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1,3,2(1,4,2)-Dioxaphosphepins Annelated with Naphthalene Fragment: Synthesis and Steric Structure

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Abstract — Reaction of hexafluoroacetone and chloral with 2-R-naphtho-1,3,2-dioxaphosphorin-4-ones yields 2-R-2,5-dioxo-4,4-bis(trifluoromethyl)naphtho-1,3,2- and 2-R-2,5-dioxo-3-trichloromethylnaphtho-1,4,2λ^5-dioxaphosphepins. Hydrolysis of the fluorophosphepins gives naphthyl-substituted fluorinated hydroxy ketones. The steric structure of the dioxaphosphepins and some fluorinated ketones was confirmed by single crystal X-ray diffraction. A competition between the π–π and halogen–halogen interactions and hydrogen bonds of classic type in the formation of crystal packing and supramolecular structure was revealed.
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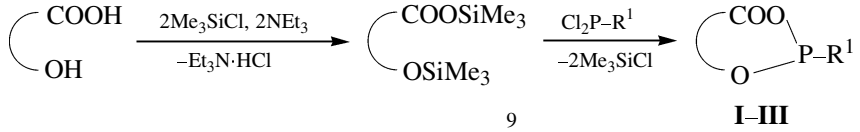
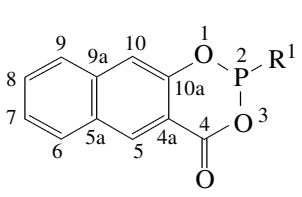
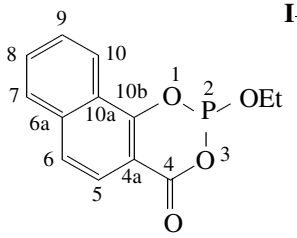
Cyclic phosphorylated derivatives of hydroxy and amino carboxylic acids are highly active P(III) derivatives capable of reacting with compounds containing an activated multiple bond. Among such cyclic anhydrides, the most studied are mixed anhydrides of salicylic and phosphoric acids, 2-R-benzo[*d*]-1,3,2-dioxaphosphorin-4-ones, or "salicyl phosphites" [1, 2]. It is presumed that their reactions with activated carbonyl compounds proceed through formation of intermediate bipolar ions with $P^+–CO^-$ and $P^+–OC^-$ bonds. The anionic center of such ion attacks the carbon atom of the endocyclic carbonyl group of the PO–C(O) fragment, which leads finally to the formation of the derivatives of five- and four-coordinate phosphorus atom: pentaalkoxyspirophosphoranes, seven-membered P-heterocycles (benzo-1,3,2- and benzo-1,4,2-dioxaphosphepins), and oxidation products [3]. Among cyclic phosphorylated derivatives of hydroxy and amino carboxylic acids and products of their transformations, substances possessing fungicidal, herbicidal, insecticidal, antiviral, and antitumor activity and also showing some catalytic properties in hydroformylation were found [1, 2, 4–8]. The synthesis and properties of the cyclic P-derivatives of hydroxy and amino carboxylic acids containing five-coordinate phosphorus are of a great interest. Such structures may act as intermediates in biochemical processes and can cause autocatalysis in the peptide biosynthesis [9–18]. Thus, further studies of the reactions of mixed cyclic anhydrides of phosphoric and hydroxy carboxylic acids are quite topical. This paper deals with the synthesis and study of reactions of the close structural analogs of "salicyl phosphites," namely, of cyclic derivatives of phosphoric and hydroxynaphthoic acids, 2-R-naphtho[*d*]-1,3,2-dioxaphosphorin-4-ones **I**–**III**, with hexafluoroacetone and chloral.

Compounds **I**–**III** were prepared by the reaction of alkyl phosphorodichloridites and phenyldichlorophosphine with the trimethylsilyl derivatives of the corresponding naphthoic acids in an inert atmosphere, followed by removal of trimethylchlorosilane. The starting trimethylsilyl derivatives of naphthoic acids were prepared by silylation of the corresponding acids with trimethylchlorosilane (the reaction was monitored by IR spectroscopy, by disappearance of the OH bands) and used without additional purification. This route is milder than the reactions of alcohols with cyclic phosphoric and hydroxynaphthoic acid chlorides [8] and ensures almost quantitative formation of derivatives **I**–**III** which do not require additional purification. This fact is significant, taking into account low stability of compounds **I**–**II** to vacuum distillation. The $^{31}P–\{^1H\}$ NMR spectra of compounds **I**–**III** contain characteristic low-field signals at δ_P 124.5, 124.8 (**I**, **III**) and 158.4 (**II**) ppm.



I–III

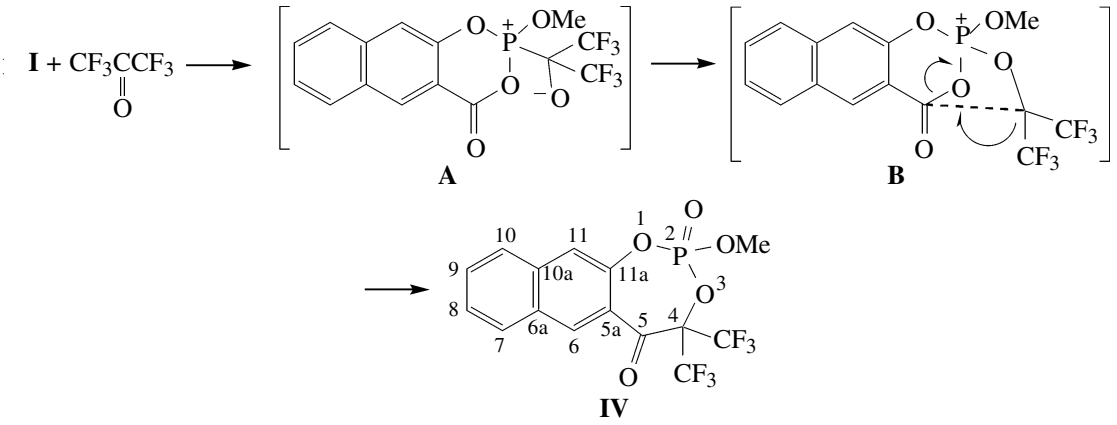




III

R^1 = OMe (**I**), Ph (**II**).

