experimental value (0.67 ppm). The chemical shifts of the protons of the cyclic fragment are also well-reproduced for the geometry corresponding to the major conformer. The following correlations between the calculated and experimental chemical shifts of the protons for two orientations of the substituent at the C(6) atom were obtained (conformations **11a** and **11b**): $y = 1.2837x - 2.5851$, $R^2 = 0.9999$ (**11a**) and $y = 0.8843x + 0.1494$, $R^2 = 0.9098$ (**11b**).

Calculations for compound **12** were carried out for the conformer with the axial orientation of the Cl atom at the phosphorus atom. The rotation about the C(6)—C(15) bond gives rise to two conformations with virtually equal energies (the difference is 0.007 kcal mol^{-1}). According to the results of calculations, the conformation of the heterocycle can be described as a boat, which is more flattened compared to that observed in the heterocycle of compound **11** (due, apparently, to the absence of a close contact between the sterically overcrowded groups) (Fig. 5). It should also be noted that the aromatic fragment of the molecule is not deformed.

The results of calculations of the ^{13}C chemical shifts for the optimized geometry are also in good agreement with the experimental data for most of the C atoms (Fig. 6). A substantial disagreement between the experimental and calculated data is observed for the C(8) atom, and a somewhat smaller discrepancy is observed for C(6). The best correspondence was obtained for the C(3) atom. Nevertheless, the observed agreement is diagnostically

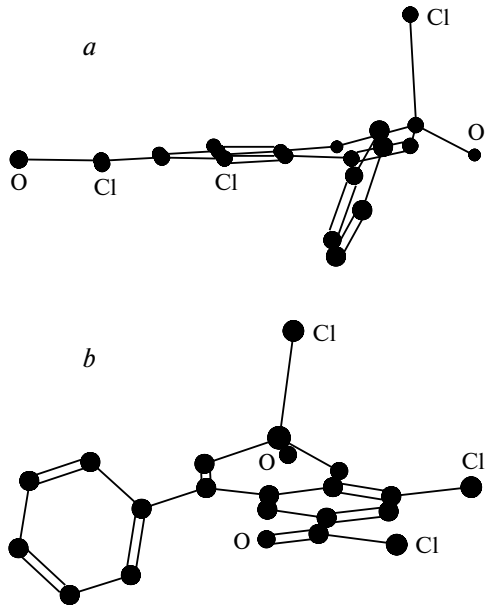


Fig. 5. Structure of the major conformer of compound **12** as viewed from the phenyl substituent (*a*) and the P atom (*b*).

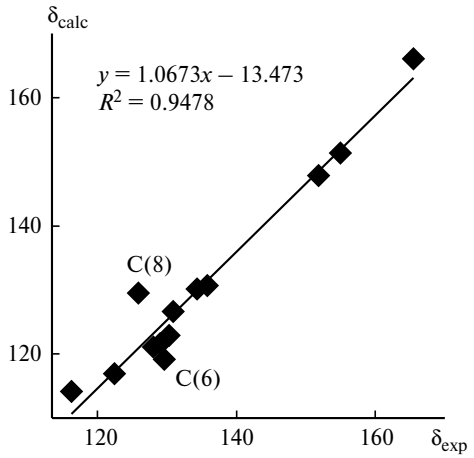
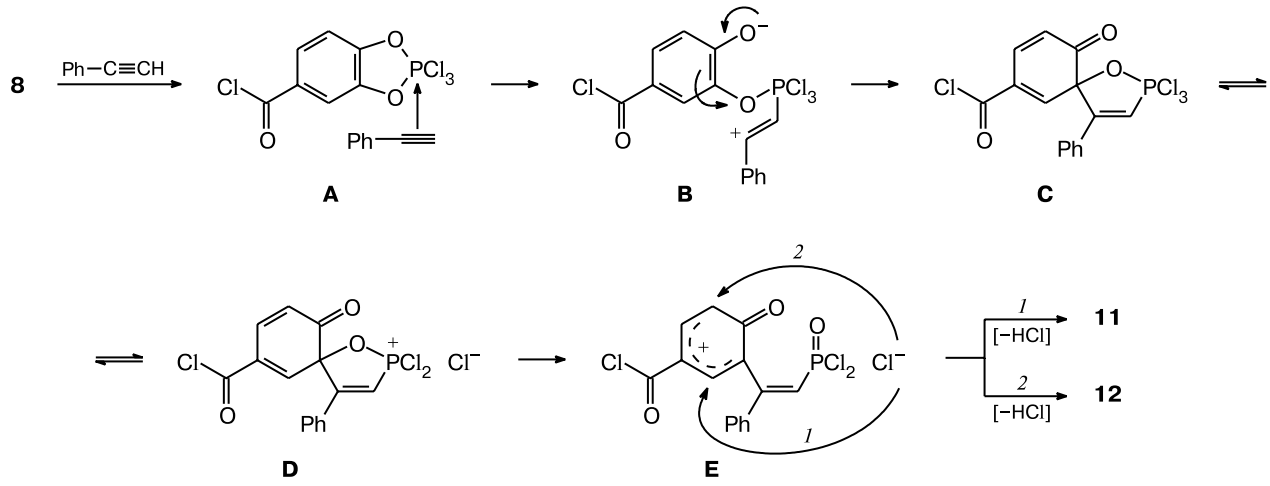


Fig. 6. Correlation between the experimental and calculated chemical shifts of the C atoms for compound **12**.

valuable for the identification of the structure, because attempts to obtain a correlation with the experimental data within the framework of any other hypothetical structure led to an obvious disagreement with calculations. For protons, a good correlation was also obtained: $y = 1.2961x - 2.6782$, $R^2 = 0.9905$.

Hence, the reaction of chlorocarbonyl-substituted phosphole **8**, unlike those of unsubstituted phosphole **1** and monohalogen-substituted derivatives **3** and **5**, with phenylacetylene follows two pathway. The first path is similar to the reaction of PCl_5 with phenylacetylene and involves the electrophilic addition to the triple bond of acetylene with retention of coordination of the P atom. The second path involves the formation of the hetero-

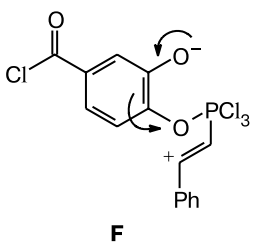
Scheme 6



cyclic benzo[*e*]-1,2-oxaphosphorinine system accompanied by regioselective *ipso*-substitution of the O atom, which is in the *meta* position with respect to the chlorocarbonyl group, in the starting phosphole giving rise to the C—C bond. The process is attended with chlorination of the phenylene substituents in the *ortho* and *meta* positions with respect to this group. Apparently, these results can be explained within the framework of the general scheme of the process proposed earlier.[3] As the first step, the reaction involves the formation of the π complex **A** of phenylacetylene (as Lewis base) with benzophosphole **8** (as Lewis acid) (Scheme 6). Then, this complex is transformed into the structure **B** with charge separation, which is converted into more stable quinoid phospholene **C**. Earlier,[20] we have described the formation of analogous compounds as final products in the phenanthrenequinone—phosphorus trichloride—arylacetylene system.

λ^5-Phospholenes analogous to the intermediate **C** can be in equilibrium with a quasiphosphonium structure of the type **D**.[21] The structure **D** is analogous to a quasiphosphonium-type intermediate produced in the Arbuzov reaction and is further transformed into vinylphosphonate **E** containing the nonclassical carbocation, whose reaction with the chloride anion can follow two pathways (*1* and *2*). Both directions of the attack of the chloride anion are accompanied by cyclization giving benzooxaphosphorinines **11** and **12**.

In the context of this scheme, the regiochemistry of the reaction can be explained by the fact that the key intermediate **B** is much more stable than its isomer **F** due to more efficient delocalization of the negative charge on the O atom by the *para*-chlorocarbonyl substituent. The stability of the structure **B** provides the exclusive formation of compounds **11** and **12**, which are derivatives of the same bicyclic system.



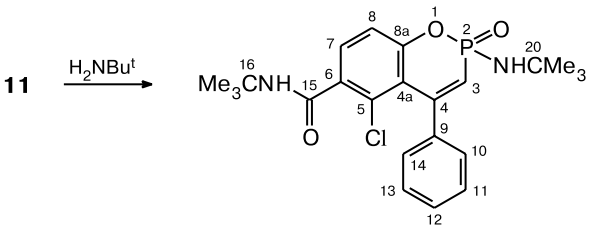
F

The reaction is accompanied by elimination of HCl, which can add to the starting phenylacetylene giving rise to chlorostyrene. Taking into account the experimental data,[3–5] bubbling with argon can be used. In this case, the major portion of HCl is purged from the reaction mixture. As a result, the ratio between the starting reagents (phosphole : phenylacetylene) can be decreased from 1 : 2 to 1 : 1.2.

The major isomer was isolated from a mixture of **11** and **12**. The fact that this isomer has the structure of benzooxaphosphorinine **11**, was confirmed by ^{1}H, ^{31}P (see the Experimental section), and ^{13}C NMR spectroscopy (see Table 1; the chemical shifts of a pure sample are given in braces). Interestingly, the spectrum of the pure sample has the resonance of C(6) at lower field compared to that of C(5), whereas the reverse pattern is observed in the ^{13}C NMR spectrum of the reaction mixture, in which the signal of the C(5) atom appears at higher field. This is, presumably, attributed to the fact that in the ^{13}C NMR spectroscopic study of the reaction mixture, the concentration of phosphorus-containing compounds in $CDCl_3$ is higher, which, in turn, influences the hindered rotation of the phenyl group about the C(4)—C(9) bond. In the ^{13}C NMR spectra, like in the ^{1}H NMR spectra (25 °C), the signals of the carbon atoms and protons belonging to the phenyl fragment are substantially broadened.

Compound **11** was transformed into hydrolytically more stable amide **13** by treatment with *tert*-butylamine (Scheme 7). Compound **13** gradually precipitated from diethyl ether. This compound can easily be recrystallized from acetone to form a solvate with the latter. This fact was established by IR (ν(C=O) = 1713 cm^{-1}), ^{1}H NMR

Scheme 7



13

(δ 2.09), and ^{13}C NMR spectroscopy (Table 2). Compound **13** is amide rather than phosphonate, which was unambiguously confirmed by the ^{13}C NMR spectrum in which the signals of the C atoms of the *tert*-butylamino group bound to the P(2) atom are observed as doublets with the constants $^2J_{P,C} = 2.6$ Hz and $^3J_{P,C} = 4.4$ Hz. In the ^1H NMR spectrum, the signal of the amide proton of the PNH fragment also appears as a doublet ($^2J_{P,H} = 9.9$ Hz). The spectral pattern depends on the solvent, particularly, for the proton of the PNH fragment. For example, in going from DMSO-d_6 to CD_3CN (with a small additive of DMSO-d_6), the signal of this proton is shifted upfield (from 5.35 to 4.81 ppm, respectively). In the spectrum in CD_3CN, the protons of the Bu^{t}NH group bound to the P atom are observed as a doublet with the constant $^4J_{P,H} = 0.6$ Hz. In the ^{31}P NMR spectrum in acetone, the signal of the phosphorus nucleus appears as a doublet of doublets ($^2J_{P,CH} = 20.3$ Hz, $^2J_{P,NH} = 10.0$ Hz). The spectrum of compound **13**, unlike that of compound **11**, shows a signal of the C(3) atom bound to the P atom at lower field (δ_C 124.37).

Quantum-chemical calculations analogous to those described above were carried out for the molecule of compound **13**. According to these calculations, the structure with the axial orientation of the O atom at the P atoms is ~2 kcal mmol^{-1} more favorable than the structure with the equatorial orientation of this substituent (Fig. 7). This fact is consistent with the X-ray diffraction data considered below.

The rotation of the substituent at the C(6) atom gives rise to two stable conformers with the *cis* and *trans* orientations of the carbonyl and phosphoryl groups. The energy difference between the conformers is 0.5 kcal mmol^{-1}, the conformer with the *trans* orientation of the C=O group being more favorable.

On the whole, the calculated ^{13}C chemical shifts correlate well with the experimental data (Fig. 8). However,

Table 2. Parameters of the $^{13}C\{^1H\}$ and ^{13}C NMR spectra of compounds **13** and **16** in DMSO-d_6

Atom	δ (*J*/Hz)	
	13*	**16****
C(3)	124.37 (d [dd], $J_{P,C(3)} = 158.6$, $J_{H,C(3)} = 164.1$)	122.75 (d [dd], $J_{P,C(3)} = 164.9$, $J_{H,C(3)} = 157.2$)
C(4)	152.54 (s [m], $J_{H(10),C(4)} = 4.5$—4.7, $J_{H(3),C(4)} = 3.3$—3.5)	144.63 (s [br.m])
C(4a)	123.26 (d [ddd], $J_{P,C(4a)} = 16.3$, $J_{H(3),C(4a)} = 9.2$, $J_{H(8),C(4a)} = 6.8$)	123.20 (d [dd], $J_{P,C(4a)} = 15.4$, $J_{H(3),C(4a)} = 8.7$)
C(5)	137.25 (s [d], $J_{H(7),C(5)} = 8.0$)	125.26 (s [dd], $J_{H,C(5)} = 163.4$, $J_{H(7),C(5)} = 7.4$)
C(6)	131.02 (d [br.d], $J_{H(8),C(6)} = 11.5$, $J_{P,C(6)} = 1.7$)	126.65 (s [br.s])
C(7)	130.73 (s [d], $J_{H,C(7)} = 166.6$)	126.49 (s [dd], $J_{H,C(7)} = 166.4$, $J_{H(5),C(7)} = 7.3$)
C(8)	119.64 (d [br.dd], $J_{H,C(8)} = 167.6$, $J_{P,C(8)} = 5.9$)	121.30 (d [dd], $J_{P,C(8)} = 5.7$, $J_{H(7),C(8)} = 5.1$—5.2)
C(8a)	153.75 (d [ddd], $J_{H(7),C(8a)} = 11.7$, $J_{P,C(8a)} = 8.3$, $J_{H(8),C(8a)} = 4.0$—4.3)	149.76 (d [ddd], $J_{H(7),C(8a)} = J_{H(5),C(8a)} = 6.5$—$6.8$, $J_{P,C(8a)} = 6.4$)
C(9)	142.54 (d [m], $J_{P,C(9)} = 16.9$)	138.70 (d [dm], $J_{P,C(9)} = 16.9$, $J_{H(11),C(9)} = 7.8$, $J_{H(3),C(9)} = 7.0$)
C(10), C(14)	128.13 (s [dm], $J_{H,C(10)} = 160.1$)	126.92 (s [dm], $J_{H,C(10)} = 161.2$, $J_{H(12),C(10)} = J_{H(14),C(10)} = 6.5$—$6.8$)
C(11), C(13)	129.62 (s [dd], $J_{H,C(11)} = 161.1$, $J_{H(13),C(11)} = 4.8$)	127.18 (s [dd], $J_{H,C(11)} = 161.4$, $J_{H(13),C(11)} = 7.7$)
C(12)	129.48 (s [dt], $J_{H,C(12)} = 161.2$, $J_{H(10),C(12)} = J_{H(14),C(12)} = 7.5$)	126.82 (s [dt], $J_{H,C(12)} = 160.2$, $J_{H(10),C(12)} = J_{H(14),C(12)} = 7.8$)
C(15)	167.13 (s [dd], $J_{H(7),C(15)} = 3.1$, $J_{HCN} = 3.1$)	164.15 (s [d], $J_{H(7),C(15)} = 5.1$)

* The solvate with acetone; ^{13}C NMR of the $(CH_3)_3C(16)NH$ fragment, δ: 28.98 (s [qm], CH_3, $^1J_{H,C} = 126.7$ Hz, $^3J_{H,C} = 3.5$—4.0 Hz); 52.67 (s [m], C(16)). ^{13}C NMR of the $(CH_3)_3C(20)NH$ fragment: 32.16 (d [qm], CH_3, $^1J_{H,C} = 126.5$ Hz, $^2J_{P,C} = 4.4$ Hz, $^3J_{H,C} = 3.7$—4.0 Hz); 53.08 (d [m], C(20), $^2J_{P,C} = 2.6$ Hz). ^{13}C NMR of the $(CH_3)_2C{=}O$ fragment: 30.94 (s [br.q], CH_3, $^1J_{H,C} = 126.3$ Hz); 207.29 (s [sept], C=O, $^2J_{H,C} = 6.3$ Hz).

** ^{13}C NMR of the $(CH_3)_2C(16)HNH$ fragment, δ: 20.63 (s [br.qm], CH_3, $^1J_{H,C} = 126.3$ Hz, $^2J_{H,C} = 3.7$ Hz); 41.65 (s [dm], C(16), $^1J_{H,C} = 142.9$ Hz, $^2J_{H,NC} = 4.4$ Hz, $^2J_{H,CC} = 3.6$—3.7 Hz). ^{13}C NMR of the $(CH_3)_2C(19)HN^+$ fragment: 18.88 (s [br.qm], CH_3, $^1J_{H,C} = 127.4$ Hz); 39.89 (s [dm], C(19), $^1J_{H,C} = 140.5$ Hz).

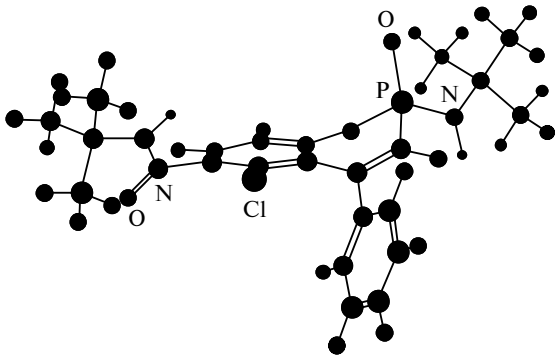


Fig. 7. Structure of the major conformer of compound **13**.