The reaction of 2-methoxynaphtho[2,3-*d*]-1,3,2-dioxaphosphorin-4-one **I** with hexafluoroacetone is carried out under mild conditions (a mixture of methylene chloride and carbon tetrachloride, –40°C) and results in almost quantitative formation of 2-methoxy-2,5-dioxo-4,4-bis(trifluoromethyl)naphtho[2,3-*e*]-1,3,2λ^5-dioxaphosphepin **IV**.



The structure of naphthophosphepin **IV** is confirmed by ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR and IR spectroscopy (see Experimental). In particular, in the ^{19}F NMR spectrum the trifluoromethyl groups are manifested as A_3B_3 system (δ_F 72.54 and 72.65 ppm, $^4J_{FF}$ 7.3 Hz). In the IR spectrum, the following characteristic absorption bands are observed (ν, cm^{-1}): 1709 (C=O), 1602–1645 (CH_{arom}), 1042–1085 (P–O–C), 1278 (P=O). In the ^{13}C–{^{1}H} NMR spectrum, the signals of carbon nuclei C^4 and C^5 (δ_C 83.40 and 186.12 ppm) were found, confirming the presence of the $C^5(O)C^4OP$ fragment. In the electron impact (EI) mass spectrum of compound **IV**, there is a peak of the molecular ion with *m/z* 414 $[M]^{+\cdot}$. The fragmentation pattern of **IV** under electron impact is in agreement with its chemical structure. The peak with *m/z* 395 corresponds to the $[M - F]^+$ ion. The strongest peak with *m/z* 170 probably corresponds to the ion formed by cleavage of the P^2–O^1 and C^4–O^5 bonds in the seven-membered ring.

The reaction in question presumably involves the initial attack of the phosphorus atom of phosphite **I** at the carbon atom of the hexafluoroacetone carbonyl group to form bipolar ion *A* containing a P–C bond, which then rearranges into ion *B* with the P^+–OC^- bond. The system is stabilized by intermolecular nucleophilic attack of the carbanion center at the carbon atom of the endocyclic carbonyl group to form phosphepin **IV**.

The structure of phosphepin **IV** was also proved by single crystal X-ray diffraction (Fig. 1). The selected geometric parameters of the molecule (bond lengths, bond and torsion angles) are listed in Table 1. The heteroring conformation is unsymmetric *twist-boat*: the four-centered fragment $O^1C^{11a}C^{5a}C^5$ is

Table 1. Selected bond lengths, bond angles, and torsion angles in the molecule of **V**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
P^2–O^1	1.570(3)	C^{10a}–C^{11}	1.413(6)	C^8–C^9	1.397(7)
P^2–O^2	1.452(3)	C^4–C^{13}	1.539(6)	O^1–C^{11a}	1.403(5)
P^2–O^3	1.601(3)	C^{5a}–C^5	1.490(6)	C^{10}–C^{10a}	1.410(6)
P^2–O^{31}	1.517(3)	C^{5a}–C^{11a}	1.408(6)	O^{31}–C^{12}	1.408(7)
C^7–C^8	1.358(7)	C^{6a}–C^6	1.397(6)	C^4–C^5	1.569(6)
O^3–C^4	1.411(5)	C^{6a}–C^7	1.404(6)	C^4–C^{14}	1.528(5)
O^5–C^5	1.200(5)	C^{6a}–C^{10a}	1.408(6)	C^{5a}–C^6	1.366(6)
Angle	φ, deg	Angle	φ, deg	Angle	φ, deg
$O^1P^2O^2$	115.6(2)	$O^3C^4C^{13}$	106.3(3)	$O^2P^2O^3$	113.5(2)
$O^1P^2O^{31}$	104.8(2)	$C^{13}C^4C^{14}$	110.6(3)	$O^3P^2O^{31}$	103.6(2)
$O^2P^2O^{31}$	116.2(2)	$C^5C^{5a}C^{11a}$	128.2(4)	$P^2O^3C^4$	119.8(2)
$P^2O^1C^{11a}$	121.0(3)	$O^5C^5C^4$	116.9(4)	$O^3C^4C^5$	116.2(3)
$P^2O^{31}C^{12}$	126.9(3)	$O^1P^2O^3$	101.4(1)	$O^3C^4C^{14}$	105.6(3)
Angle	τ, deg	Angle	τ, deg	Angle	τ, deg
$O^2P^2O^1C^{11a}$	–44.4(3)	$C^{13}C^4C^5O^5$	–15.2(5)	$P^2O^1C^{11a}C^{5a}$	–24.1(5)
$O^{31}P^2O^1C^{11a}$	–173.7(3)	$C^{14}C^4C^5O^5$	105.6(4)	$P^2O^3C^4C^5$	12.4(4)
$O^2P^2O^3C^4$	44.6(3)	$C^6C^{5a}C^5O^5$	–29.7(5)	$P^2O^3C^4C^{14}$	131.5(3)
$O^1P^2O^{31}C^{12}$	–39.5(4)	$C^{11a}C^{5a}C^5O^5$	149.7(4)	$O^3C^4C^5C^{5a}$	51.4(5)
$O^3P^2O^{31}C^{12}$	66.4(4)	$O^3P^2O^1C^{11a}$	78.8(3)	$C^{13}C^4C^5C^{5a}$	172.5(3)
$P^2O^1C^{11a}C^{11}$	155.7(3)	$O^1P^2O^3C^4$	–80.1(3)	$C^{14}C^4C^5C^{5a}$	–66.7(5)
$P^2O^3C^4C^{13}$	–111.0(3)	$O^{31}P^2O^3C^4$	171.5(3)	$C^6C^{5a}C^5C^4$	142.2(4)
$O^3C^4C^5O^5$	–136.3(4)	$O^2P^2O^{31}C^{12}$	–168.4(4)	$C^{11a}C^{5a}C^5C^4$	–38.4(6)