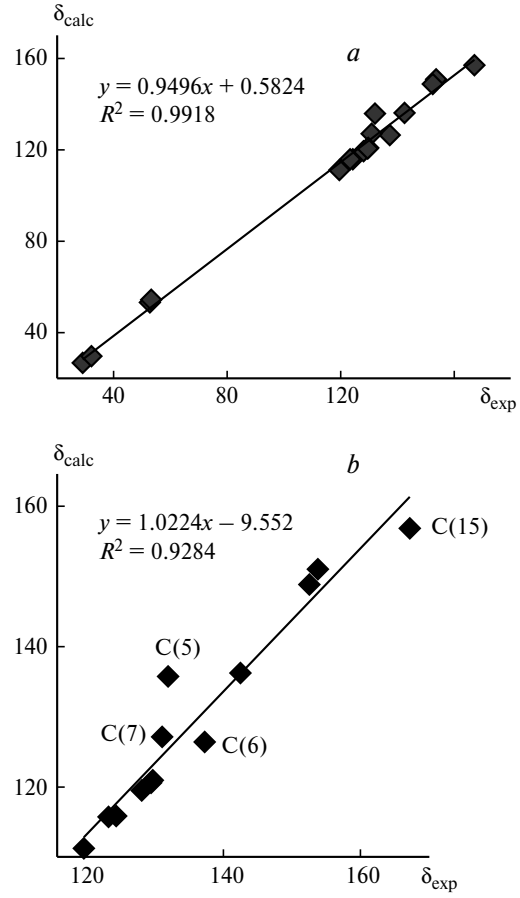


Fig. 8. Correlation between the experimental and calculated chemical shifts of the C atoms for the *trans* conformation of compound **13**: the overall correlation (*a*) and the low-field region (*b*).

like in the above-considered cases, there are some discrepancies. In particular, there is a noticeable disagreement between the calculated and experimental shifts of the C(5) atom and an incomplete agreement for the C(6) and C(7) atoms. The chemical shift of the C(15) atom is somewhat underestimated. It should be noted that the deviation of the calculated chemical shift of the C(5) atom from the experimental value and the situation with the C atoms bound to the Cl atom in the above-considered compounds **11** and **12** have, apparently, a common nature, whereas a slight disagreement for the C(6), C(7), and C(15) atoms is, presumably, caused by hydrogen bonding with the solvent (acetone or DMSO) or the formation of dimers in solutions. This is indirectly confirmed also by calculations of the ^{1}H chemical shifts, according to which the protons of NH should come into resonance at substantially higher field (at δ 4.36 (C(6)NH) and 1.79 (P(2)NH)), whereas the experimental resonanses are observed at δ 7.81 and 5.35, respectively. This downfield shift by more than 3 ppm is, apparently, indicative of the formation of hydrogen-bonded dimers.

On the whole, the calculated chemical shifts correlate well with the experimental data. The maximum deviations are observed for the C atoms directly bound to the Cl atom (C(5) in compound **11** and C(8) in compound **12**), and smaller discrepancies are observed for the carbon atoms bound to the P atom (C(3)). On the one hand, this is, apparently, attributed to the fact that the method used for geometry optimization is inapplicable to systems containing Group III elements[22] (for example, the calculated C—Cl bond lengths are in the range of 1.811—1.813 Å, whereas the corresponding bond lengths determined by X-ray diffraction study are in the range of 1.743—1.747 Å [23]). An analogous disagreement is also observed for the P—C bond length. On the other hand, this discrepancy may result from limitations of the method used for estimations of the chemical shifts in such systems.[19] For example, trial calculations of the ^{13}C chemical shifts for the structure with the fixed C—Cl bond length (1.73 Å) gave a much better correlation with the experimental data (the chemical shift decreases by 5.4 ppm). Therefore, a comparison of the chemical shifts provides a reliable criterion for the identification of not only the structure but also of the conformation.

The structure of the solvate of compound **13** with acetone was established by X-ray diffraction analysis. The overall view of molecule **13** in the crystal is shown in Fig. 9. The selected bond lengths, bond angles, and torsion angles are given in Table 3.

The heterocycle of molecule **13** contains two planar fragments, *viz.*, O(1)C(8a)C(4a)C(4) and P(2)C(3)C(4)C(4a); the dihedral angle between these fragments is 20.0(3)°. The C(3) and P(2) atoms of the heterocycle deviate from the O(1)C(8a)C(4a)C(4) plane in the same direction by −0.367(4) and −0.887(1) Å, respectively. The O(1) and C(8a) atoms of the heterocycle deviate from the P(2)C(3)C(4)C(4a) fragment also in the same direction by 0.811(3) and 0.487(4) Å respectively. Therefore, the oxaphosphorine ring in molecule **13** adopts a distorted boat conformation, which is less flat-

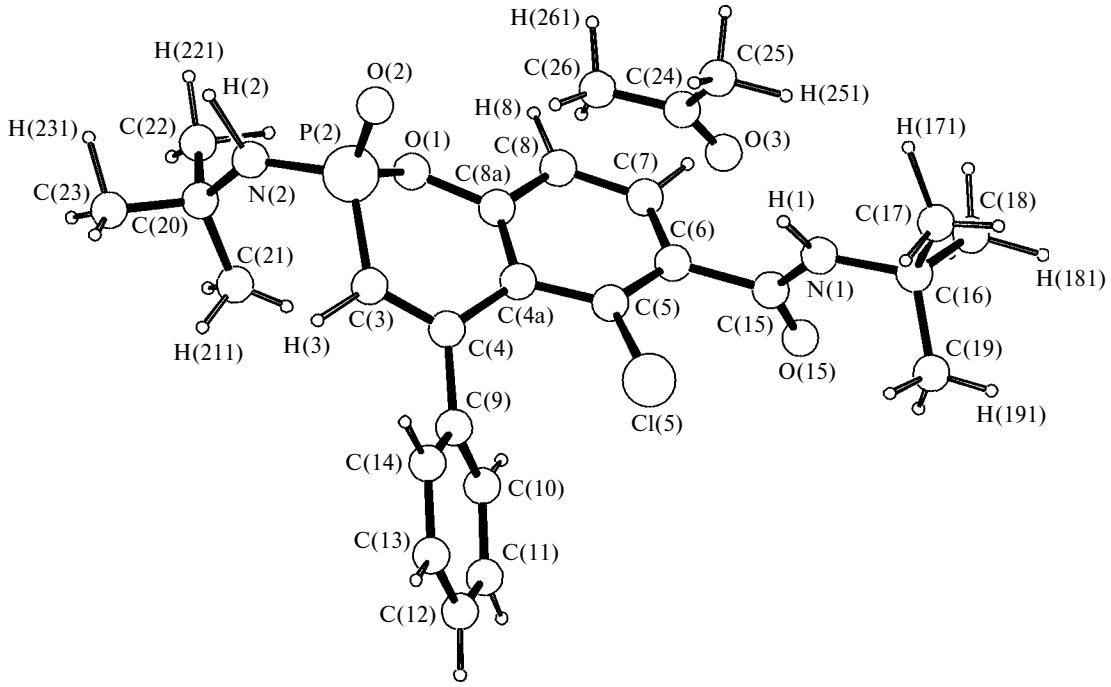
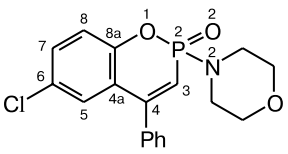


Fig. 9. Geometry of molecule **13** (solvate with acetone) in the crystal.

Table 3. Selected bond lengths (*d*), bond angles (ω), and torsion angles (τ) in amide **13** and salt **16**