planar within 0.003(4) Å, but the phosphorus atom P^2 deviates from the plane to one side by –0.561(1) Å, and the O^3 and C^4 atoms deviate to the other side of the plane by distances of 0.664(3) and 0.847(4) Å, respectively. The O^5 oxygen atom of the carbonyl group also deviates from the planar fragment by –0.517(3) Å, which corresponds to the dihedral angle $O^5C^5C^{5a}C^6$ of 29.7(6)°. The phosphoryl group occupies a pseudoaxial position [the O^2 atom deviates from the $O^1C^{11a}C^{5a}C^5$ plane by –1.816(3) Å], whereas the methoxy group is pseudoequatorial [the O^{31} atom deviates from the $O^1C^{11a}C^{5a}C^5$ plane by –0.539(3) Å]. Recently we showed [19] that the hererоring in 2-oxo-2-fluoroalkoxy-4,4-bis(trifluoromethyl)benzo[*d*]-1,3,2λ^5-dioxaphosphepin, unlike compound **IV**, has the conformation of a distorted *boat* in which the P^2, O^3, and C^4 atoms deviate from the planar disubstituted phenylene fragment to the same side by different distances.

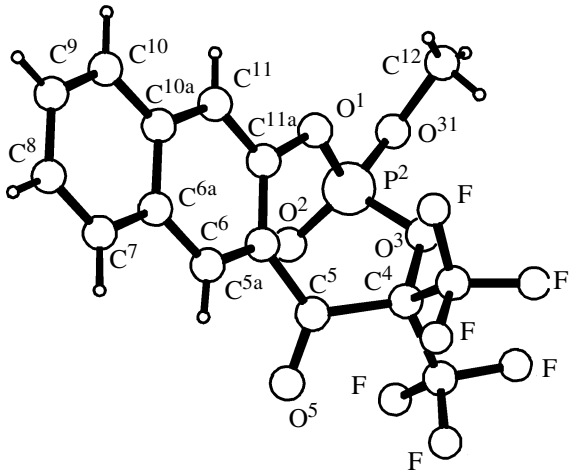


Fig. 1. Geometry of phosphepin **V** in crystal.

In the crystal of phosphepin **IV**, we detected intramolecular interactions of the C–H···O type and contacts of the π–π type between aromatic fragments of the molecules. The intramolecular hydrogen bond C^6–H^6···O^2 [1/2 + *x*, 1/2 – *y*, *z*] between the phosphoryl oxygen atom O^2 and the hydrogen atom of the naphthylene moiety H^6 leads to the formation of infinite molecular zigzag chains along the 0*x* axis. Parameters of the interaction: C^6–H^6 0.87(3), H^6···O^2

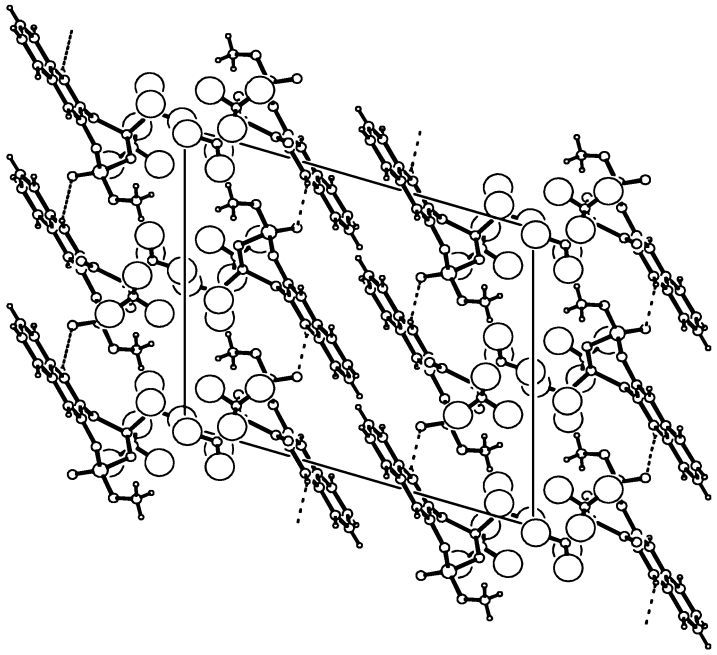
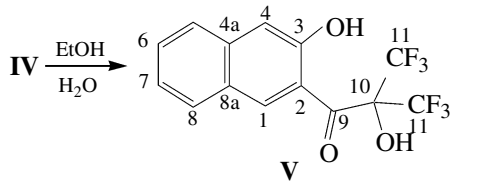


Fig. 2. Packing of molecules of phosphepin **IV** in the crystal. The CH···O interactions are shown by dotted lines, and the F atoms, as big apheres. View aling O_y axis.