Bond	*d*/Å		Angle	ω/deg		Angle	τ/deg	
	13	**16**		**13**	**16**		**13**	**16**
P(2)—O(1)	1.625(3)	1.635(3)	O(1)—P(2)—O(2)	113.8(2)	105.8(2)	O(2)—P(2)—O(1)—C(8a)	78.4(3)	160.3(3)
P(2)—O(2)	1.460(3)	1.474(4)	O(1)—P(2)—C(3)	99.3(2)	100.5(2)	C(3)—P(2)—O(1)—C(8a)	−45.4(3)	44.2(3)
P(2)—C(3)	1.762(4)	1.771(5)	O(2)—P(2)—C(3)	115.9(2)	111.5(2)	O(1)—P(2)—C(3)—C(4)	28.9(4)	−25.9(4)
O(1)—C(8a)	1.383(5)	1.371(5)	P(2)—O(1)—C(8a)	120.5(2)	119.4(3)	O(1)—P(2)—C(3)—H(3)	−154	148.5(4)
O(15)—C(15)	1.222(5)	1.242(5)	C(15)—N(1)—C(16)	125.6(4)	121.8(3)	O(2)—P(2)—C(3)—C(4)	−93.3(4)	−137.7(4)
N(1)—C(15)	1.336(6)	1.348(5)	P(2)—C(3)—C(4)	121.4(3)	122.0(3)	O(2)—P(2)—C(3)—H(3)	84.2(4)	36.7(5)
N(1)—C(16)	1.467(6)	1.472(5)	P(2)—C(3)—H(3)	118	124.4(3)	P(2)—O(1)—C(8a)—C(4a)	31.2(5)	−36.9(5)
C(3)—C(4)	1.357(5)	1.349(6)	C(4)—C(4a)—C(5)	125.8(3)	121.2(4)	P(2)—O(1)—C(8a)—C(8)	−149.5(3)	144.3(3)
C(3)—H(3)	1.11	1.113(4)	C(4)—C(4a)—C(8a)	119.8(3)	120.9(4)	C(16)—N(1)—C(15)—O(15)	−4.7(7)	−1.6(6)
C(4)—C(4a)	1.467(5)	1.484(5)	O(15)—C(15)—N(1)	124.8(4)	122.8(4)	C(16)—N(1)—C(15)—C(6)	177.8(4)	177.0(3)
C(4a)—C(5)	1.409(5)	1.380(6)	O(15)—C(15)—C(6)	120.0(4)	122.0(3)	C(15)—N(1)—C(16)—C(17)	−176.3(4)	−158.9(4)
C(4a)—C(8a)	1.402(5)	1.409(6)	N(1)—C(15)—C(6)	115.1(4)	115.2(4)	C(15)—N(1)—C(16)—C(18)	67.1(6)	77.1(5)
C(4)—C(9)	1.493(5)	1.482(6)	N(1)—C(16)—C(17)	104.9(4)	107.5(4)	C(3)—C(4)—C(4a)—C(5)	155.4(4)	−162.8(4)
C(5)—C(6)	1.375(6)	1.391(5)	N(1)—C(16)—C(18)	109.7(4)	110.8(4)	C(9)—C(4)—C(4a)—C(5)	−30.8(6)	17.8(6)
C(6)—C(7)	1.385(6)	1.396(6)	C(17)—C(16)—C(18)	108.7(5)	113.1(4)	C(3)—C(4)—C(4a)—C(8a)	−25.5(6)	16.8(6)
C(6)—C(15)	1.517(6)	1.492(6)	C(5)—C(4a)—C(8a)	114.4(3)	118.0(4)	C(9)—C(4)—C(4a)—C(8a)	148.3(4)	−162.5(4)
C(7)—C(8)	1.368(6)	1.370(6)	C(3)—C(4)—C(4a)	119.9(3)	119.8(4)	C(3)—C(4)—C(9)—C(10)	128.7(4)	−128.6(4)
C(8)—C(8a)	1.384(6)	1.385(6)	C(3)—C(4)—C(9)	118.9(4)	120.5(4)	C(3)—C(4)—C(9)—C(14)	−46.8(6)	46.7(6)
C(9)—C(10)	1.397(6)	1.399(5)	C(4a)—C(4)—C(9)	120.9(3)	119.7(3)	C(4a)—C(4)—C(9)—C(10)	−45.2(6)	50.7(5)
C(9)—C(14)	1.376(6)	1.379(6)	C(4a)—C(5)—C(6)	123.4(4)	121.8(4)	C(4a)—C(4)—C(9)—C(14)	139.3(4)	−133.9(4)
C(10)—C(11)	1.379(6)	1.398(7)	C(5)—C(6)—C(7)	118.6(4)	119.4(4)	C(7)—C(6)—C(15)—O(15)	−75.7(5)	151.6(4)
C(11)—C(12)	1.366(8)	1.360(7)	C(5)—C(6)—C(15)	122.5(4)	118.2(4)	C(5)—C(6)—C(15)—O(15)	102.0(5)	30.0(6)
C(12)—C(13)	1.364(8)	1.392(7)	C(7)—C(6)—C(15)	118.9(4)	122.4(3)	C(5)—C(6)—C(15)—N(1)	−80.3(5)	−148.6(4)
C(13)—C(14)	1.389(7)	1.385(8)	C(6)—C(7)—C(8)	120.7(4)	119.3(4)	C(7)—C(6)—C(15)—N(1)	101.9(5)	29.7(5)
C(16)—C(17)	1.544(8)	1.508(6)	O(1)—C(8a)—C(4a)	120.9(3)	121.5(4)			
C(16)—C(18)	1.528(7)	1.495(7)	O(1)—C(8a)—C(8)	116.3(3)	118.5(4)			

tened than those in the compounds described earlier.[3–5] This is reflected in the direction of deviations of the O(2) and N(2) atoms, which are located on one side of the O(1)C(8a)C(4a)C(4) plane at distances of –2.324(3) and –0.288(3) Å, respectively, from this plane. In structurally similar 6-chloro-2-morpholino-4-phenylbenzo[*e*]-1,2-oxaphosphorinine (**14**),[3] these atoms deviate from the above-mentioned plane in opposite directions by smaller distances (O(2), by –2.12(1) Å; N(2), by 0.12(1) Å). These atoms in molecules **13** deviate from another plane, *viz.*, P(2)C(3)C(4)C(4a), in opposite directions (the same situation is observed in the structure of **14**) by –1.303(3) (O(2)) and 0.983(3) Å (N(2)) (in compound **14**, these deviations are –1.28(1) (O(2)) and 1.12 Å (N(2))). The larger deviations of the O(2) atom are indicative of its axial orientation, whereas the N(2) atom is in the equatorial position.



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The P(2)—O(1) bond in molecule **13** (1.625(3) Å) is somewhat elongated, which may be caused by the reverse anomeric effect (interaction between the lone electron pair of the N(2) atom and the antibonding orbital of the endocyclic O(1)—P(2) bond). This effect is favored by the virtually eclipsed conformation along the P(2)—N(2) bond (the O(2)—P(2)—N(2)—C(20) torsion angle is 169.8(4)°). The N(2) atom has a trigonal-planar configuration (the sum of the bond angles at this atom is 359.8(3)°). It should be noted that the attachment of the bulky Bu^{t}NH substituent at the P(2) atom has virtually no effect on the bond angles at the P atom (these angles are close to those in the structure of **14**). The exocyclic O(2)—P(2)—N(2) (111.3(2)°) and O(2)—P(2)—C(3) (115.9(2)°) bond angles are larger than the endocyclic O(1)—P(2)—C(3) bond angle (99.3(2)°).

The presence of the Cl atom at C(5), the Ph substituent at C(4), and the *tert*-butylaminocarbonyl group at position 6 leads to repulsions between these substituents resulting in an increase in the C(4a)—C(5)—C(6) (123.4(4)°), C(4)—C(4a)—C(5) (125.8(3)°), and C(5)—C(6)—C(15) (122.5(4)°) bond angles compared to the ideal value for the sp^2-hybridized atom. Compound **13** contains 1,2,3,4-tetrasubstituted benzene as the benzo fragment. Steric repulsions between the substituents lead also to deviations of the O(1), C(4), and Cl atoms from the plane of the benzene ring in opposite directions by –0.160(3), +0.226(4), and –0.210(1) Å, respectively. The deviation of the C(15) atom is very small (–0.040(5) Å). Nevertheless, the carbonyl group is substantially twisted with respect to the plane of the benzene ring (O(5)—C(15)—C(6)—C(7) torsion angle is –75.7(5)°). This rotation is, presumably, caused by steric repulsion between the C(15) and Cl atoms. Molecule **13** contains one more planar (within 0.015(4) Å) fragment, *viz.*, C(6)C(15)N(1)C(16); the deviations of the O(15) and C(17) atoms from this plane are very small (–0.059(3) and 0.086(7) Å, respectively). Hence, the overall C(6)C(15)(O(15))N(1)C(16)C(17) six-membered fragment can be considered as a planar moiety. This structure is favorable because of the efficient amide n—π conjugation and the minimum steric interactions with the Me groups of the Bu^t substituent. The N(1) atom has a trigonal-planar configuration (the sum of the bond angles at this atom is 359.5(4)°). The dihedral angle between the planes of the C(6)C(15)N(1)C(16) and C(4a)C(5)C(6)C(7)C(8)C(8a) fragments is 80.6(2)°. The C(5) and C(7) atoms virtually symmetrically deviate from the C(6)C(15)N(1)C(16) plane (by 1.162(4) and –1.171(4) Å, respectively). Hence, conjugation between the carbonyl group and the benzene ring in molecule **13** is impossible, but there is conjugation between the lone electron pair of the N atom and the C=O bond. The observed shortening of the N(1)—C(15) bond and elongations of the C(15)=O(15) and C(6)—C(15) bonds are consistent with this assumption. The phenyl substituent at the C atom of the heterocycle at position 4 is twisted with respect to the P(2)C(3)C(4)C(4a) plane; the dihedral angle between these planes is large (132.7(1)°).

In the crystals of compound **13**, the molecules are linked by various types of short intermolecular contacts. Analysis of these interactions reveals supramolecular isomerism in the crystal, *i.e.*, the formation of different types of supramolecular structures depending on the type of the contacts. For example, the classical N(2)—H(2)...O(2′) hydrogen bonds ($1 - x$, $-y$, $1 - z$) (d(H(2)...O(2′)) = 2.09 Å, N(2)—H(2)...O(2′) = 174°) give rise to centrosymmetrical dimers (Fig. 10), each molecule **13** being linked to one acetone molecule through a hydrogen bond (d(H(1)...O(3)), 1.91 Å; N(1)—H(1)...O(3), 175°). The H(3) and H(14) protons of the initial molecule are involved in a bifurcate C—H...O hydrogen bond with the O(15″) atom of the carbonyl group of another molecule ($1 + x$, y, z) (d(H(3)...O(15″)), 2.36 Å; C(3)—H(3)...O(15″), 147°; and d(H(14)...O(15″)), 2.50 Å; C(14)—H(14)...O(15″), 141°). As a result, the molecules in the crystal are linked in ribbon-like infinite chains along the crystallographic axis 0x (Fig. 11), because each molecule of the dimer is involved in two such contacts (both as a donor and an acceptor). In the crystal, there are also interactions of C—H...π and π...π types. Taking into account two different types of intermolecular contacts, the crystal structure of **13** can be described as a 1D-type supramolecular structure rather than as a structure consisting of 0D dimers. On the whole, the molecular packing in the crystal can

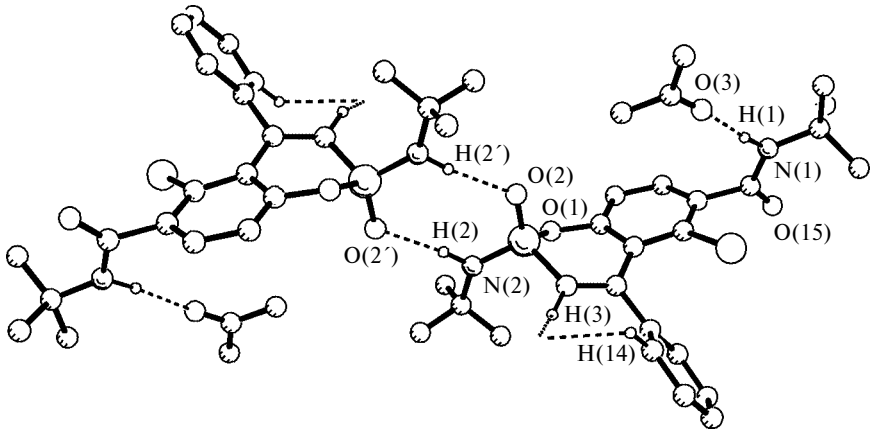


Fig. 10. Formation of dimers in the crystal of compound **13**. Only protons involved in hydrogen bonding are shown.

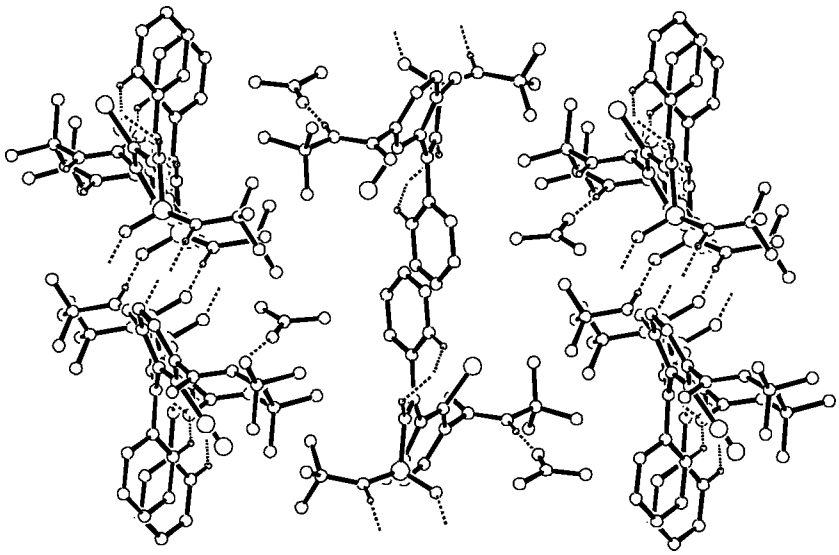


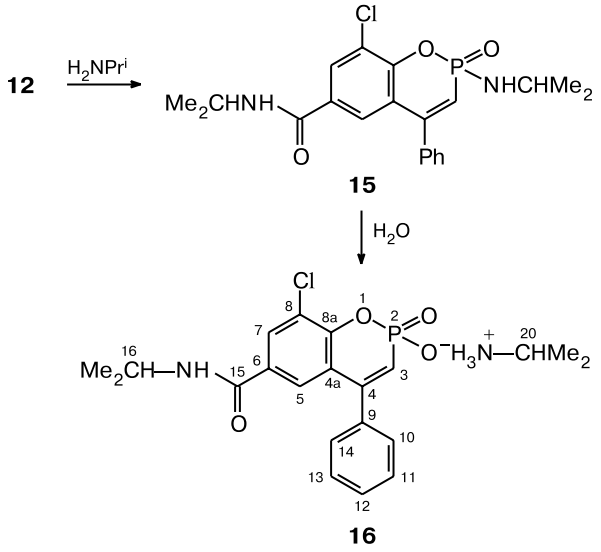
Fig. 11. Molecular packing of compound **13** in the crystal projected along the crystallographic axis 0*x*.

be represented as follows. A parallel packing of such ribbon-like structures forms a layer parallel to the *x*0*z* plane of the crystal, so that the Ph substituents of the adjacent chains in the layer are in contact with each other. The next layer is rotated with respect to this layer by 90°, the Bu^t substituents and the acetone molecules forming a pseudolayer.

After separation of the major portion of benzooxaphosphorinine **11**, the filtrate was thoroughly dried *in vacuo* and treated with isopropylamine. Then less soluble isopropylamide **15** was isolated (Scheme 8). The latter was readily hydrolyzed in the course of crystallization from DMSO to give salt **16** (see the Experimental section). In the ^{31}P NMR spectrum of compound **16** (DMSO-d_6), the signal of the P atom appears as a doublet with the constant $^2J_{P,CH}$, *i.e.*, spin-spin coupling with the proton of the NH group is not manifested. The results of ^1H and ^{13}C NMR spectroscopy (see Table 2) are also consistent with the structure of the salt. The spectroscopic data were interpreted taking into account the above-described spectra of compounds **11** and **12**. The absence of the spin-spin coupling of the P atom with the C atoms of the CH and Me groups of the Pr^iNH fragment is indicative of the absence of the P—NH bond, *i.e.*, the amidophosphonate fragment rather than the amide group $C(O)NHCHMe_2$ is subjected to hydrolysis. The IR spectrum of compound **16** shows a band belonging to vibrations of the amide group (ν(NC=O) = 1634 cm^{-1}).

The structure of salt **16** was unambiguously established by X-ray diffraction analysis. The three-dimensional structures of the anion and cation of salt **16** in the crystal are shown in Fig. 12. The selected geometric parameters (bond lengths, bond angles, and torsion angles) are given in Table 3. The heterocycle in molecule **16**, like that in the structure of **13**, has two planar fragments, *viz.*, O(1)C(8a)C(4a)C(4) and P(2)C(3)C(4)C(4a); the di-

Scheme 8



hedral angle between these planes is 17.4(3)°. The C(3) and P(2) atoms of the heterocycle deviate from the former plane by 0.396(5) and 0.821(1) Å, respectively, *i.e.*, are located on the same side of this plane. The O(1) and C(8a) atoms of the heterocycle deviate from the latter plane also in the same direction (by −0.718(3) and −0.335(4) Å, respectively). The deviations of these atoms in the same direction and the different values of these deviations indicate that the oxaphosphorine ring adopts a distorted boat conformation. This conformation of the heterocycle in **16**, like that in the structure of **13**, is less flattened (the deviations of the above-mentioned atoms from the above two planar fragments are larger) compared to that observed in benzophosphorinines studied earlier.[3–5] Correspondingly, the exocyclic O(2) and O(3) atoms deviate more substantially from the O(1)C(8a)C(4a)C(4) plane (by −0.241(4) and 2.264(3) Å, respectively). These atoms deviate from the P(2)C(3)C(4)C(4a) plane by −0.917(4) and 1.384(3) Å, respectively. The deviations of the O(2) and O(3) atoms are indicative of their equatorial and axial positions, respectively. The P(2)O(2)O(3) fragment bears a negative charge (*i.e.*, this fragment is an anion). This leads to an elongation and equalization of the P(2)—O(2) (1.474(4) Å) and P(2)—O(3) (1.485(3) Å) bonds compared to the P(2)=O(2) bond in 4-(4-bromophenyl)-6-chloro-2-hydroxybenzo[*e*]-1,2-oxaphosphorinine (**17**) (1.468(6) Å).[3] Nevertheless, in spite of delocalization of the negative charge in the P(2)O(2)O(3) fragment, the P(2)—O(2) and P(2)—O(3) bond lengths are slightly different. This may be associated, first, with the different positions of the O atoms in the ring (the O(3) and O(2) atoms are in the axial and equatorial positions, respectively) and, second, with the different hydrogen bonds involving these atoms as acceptors.

The O(2)P(2)O(3) bond angle (119.6(3)°) in **16** is larger than that in molecule **17** (112.2(3)°). The endocyclic