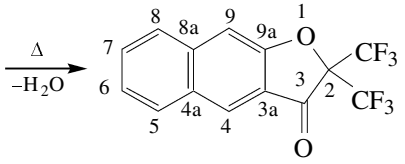
2.49(3), $C^6\cdots O^2$ 3.253(5) Å, angle $C^6–H^6\cdots O^2$ 147(2)°. The contacts of the π–π type between the electronic systems of naphthylene fragments in centrosymmetric pairs of phosphepin molecules bind the chains in layers parallel to the 0*xy* plane (the shortest distance between the ring centers is 3.43 Å, and the dihedral angle between the planes is 0°). Thus, the combination of these interactions leads to formation of layered structures differing in the type of interaction in two perpendicular directions. The naphthylene fragments of the molecules form separate layers, and the crystal packing presents alternation of the layers consisting of naphthylene and phosphorus-containing heterocyclic fragments of the molecules (Fig. 2). Such arrangement of the molecules provides fairly high density of the crystal packing: the calculated packing coefficient is equal to 0.69.

The observed short contacts between fluorine atoms of the molecules [with the distances of 2.945(4) and 2.996(4) Å] result in association in the crystal of fluorine-containing fragments as cylindrical supramolecular structures along the 0*y* axis; the F···F distance between the neighboring cylindrical structures is no shorter than 3.57 Å.

Hydrolysis of phosphepin **IV** with a 1 : 1 ethanol–water mixture leads to the formation of functionally substituted fluorinated hydroxy ketone **V** whose distillation at high temperature is accompanied by water elimination and formation of naphthofuranone derivative **VI**.



V



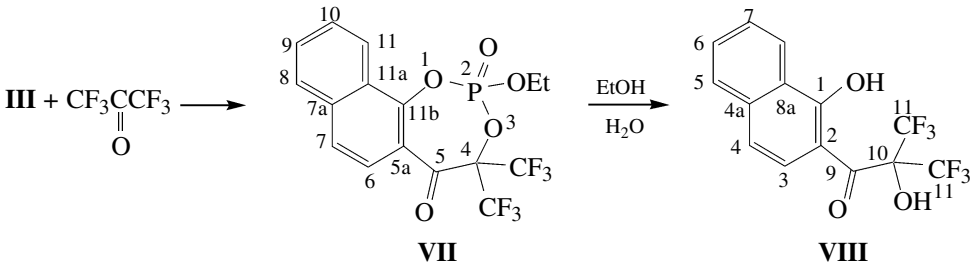
VI

In the IR spectrum of **V** there are the following bands (ν, cm^{-1}): 3000–3400, (ν_{OH}), 1715–1740 ($\nu_{C=O}$), 1605 and 1640 ($\nu_{C=C}$), and 1200–1300 (ν_{CF}). In the ^{19}F NMR spectrum of **V**, there is a singlet at δ_F –74.62 ppm. The $^{13}C–\{^1H\}$ NMR spectrum (see Experimental) confirms the structure of fluorinated ketone **V**.

In the IR spectrum of **VI**, there is a characteristic band at 1756 cm^{-1} ($\nu_{C=O}$) and the absorption bands of hydroxy groups are absent. In the mass spectrum of naphthofuranone **VI**, the peak with *m/z* 320 corresponds to the molecular ion $[M]^{+\cdot}$. The fragmentation

pattern of **VI** under electron impact is in agreement with its chemical structure: the peak with *m/z* 301 corresponds to the $[M - F]^+$ ion, and the peak with *m/z* 251, to the $[M - CF_3]^+$ ion. A strong peak with *m/z* 154 in the mass spectrum probably corresponds to the ion formed by cleavage of the C^{9a}–O^1 and C^2–C^3 bonds in the five-membered ring with the charge localization on the aromatic fragment. The strongest peak with *m/z* 126 corresponds to the $[C_{10}H_6]^+$ ion apparently formed by cleavage of the C^{9a}–O^1 and C^{2a}–C^3 bonds. The data of the ^{13}C and ^{13}C–$\{^1H\}$ NMR spectra are also in agreement with the cyclic structure of naphthofuranone **VI**.

Naphthylene phosphite **III**, a derivative of 1-hydroxy-2-naphthoic acid, reacts with hexafluoroacetone to form 1,3,2-dioxaphosphepin **VII** which is hydrolyzed similarly to **IV** to form a product with an open-chain structure, functionally substituted fluorinated hydroxy ketone **VIII**.



The structure of compound **VII** is confirmed by spectral methods. In the ^{31}P–$\{^1H\}$ NMR spectrum, the singlet at δ_P –13.1 ppm corresponds to phosphepin **VII**. In the ^{19}F NMR spectrum, the trifluoromethyl groups give an A_3B_3 pattern with δ_F –72.10 and –72.34 ppm ($^4J_{FF}$ 9.2 Hz). In the ^1H NMR spectrum of **VII**, the signals of the CH_3CH_2O protons are observed at δ 1.68 ppm, t.d ($^3J_{HH}$ 7.0, $^4J_{POCCH}$ 1.2 Hz) and at δ 4.75 ppm, d.q ($^3J_{HH}$ 7.0, $^3J_{POCCH}$ 9.3 Hz).

The ^{19}F NMR spectrum of fluorinated ketone **VIII** consists of a single signal at δ_F –75.89 ppm. In the ^1H NMR spectrum, there are two broad singlets corresponding to OH groups involved in inter- and intramolecular hydrogen bonds (5.85 and 13.60 ppm). In the electron impact mass spectrum, a peak with *m/z* 338 corresponds to the molecular ion $[M]^{+\cdot}$ of **IX**. The strongest peak with *m/z* 171 probably belongs to the ion formed by cleavage of the C(O)–$C(CF_3)_2OH$ bond. The ^{13}C and ^{13}C–$\{^1H\}$ NMR data are in agreement with the structure of hydroxy ketone **VIII** (see Experimental).