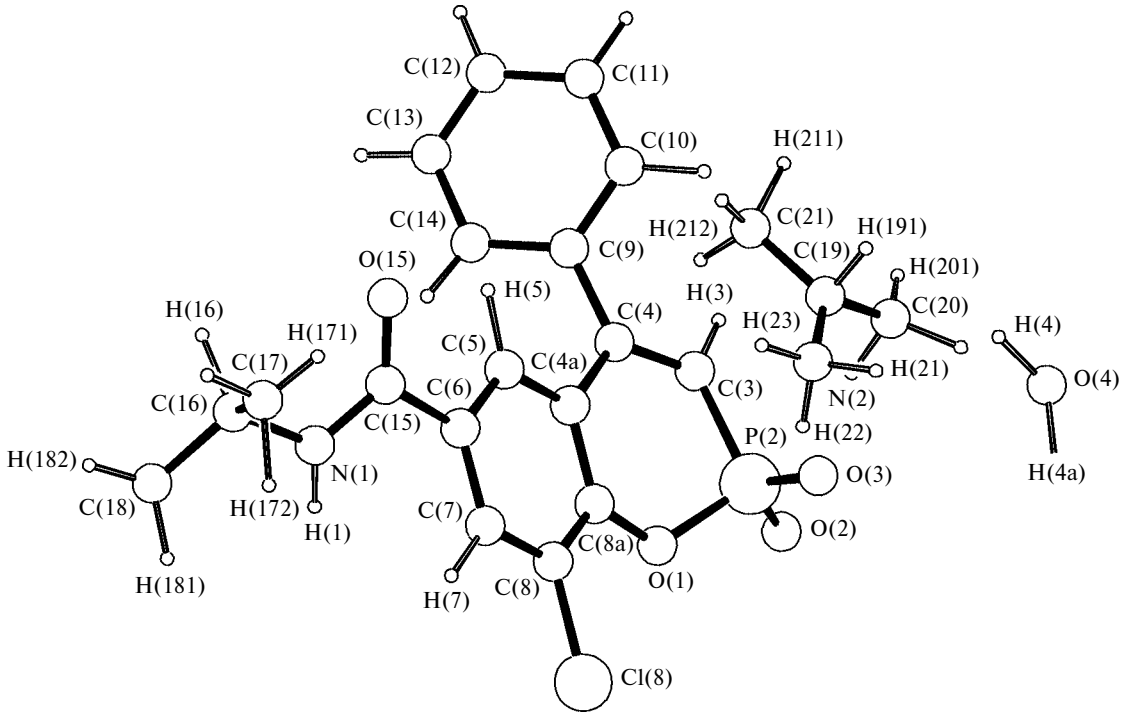
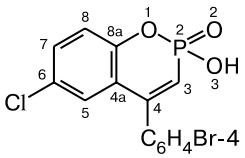


Fig. 12. Geometry of the crystal hydrate of compound **16** in the crystal.

P(2)—O(1) bond in salt **16** (1.635(3) Å), like that in compound **13**, is somewhat longer than that in compound **17** (1.593(6) Å), and, *vice versa*, the O(1)—C(8a) bond (1.371(5) Å) is shorter (in compound **17**, 1.40(1) Å). The endocyclic P(2)—C(3) bond is also somewhat elongated (1.771(5) Å; *cf.* 1.753(9) Å in molecule **17**). These changes in the bond lengths in molecule **16** may be indicative of partial σ—π delocalization of the negative charge from the exocyclic O atoms to the endocyclic O(1)—P(2) and C(3)—P(2) bonds as well as of the efficient conjugation between the lone electron pairs of the O(1) atom and the electron-withdrawing benzo fragment (bearing the *para*-chlorocarbonyl substituent). Salt **16** contains not only the Ph ring but also the virtually planar five-membered C(6)C(15)(O(15))N(1)C(16) fragment; the dihedral angle between this fragment and the benzene ring is 30.8(2)°, which does not exclude conjugation of this fragment with the benzene ring. The N(1) atom has a trigonal-planar configuration (the sum of the bond angles at this atom is 360.0(4)°). The C(6)—C(15) bond length (1.492(6) Å) is smaller than that in compound **13** (1.517(6) Å), which is also consistent with a more efficient conjugation of the carbonyl group with the aromatic system in salt **16**. The dihedral angle between the planes of the Ph substituent and the P(2)C(3)C(4)C(4a) fragment is rather large (49.3(2)°), which decreases the possibility of conjugation between these fragments.



17

In the crystals of this compound, the molecules are linked through various intermolecular contacts involving both classical hydrogen bonds and weak C—H...N and C—H...π intermolecular interactions. It should be noted that this compound crystallizes with a water molecule of solvation. In the crystal, this water molecule occupies a special position and is also involved in hydrogen bonding. The parameters of the strongest interactions (hydrogen bonds) in the crystal structure are given in Table 4.

Table 4. Parameters of the hydrogen bonds in the crystal structure of compound **16** (D is a donor and A is an acceptor)

DH...A Bond	D—H	H...A	D...A	Angle D—H...A /deg
	Å			
N(1)—H(1)...O(15)#1	1.00	1.96	2.890(4)	153
N(2)—H(21)...O(3)#2	1.09	1.76	2.760(5)	150
O(4)—H(4)...O(2)#3	1.09	1.91	2.944(4)	156
N(2)—H(22)...O(2)#3	0.98	1.80	2.759(5)	163
N(2)—H(23)...O(3)	0.98	1.93	2.857(6)	155
C(5)—H(5)...O(15)	1.12	2.50	—	—
C(16)—H(16)...O(15)	1.18	2.69	—	—
C(12)—H(12)...O(15)#4	1.07	2.69	—	—
C(18)—H(183)...Cg(2)	0.98	2.70	3.621(6)	157
C(17)—H(172)...Cg(3)	1.08	2.93	3.644(6)	124

Note. Symmetry operations: #1 $x, -y, 1/2 + z$; #2 $-x, y, 1/2 - z$; #3 $x, 1 - y, -1/2 + z$; #4 $1/2 - x, 1/2 + y, 1/2 - z$. Cg(2) is the center of gravity of the fused benzene ring; Cg(3) is the center of gravity of the Ph substituent.

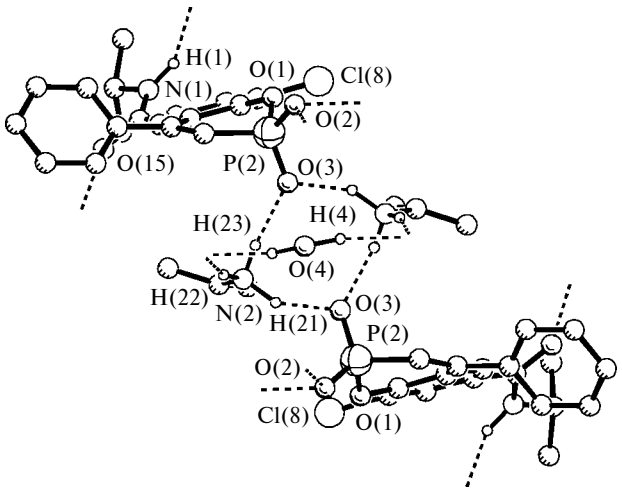


Fig. 13. Formation of a tetramer in the crystal of compound **16**. Only protons involved in hydrogen bonding are shown.

The crystal structure of compound **16** is characterized by the formation of centrosymmetrical hydrogen-bonded tetramers involving two anion-cation pairs (Fig. 13). The water molecule also participates in stabilization of the tetramer. The H atoms of the water molecule are involved in bifurcate hydrogen bonds with the O atoms of the phosphoryl groups of molecules **16** adjacent to the tetramer. In addition, each anion is involved in two hydrogen bonds (both as a donor and acceptor) between the H(1) proton of the amino group and the carbonyl O(15) atom giving rise to an infinite chain along the crystallographic axis 0*z* (Fig. 14). As a result, the tetramers are

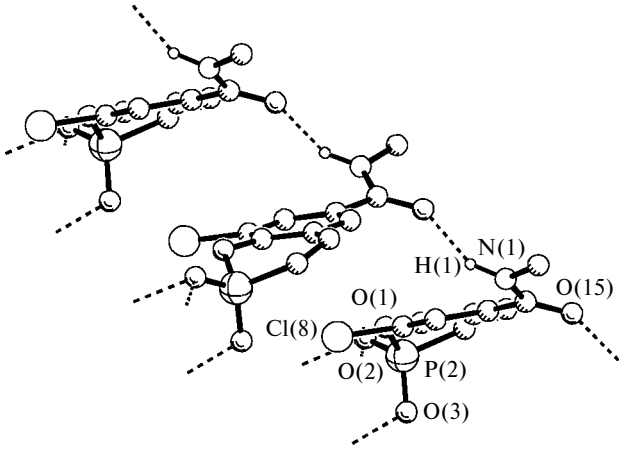


Fig. 14. Fragment of an infinite chain of the hydrogen-bonded molecules in the crystal of compound **16**.

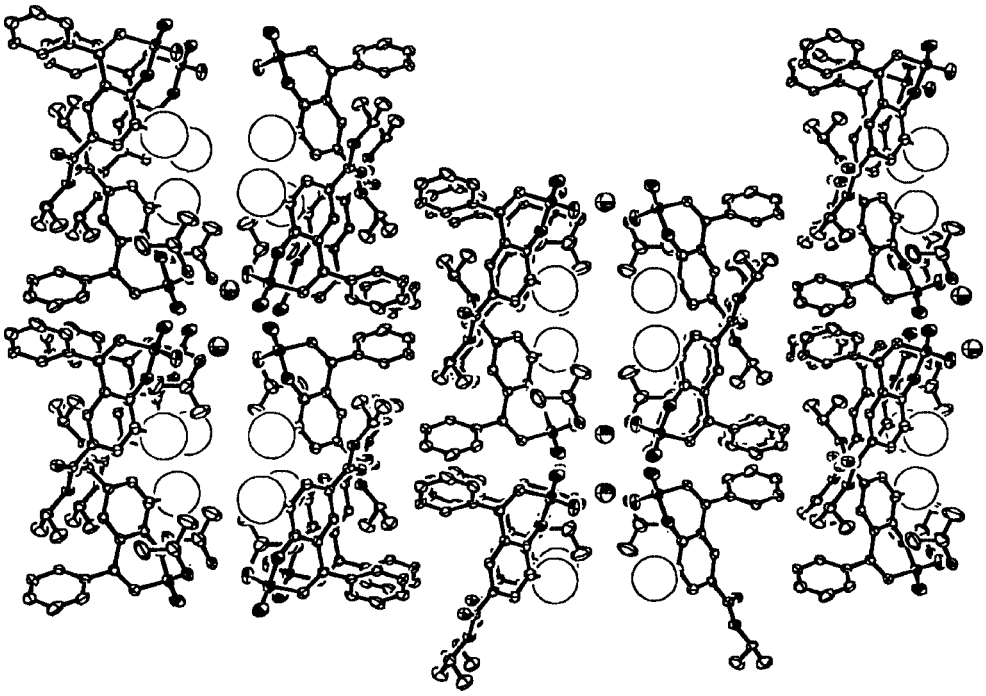


Fig. 15. Molecular packing of compound **16** in the crystal containing pseudochannels formed by chlorine atoms (Cl atoms are represented by large circles). The projection along the crystallographic axis 0*z*.

linked to each other to form finally a two-dimensional supramolecular structure in the crystal.

Interestingly, the molecular packing in the crystal, which can be described as a packing of parallel hydrogen-bonded layers along the direction 0*z* results in localization of regions with the Cl atoms and the formation of pseudochannels (Fig. 15). The packing coefficient of this structure is not high (64.6%). The calculations demonstrated that the unit cell has cavities with a total volume of 149 Å^3. One would expect that the crystals of compound **16**, which have such a special direction, could exhibit substantial anisotropy of the physical properties.

To summarize, it was demonstrated that 2,2,2-trichloro-5-chlorocarbonylbenzo[*d*]-1,3,2-dioxaphosphole (**8**) rather readily reacts with arylacetylenes to give the benzo[*e*]-1,2-oxaphosphorinine heterocyclic system. The unusual feature of this reaction is the introduction of the Cl atom at the *ortho* position with respect to either the O atom or the C atom of the annelated oxaphosphorinine heterocycle. Apparently, this reaction is common to phosphorylated derivatives of *o*-dihydroxyarenes. However, in each particular case, the regiochemistry of the process is determined by the nature of the substituents in the arene fragment. This problem calls for further investigation.

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 (400 (^{1}H), 162.0 (^{31}P), 100.6 MHz (^{13}C)), and Bruker CXP-100 (36.48 MHz (^{31}P)) instruments in DMSO-d_6 (45 °C) or $CDCl_3$, CD_3CN (25 °C). The chemical shifts are given in the δ scale with respect to Me_4Si using signals of the residual protons of the deuterated solvent or carbon nuclei of DMSO or $CHCl_3$ (^{1}H and ^{13}C) as the internal standard or H_3PO_4 as the external standard. The IR spectra were measured on a Vector-22 (Bruker) Fourier-transform spectrometer in Nujol mulls or KBr pellets. The EI mass spectra were obtained on a MAT-212 (Finnigan) instrument; the energy of ionizing electrons was 70 eV. The masses were precisely determined by fitting to the reference peaks of perfluorokerosene. The temperature of the ion source was 120 °C. The samples were introduced into the ion source using a direct inlet system. The temperature of the evaporator tube was 100 °C. The mass-spectrometric data were processed using the MASPEC 2 system program.

Ab initio quantum calculations were carried out using the GAUSSIAN98 program package[24] on a computer cluster at the A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Research Center of the Russian Academy of Sciences consisting of nine Compaq Alpha DS10L workstations (Alpha-264-466MHz/256 Mb/10 Gb) and an Alpha DS20E workstation (2*Alpha-264-667MHz/512 Mb/20 Gb) with 100 Mbps Fast Ethernet system. All molecular geometries were optimized at the HF/6-31G level of theory. The absolute values of shielding were calculated by the DFT/GIAO (density functional theory/gauge-including atomic orbital) method with the 6-31G(d) basis set and the B3LYP functional. Calculations were carried out for the isolated molecule in the gas phase without regard for the solvent effects. The chemical shifts are given relative to the signal of Me_4Si calculated in the identical conditions.

2-Chloro-5-chlorocarbonylbenzo[*d*]-1,3,2-dioxaphosphole (9). A mixture of PCl_3 (13.7 g, 0.1 mol) and protocatechuic acid

(5 g, 0.032 mol) was heated with stirring for 2 h. Then the reaction mixture was distilled off. Benzophosphole **9** was isolated in a yield of 1.6 g (21%) as a colorless viscous liquid, b.p. 89—90 °C (0.8 Torr). ^{31}P NMR (CH_2Cl_2): δ_P 179.8. Found (%): Cl, 30.05. $C_7H_3Cl_2O_3P$. Calculated (%): Cl, 29.96.

2,2,2-Trichloro-5-chlorocarbonylbenzo[*d*]-1,3,2-dioxaphosphole (8). ***A.*** Phosphorus pentachloride (32.7 g, 0.157 mol) suspended in benzene (50 mL) was placed in a three-neck flask equipped with a stirrer and a reflux condenser. Then benzene (150 mL) was added, and protocatechuic acid (9.7 g, 0.06 mol) was gradually added portionwise with stirring at 20 °C (for 40 min). The reaction mixture was stirred for 1 h and the benzene was distilled off under atmospheric pressure. The residue was kept *in vacuo* (12 Torr) at 120 °C until distillation of $POCl_3$ and sublimation of excess PCl_5 ceased and then distilled. Benzophosphole **8** was isolated in a yield of 10.9 g (56.2%) as a viscous yellowish liquid, b.p. 129—130 °C (0.5 Torr). Found (%): Cl, 46.18. $C_7H_3Cl_4O_3P$. Calculated (%): Cl, 46.1. MS*, *m/z* (I_{rel} (%)): 312 (2.0), 311 (0.63), 310 (8.8), 309 (1.0), 308 (18.7), 307 (1.7), 306 $[M]^{\bullet+}$ (14.6), 273 (100.0), 201 (14.7), 119 (24.4), 107 (34.1), 79 (45.7), 63 (32.4), 47 (16.0), 36 (15.7), 35 (4.5). ^{31}P NMR ($CDCl_3$): δ_P −23.5. ^{13}C NMR (signals in the $^{13}C\{^1H\}$) NMR spectrum are given in brackets ($CDCl_3$)), δ: 110.64 (dd [d], C(7), $^1J_{H,C(7)}$ = 170.6 Hz, $^3J_{P,C(4)}$ = 17.0 Hz); 113.49 (ddd [d], C(4), $^1J_{H,C(4)}$ = 170.7 Hz, $^3J_{P,C(4)}$ = 19.6 Hz, $^3J_{H(6),C(4)}$ = 6.7 Hz); 127.73 (br.d [br.s], C(5), $^3J_{H(7),C(5)}$ = 8.4 Hz); 128.75 (dd [s], C(6), $^1J_{H,C(6)}$ = 170.7 Hz, $^3J_{H(4),C(6)}$ = 5.9 Hz); 141.53 (dd [s], C(4a), $^3J_{H(7),C(4a)}$ = 7.0 Hz, $^2J_{H(4),C(4a)}$ = 4.9 Hz); 148.15 (ddd [s], C(7a), $^3J_{H(6),C(7a)}$ = 11.4 Hz, $^3J_{H(4),C(7a)}$ = 6.7 Hz, $^2J_{H(7),C(7a)}$ = 2.9 Hz); 165.89 (dd [s], COCl, $^3J_{H(6),C}$ = $^3J_{H(4),C}$ = 5.0—5.4 Hz).

B. A cooled (from 0 to −10 °C) solution of chlorine (0.5 g, 0.07 mol) in CH_2Cl_2 (20 mL) was added dropwise with stirring to a solution of benzophosphole **9** (1.5 g, 0.006 mol) in CH_2Cl_2 (5 mL) under argon at −20 °C. An excess of chlorine was removed *in vacuo* (12 Torr). Tetrachlorobenzophosphole **8** was obtained in a nearly quantitative yield. The resulting solution of phosphorane **8** was used without additional purification.

Reaction of benzophosphole 8 with phenylacetylene. A solution of phenylacetylene (2.93 g, 0.029 mol) in CH_2Cl_2 (5 mL) (5—15 °C) was added dropwise with stirring to a solution of benzophosphole **8** (5.9 g, 0.019 mol) in CH_2Cl_2 (20 mL) through a thin capillary using a stream of dry argon. The reaction mixture was kept at 20 °C for 4 h and then the solvent was removed *in vacuo* (12 Torr). According to the ^{31}P NMR spectroscopic data, a mixture of 2,5-dichloro-6-chlorocarbonyl-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinine (**11**), 2,8-dichloro-6-chlorocarbonyl-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinine (**12**) (~83%), and 2,2-dichloro-2-(2-chloro-2-phenylethen-1-yl)benzo[*d*]-1,3,2-dioxaphosphole (**10**) (~17%) was obtained. MS of a mixture of isomers of **11** and **12**, *m/z* (I_{rel} (%)): 377 (0.7), 376 (5.3), 375 (2.5), 374 (16.0), 373 (3.7), 372 $[M]^{\bullet+}$ (16.5), 337 (100.0), 273 (6.3), 274 (3.0), 217 (8.0), 183 (10.5), 163 (15.8), 102 (15.3), 79 (11.6), 51 (15.0), 63 (10.5), 47 (7.6), 36 (8.9), 35 (1.1). The resulting mixture was kept *in vacuo* (0.05 Torr) at 20 °C to remove volatile impurities. The residue was kept at 0—5 °C for 2—3 days, after which it partially crystallized. The crystals were washed with a 10 : 1 light petroleum—CH_2Cl_2 mixture and dried *in vacuo* to prepare compound **11** in a yield of 2.2 g (29.4%), m.p. 136—138 °C. ^{31}P NMR ($CDCl_3$): δ_P 17.0 (d, $^2J_{P,CH}$ = 25.3 Hz). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.58 (d, PCH, $^2J_{P,CH}$ = 25.5 Hz); 7.24—7.25 and 7.43—7.45 (both br.m, Ph); 7.43 (dd, H(8), $^3J_{H(7),H(8)}$ = 8.8 Hz, $^4J_{P,H(8)}$ = 0.8 Hz); 8.10 (dd, H(7), $^3J_{H(7),H(8)}$ = 8.8 Hz, $^5J_{P,H(7)}$ = 1.6 Hz). After separation of the crystals of compound **11**, the residue was kept at 150 °C to remove volatile impurities. Then the resulting glassy amber-colored compound (4.8 g) was cooled and used for the synthesis of amide **16**.