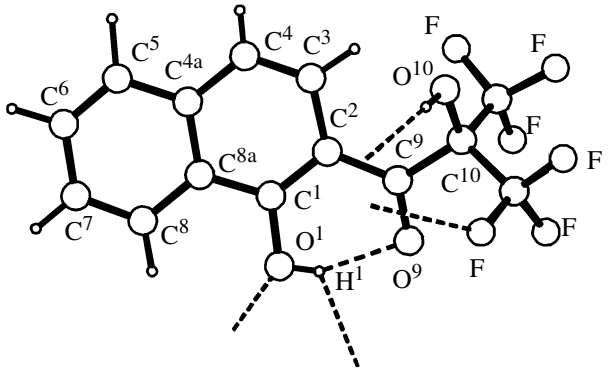


Fig. 3. Geometry of fluorinated ketone **VIII** in crystal.

The structure of **VIII** is also confirmed by single crystal X-ray diffraction (Fig. 3). Selected geometric parameters of the molecule are listed in Table 2. The carbonyl group deviates insignificantly from the plane of the naphthalene fragment [dihedral angle $C^1C^2C^9O^9$ 10.0(8)°], which is favorable for their conjugation. The bond lengths and bond angles (the main of them are given in Table 2) have typical values. The crystal of **VIII** is characterized by a large number of inter- and intramolecular hydrogen bonds of different types. Among the intermolecular H-bonds, first of all we should note the hydrogen bond between the hydroxyl hydrogen of the naphthalene fragment and carbonyl oxygen, O^1–$H^1\cdots O^9$, O^1–H^1 0.77(3), $H^1\cdots O^9$ 1.81(4), $O^1\cdots O^9$ 2.520(6) Å, angle O^1–$H^1\cdots O^9$ 153(4)°. The intramolecular hydrogen bond O^{10}–$H^{10}\cdots O^{1'}$ [–1/2 + *x*, 1/2 – *y*, *z*], O^{10}–H^{10} 0.77(4), $H^{10}\cdots O^{1'}$ 2.09(4), $O^{10}\cdots O^{1'}$ 2.838(6) Å, angle O^{10}–$H^{10}\cdots O^{1'}$ 163(4)°, and the O^1–$H^1\cdots F^{2''}$ [1/2 + *x*, 1/2 – *y*, *z*] bond, O^1–H^1 0.77(3), $H^1\cdots F^{2''}$ 2.51(3), $O^1\cdots F^{2''}$ 2.942(5) Å, angle O^1–$H^1\cdots F^{2''}$ 117(3)°, lead to the formation of cylindrical supramolecular structures in the form of molecular stacks arranged along the crystallographic axis 0*x* (Fig. 4).

Table 2. Selected bond lengths, bond angles, and torsion angles in the molecule of **VIII**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
C^{4a}–C^{4}	1.404(7)	C^{2}–C^{3}	1.443(7)	O^{10}–C^{10}	1.411(6)
C^{4a}–C^{8a}	1.415(7)	C^{2}–C^{9}	1.453(7)	C^{1}–C^{2}	1.379(7)
O^{1}–C^{1}	1.365(6)	C^{3}–C^{4}	1.336(7)	C^{1}–C^{8a}	1.417(7)
O^{9}–C^{9}	1.222(6)	C^{4a}–C^{5}	1.417(7)	C^{9}–C^{10}	1.549(7)
C^{7}–C^{8}	1.365(7)	C^{5}–C^{6}	1.347(8)	C^{10}–C^{11}	1.543(7)
C^{8a}–C^{8}	1.406(7)	C6–C^{7}	1.394(8)	C^{10}–C^{12}	1.521(7)
Angle	φ, deg	Angle	φ, deg	Angle	φ, deg
$O^{1}C^{1}C^{2}$	121.7(4)	$O^{10}C^{10}C^{9}$	114.2(4)	$C^{3}C^{2}C^{9}$	124.6(4)
$C^{2}C^{1}C^{8a}$	124.6(5)	$O^{10}C^{10}C^{12}$	105.5(4)	$C^{2}C^{9}C^{10}$	122.4(4)
$C^{1}C^{2}C^{9}$	119.4(4)	$C^{9}C^{10}C^{12}$	110.2(4)	$O^{10}C^{10}C^{11}$	106.9(4)
$C^{2}C^{3}C^{4}$	120.8(5)	$O^{1}C^{1}C^{8a}$	113.7(4)	$C^{9}C^{10}C^{11}$	109.7(4)
$O^{9}C^{9}C^{10}$	115.8(4)	$C^{1}C^{2}C^{3}$	116.0(4)	$C^{11}C^{10}C^{12}$	110.1(4)
Angle	τ, deg	Angle	τ, deg	Angle	τ, deg
$O^{9}C^{9}C^{10}O^{10}$	–147.7(4)	$C^{2}C^{9}C^{10}C^{11}$	145.4(5)	$C^{2}C^{9}C^{10}O^{10}$	25.4(6)
$O^{9}C^{9}C^{10}C^{12}$	93.7(5)	$O^{9}C^{9}C^{10}C^{11}$	–27.6(6)	$C^{2}C^{9}C^{10}C^{12}$	–93.2(5)

The π–π contacts between the electronic systems of the naphthylene fragments of the phosphepin molecule act in the same direction. Each molecule participates in two such contacts with the neighboring molecules related to it by a center of symmetry and translation of ±1 along the 0*x* axis. The shortest distances between the planes of naphthylene rings are 3.42 and 3.45 Å, and the dihedral angles are 1.8° and 1.8°. On the whole, the molecular packing in the crystal consists in parallel arrangement of the octahedral type of cylindrical supramolecular structures described previously (Fig. 5); a high packing density is achieved: the calculated packing coefficient is 0.72. The naphthylene fragments of the molecules do not form separate layers and are surrounded by the fluorine-containing fragments of the molecules. Moreover, the short contacts between the fluorine atoms in the crystal of fluorinated ketone **VIII** cause formation of centrosymmetrical dimers of molecules only [the F···F distances are equal to 3.056(6) Å], and the contacts between the fluorine atoms belonging to the neighboring dimers are observed only when the distances exceed 3.5 Å.