2-*tert*-Butylamino-6-*tert*-butylaminocarbonyl-5-chloro-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinine (13). *tert*-Butylamine (3.5 mL, 0.069 mol) was added to a solution of compound **11** (2.0 g, 0.005 mol) in CH_2Cl_2 (20 mL) by bubbling through a capillary with a stream of argon. The reaction mixture was kept for 2 h and then the solvent and an excess of the amine were removed *in vacuo* (12 Torr). The glassy yellowish residue was mixed with dry diethyl ether (25 mL), which led to dissolution of the glassy compound to form a white precipitate. The resulting mixture was kept for 5—8 h to achieve better coagulation of the precipitate. The latter was filtered off, washed with diethyl ether, dried *in vacuo* (12 Torr), treated with water (pH 8.0) (3×10—15 mL) to dissolve *tert*-butylammonium hydrochloride, and dried in air. Compound **13** was obtained in a yield of 1.9 g (79.2%). ^{1}H NMR (400 MHz, CD_3CN + 10% DMSO-d_6), δ: 1.30 (s, C(17)H_3, C(18)H_3, C(19)H_3); 1.31 (d, C(21)H_3, C(22)H_3, C(23)H_3, $^4J_{P,H}$ = 0.6 Hz); 4.81 (br.d, PNH, $^2J_{P,NH}$ = 8.5 Hz); 6.23 (d, PCH, $^2J_{P,CH}$ = 18.0 Hz); 7.08 (dd, H(8), $^3J_{H(7),H(8)}$ = 8.3 Hz, $^4J_{P,H(8)}$ = 0.6 Hz); 7.12 (br.s, CNH); 7.25 (dd, H(7), $^3J_{H(7),H(8)}$ = 8.3 Hz, $^5J_{P,H(7)}$ = 1.0 Hz); 7.23 and 7.33 (both m, Ph). After recrystallization from acetone, the solvate of compound **13** with acetone was obtained in a yield of 1.3 g, m.p. 148—152 °C. Found (%): C, 62.27; H, 7.12; Cl, 7.11; N, 5.84. $C_{23}H_{28}ClN_2O_3P \cdot C_3H_6O$. Calculated (%): C, 61.84; H, 6.74; Cl, 7.04; N, 5.55. IR (Nujol mull), ν/cm^{-1}: 3336, 3227 (NH); 3066, 3033 (CH arom.); 1713 (C=O); 1663 (HNC=O); 1589, 1569, 1557 sh, 1538 (C=C arom., C=C); 1494, 1446, 1392, 1337, 1304, 1266, 1224—1228 (P=O), 1196 (POC), 1138, 1127, 1069, 1033, 978, 929, 907, 895, 877, 843, 830, 812, 796, 777, 758, 744, 696, 656, 596, 563, 550, 523, 500, 473, 461, 446, 412. ^{31}P NMR (acetone): δ_P 8.4 (br.dd, $^2J_{P,CH}$ = 20.0 Hz, $^2J_{P,NH}$ = 10.0 Hz). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 1.29 (s, C(17)H_3, C(18)H_3, C(19)H_3); 1.31 (s, C(21)H_3, C(22)H_3, C(23)H_3); 2.09 (s, acetone); 5.35 (br.d, PNH, $^2J_{P,NH}$ = 9.9); 6.37 (d, PCH, $^2J_{P,CH}$ = 20.2 Hz); 7.27 and 7.39 (both br.m, Ph); 7.30 (dd, H(8), $^3J_{H(7),H(8)}$ = 8.4 Hz, $^4J_{P,H(8)}$ = 0.5 Hz); 7.38 (dd, H(7), $^3J_{H(7),H(8)}$ = 8.4 Hz, $^5J_{P,H(7)}$ = 1.2 Hz); 7.81 (br.s, CNH).

Isopropylammonium 8-chloro-6-isopropylaminocarbonyl-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinin-2-oate (16). After separation of crystals of compound **11** (4.8 g), isopropylamine (6 g) was added to the residue dissolved in benzene (20 mL). The resulting mixture was kept for 8 h and washed with water with pH 8.0. The benzene solution was concentrated *in vacuo* to one-half of the initial volume. This solution was kept for 3—5 day, after which a white precipitate of salt **16** (1.0 g) was obtained. The precipitate was filtered off, dried, and recrystallized from DMSO (crystals precipitated upon prolonged storage in air).

* The peaks of ions containing the most widespread isotopes are given.

Salt **16** was obtained in a yield of 0.7 g, m.p. 227—230 °C. Found (%): C, 56.87; H, 6.11; N, 6.32. $C_{18}H_{17}ClNO_4P \cdot \cdot C_3H_{10}N \cdot 0.5H_2O$. Calculated (%): C, 56.48; H, 6.32; N, 6.27. IR (KBr), ν/cm^{-1}: 3445, 3280, 3063, 3032, 2967, 2931, 2767, 2645, 2104, 1634, 1603, 1548, 1594, 1447, 1382, 1328, 1289, 1241, 1169, 1106, 1077, 917, 878, 846, 816, 753, 703, 629, 567, 539, 520, 481, 441. ^{31}P NMR (DMSO-d_6): δ_P −1.4 (br.d, $^2J_{P,CH}$ = 16.7 Hz). ^{1}H NMR (250 MHz, DMSO-d_6), δ: 1.07 (d, $NCCH_3$, $^3J_{H,CH}$ = 7.5 Hz); 1.15 (d, N^+CCH_3, $^3J_{H,CH}$ = 6.4 Hz); 3.26 (br.m, N^+CH, $^3J_{H,CH}$ = 6.4 Hz); 4.01 (dsept, CHNC, $^3J_{H,NH}$ = 7.5 Hz, $^3J_{H,CH}$ = 7.5 Hz); 6.21 (d, PCH, $^2J_{P,CH}$ = 16.7 Hz); 7.33 and 7.44 (both br.m, Ph); 7.56 (d, H(5), $^4J_{H(5),H(7)}$ = 1.7 Hz); 8.05 (br.s, H(7)); 8.27 (br.d, NHC, $^3J_{H,NH}$ = 7.5 Hz).

X-ray diffraction analysis of compounds **13** and **16** was carried out on an automated four-circle Enraf-Nonius CAD-4 diffractometer at 20 °C (Mo-Kα radiation, λ(Mo-Kα) = 0.71073 Å). Crystals of the solvate of benzophosphorinine **13** with acetone are monoclinic. At 20 °C, a = 9.698(2) Å, b = 17.333(4) Å, c = 16.629(4) Å, β = 91.56(2)°, V = 2794(1) Å^3, Z = 4, d_{calc} = 1.20 g cm^{-3}, space group $P2_1/n$. Crystals of salt **16** are monoclinic. At 20 °C, a = 36.96(1) Å, b = 13.881(2) Å, c = 9.397(2) Å, β = 102.17(2)°, V = 4712.7(2) Å^3, Z = 8, d_{calc} = 1.28 g cm^{-3}, space group $C2/c$. The unit cell parameters and intensities of 6200 (**13**) and 4903 (**16**) reflections, of which 2797 (**13**) and 2283 (**16**) reflections were with $I \geq 2\sigma$, were measured at ~20 °C (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω/2θ (**13**) and ω scanning technique (**16**), θ ≤ 27.2°). The intensities of three check reflections showed no decrease in the course of X-ray data collection. Because of low values of the coefficient (μ(Mo) = 2.22 and 2.58 cm^{-1}, respectively), absorption was ignored. The structures were solved by direct methods using the SIR program[25] and refined first isotropically and then anisotropically. In the crystal structure of **16**, the water molecule of crystallization occupies a special position on a twofold axis. All H atoms were revealed from difference electron density syntheses. Their contributions to the structure factors were taken into account in the final steps of the least-squares refinement with fixed positional and isotropic thermal parameters. The final values of the reliability factors were as follows: R = 0.053, R_w = 0.060 based on 2536 independent reflections with $F^2 \leq \sigma$ in the structure of **13** and R = 0.054, R_w = 0.064 based on 2045 independent reflections with $F^2 \leq 3\sigma$ in the structure of **16**. All calculations were carried out using the MolEN complex program[26] on an AlphaStation 200 computer. The atomic coordinates and thermal parameters were deposited with the Cambridge Structural Database. Selected geometric parameters are given in Table 3. The molecular structures were drawn and intermolecular interactions were calculated with the use of the PLATON program.[27]

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