Salicyl phosphites quite readily form the products of heteroring expansion under the influence of another reactive compound, chloral, which also reacts with them after Perkow. The regular trends of the reactions and the structure of the resulting 1,4,2-dioxaphosphepins were studied previously, in particular, using quantum-chemical calculations [19–22]. The naphthylene-contained derivatives **I** and **II** react with chloral at equimolar reactant ratio to form 2-R-2,5-dioxo-3-trichloromethylnaphtho[2,3-*e*]-1,4,2λ^5-dioxaphosphepins **IX** and **X**. More reactive phosphonite **II** reacts with chloral with a small exothermic effect, but in the case of phosphite **I** the reaction requires keeping for 2 months. Unlike the reaction with hexa-

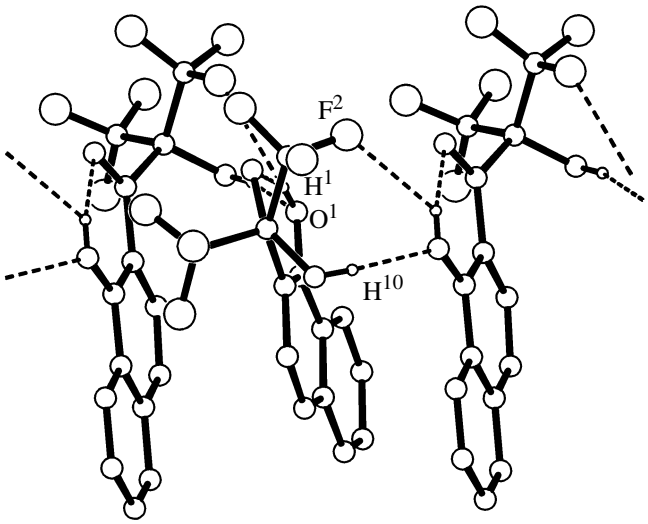


Fig. 4. System of hydrogen bonds O–H···O and O–H···F in the crystal of phosphepin **VIII** (hydrogen bonds are shown by dashed lines, and F atoms, as big spheres; only hydroxyl hydrogen atoms are shown).

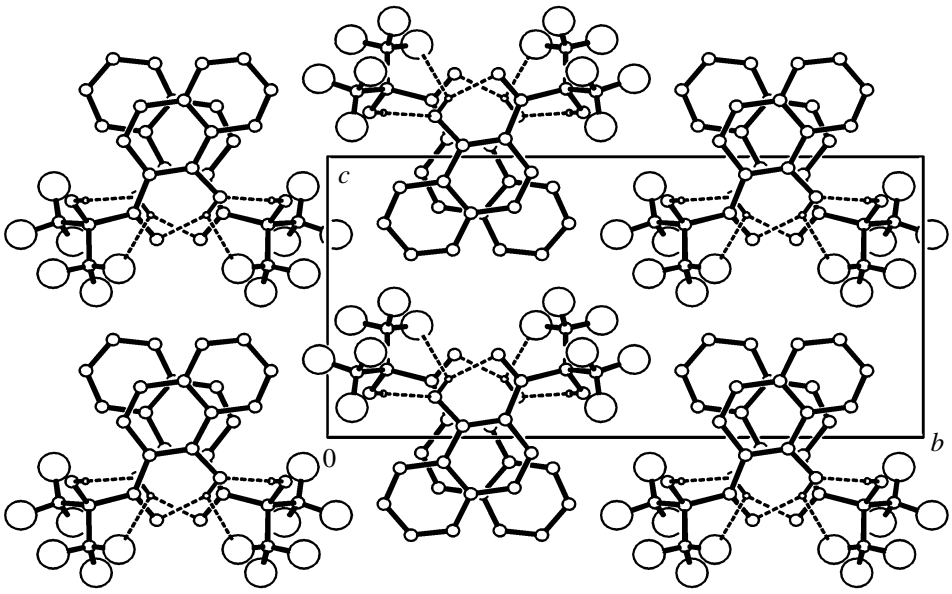
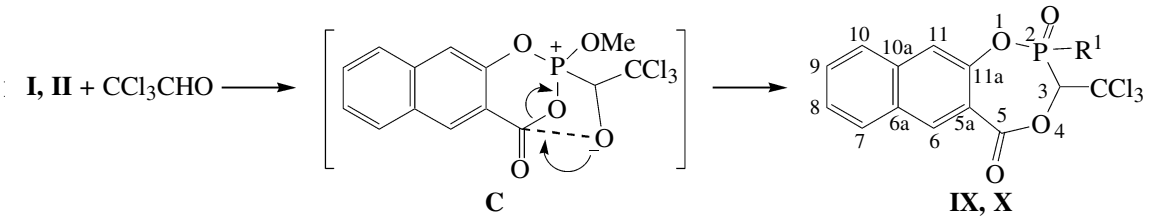


Fig. 5. Packing of molecules of phosphepin **VIII** in the crystal (O–H···O and O–H···F interactions are shown by dashed lines, and F atoms, as big spheres; only hydroxyl hydrogen atoms are shown); view along O_x axis.

fluoroacetone, the formation of 1,4,2-dioxaphosphepins proceeds evidently via bipolar ion C with the P–C bond, or, in accordance with the calculated data [21, 22], this structure should be considered as a transition state. The reactions are characterized by a high stereoselectivity (>95%).



R^1 = OMe (**I, IX**), Ph (**II, X**).

The structure of **IX** is confirmed by spectral methods (see Experimental). In the electron impact mass spectrum of phosphepin **IX**, the peak with *m/z* 394 corresponds to the molecular ion $[M]^{+\cdot}$. The ratio of the intensity of the isotopic peaks with *m/z* 394, 396, and 398 is consistent with the empirical formula $C_{14}H_{10}Cl_3O_5P$. The fragmentation pattern under electron impact is in good agreement with the chemical structure of the molecule. A peak with *m/z* 359 corresponds to the $[M - Cl]^+$ ion. Loss of the CCl_3 group by the $[M]^{+\cdot}$ ion gives the ion with *m/z* 277. The strongest peak with *m/z* 170 apparently corresponds to the ion formed by cleavage of the P^1–O^2 and O^4–C^5 bonds in the seven-membered ring.

The data of X-ray structural analysis of the isolated major diastereomer of phosphepin **IX** ($P^2_SC^3_S/P^2_RC^3_R$) also confirms the 1,4,2-dioxaphosphepin structure (Fig. 6). Table 3 lists the selected parameters of the molecule (bonds lengths, bond and torsion angles). The conformation of the seven-membered heteroring is a distorted *boat* involving, as in the case of **IV**, a planar four-atom fragment $O^1C^{11a}C^{5a}C^5$ from which the P^2, C^3, and O^4 atoms deviate to the same side by the distances of 1.311(1), 1.896(5), and 0.786(3) Å, respectively. The O^5 atom deviates from the $O^1C^{11a}\cdot C^{5a}C^5$ plane by a somewhat longer distance [–0.606(4) Å] than in **IV**, which corresponds to the

Table 3. Selected bond lengths, bond angles, and torsion angles in the molecule of **IX**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Cl^1–C^{13}	1.794(5)	O^4–C^5	1.377(5)	P^2–O^2	1.434(3)
C^{6a}–C^7	1.399(6)	O^5–C^5	1.190(7)	C^8–C^9	1.353(9)
C^{6a}–C^{10a}	1.414(7)	C^3–C^{13}	1.539(7)	O^1–C^{11a}	1.405(5)
C^7–C^8	1.35(1)	C^{5a}–C^6	1.345(6)	O^3–C^{12}	1.386(8)
P^2–O^3	1.556(4)	C^6–C^{6a}	1.423(8)	C^{10}–C^{10a}	1.430(8)
P^2–C^3	1.844(6)	Cl^2–C^{13}	1.765(5)	C^5–C^{5a}	1.492(7)
C^9–C^{10}	1.367(6)	Cl^3–C^{13}	1.734(5)	C^{10a}–C^{11}	1.366(5)
O^4–C^3	1.427(6)	P^2–O^1	1.590(3)	C^{5a}–C^{11a}	1.409(7)
Angle	φ, deg	Angle	φ, deg	Angle	φ, deg
$O^1P^2O^2$	111.6(2)	$P^2C^3C^{13}$	117.7(3)	$O^3P^2C^3$	103.4(2)
$O^1P^2C^3$	99.0(2)	$O^4C^5O^5$	117.6(5)	$P^2O^3C^{12}$	126.5(3)
$O^2P^2C^3$	119.0(2)	$O^5C^5C^{5a}$	123.8(4)	$P^2C^3O^4$	108.6(3)
$P^2O^1C^{11a}$	120.7(2)	$O^1P^2O^3$	105.2(2)	$O^4C^3C^{13}$	105.2(4)
$C^3O^4C^5$	119.7(4)	$O^2P^2O^3$	116.4(2)	$O^4C^5C^{5a}$	118.6(4)
Angle	τ, deg	Angle	τ, deg	Angle	τ, deg
$O^2P^2O^1C^{11a}$	173.6(3)	$C^3O^4C^5C^{5a}$	23.5(6)	$O^3P^2C^3O^4$	153.8(3)
$C^3P^2O^1C^{11a}$	47.4(4)	$O^4C^5C^{5a}C^{11a}$	37.0(6)	$P^2O^1C^{11a}C^{5a}$	–79.8(5)
$O^1P^2C^3C^{13}$	165.0(4)	$O^5C^5C^{5a}C^{11a}$	–143.1(5)	$C^5O^4C^3P^2$	–89.2(4)
$O^2P^2C^3C^{13}$	44.0(4)	$O^3P^2O^1C^{11a}$	–59.2(4)	$C^3O^4C^5O^5$	–156.4(4)
$O^3P^2C^3C^{13}$	–86.9(4)	$O^1P^2C^3O^4$	45.7(3)	$O^4C^5C^{5a}C^6$	–145.4(4)
$P^2O^1C^{11a}C^{11}$	104.2(4)	$O^2P^2C^3O^4$	–75.3(3)	$O^5C^5C^{5a}C^6$	34.5(7)

dihedral angle $O^5C^5C^{5a}C^6$ 34.5(7)°. The phosphoryl and trichloromethyl groups occupy pseudoequatorial positions [O^2 and C^{13} atoms deviate from the $O^1C^{11a}C^{5a}C^5$ plane by distances of 1.035(4) and 2.978(5) Å, respectively], whereas the methoxy group is pseudoaxial [O^3 atom deviates from the same plane by 2.323(3) Å]. Along the P^2–C^3 bond the conformation is close to staggered [the dihedral angle $H^3C^3P^2O^2$ is 165.1(3)°]. It is interesting that the conformation of the seven-membered heteroring in 2-methoxy-2,5-dioxo-3-trichloromethyl-6,7-benzo[*e*]-1,4,2λ^5-dioxaphosphepin, similar to phosphepin **X**, is also a distorted *boat* with a somewhat smaller deviation of the C^3 and P^2 atoms from the base plane [by –1.833(2) and –0.695(2) Å, respectively].

On the whole, realization of numerous intramolecular interactions in the crystal of phosphepin **IX** causes formation of a three-dimensional supramolecular structure. It is interesting that the interaction of the C–H···O type between the phosphoryl oxygen $O^{2'}$ (1/2 + *x*, 1/2 – *y*, –1/2 + *z*] and the H^3 atom at the chiral carbon atom C^3 also binds the molecules in a chain along the diagonal 0*xz*, but all the molecules in the chain have the same configuration. The parameters of the interaction are as follows: C^3–H^3 0.94, $H^3\cdots O^{2'}$ 2.14, $C^3\cdots O^{2'}$ 3.077(6) Å, and angle C^3–$H^3\cdots O^{2'}$ 173°. The π–π contacts between the electronic systems of the naphthylene fragments of the molecules (the shortest distance between the planes is 3.35 Å, dihedral angle 0°) bind the chains along the

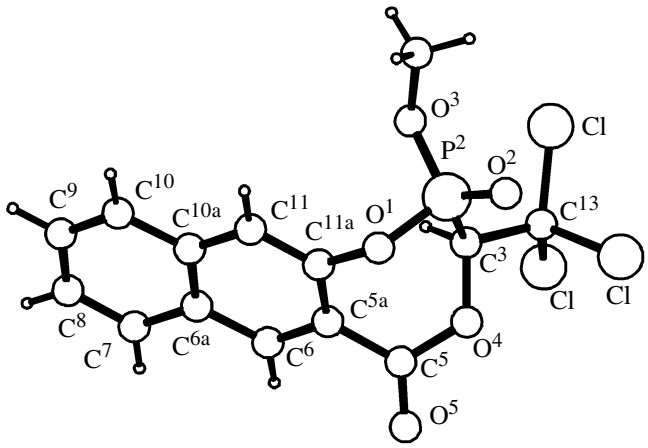


Fig. 6. Geometry of naphthophosphepin **IX** in crystal.

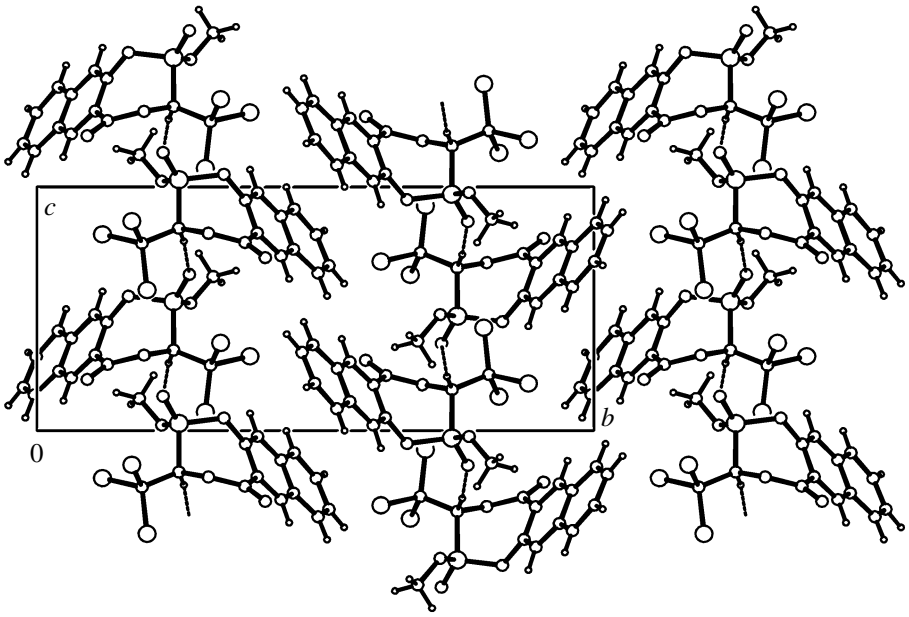


Fig. 7. Packing of molecules of **IX** in the crystal (C–H···O interactions are shown by dotted lines); view along O_x axis.

0*y* axis, and the additional interactions of the C–H···O– and C–H···Cl types provide connection of the chains in two orthogonal directions; the naphthylene fragments of the molecules form separate layers (Fig. 7). The contacts between the chlorine atoms of **IX** are observed only at distances longer than 3.59 Å. Such mutual arrangement of molecules is not favorable to their compact packing: the calculated packing coefficient is as low as 0.66.

Analysis of the crystallographic data for the three compounds containing a bulky aromatic fragment shows that, without classical strong hydrogen bonds, the crystal packing and formation of supramolecular structures are mainly governed by the contacts between the electronic systems of the aromatic fragments, leading to localization (association) of such fragments in the crystals. Association of fluorine-containing fragments of the molecules in the crystal is observed both in the presence and in absence of hydrogen bonds; at the same time, the classical hydrogen bonding favors dense packing of molecules in the crystal.

Spectral data for **X** are listed in Table 4; the whole interpretation was carried using the techniques of correlation spectroscopy (2D COSY, 2D HSQC, 2D HMBC).

Thus, phosphorylated derivatives of hydroxynaphthoic acids react with hexafluoroacetone and chloral to form seven-membered phosphorus-containing heterocycles, namely, 1,3,2λ^5- or 1,4,2λ^5-dioxaphosphepins, depending on the structure of the carbonyl compound. Hydrolysis of 1,3,2λ^5-dioxaphosphepins obtained in the reactions with hexafluoroacetone allows preparation of fluorinated hydroxy ketones containing 1- and 2-naphthyl radical as a substituent.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer from thin films or mulls in mineral oil between KBr plates, or from KBr pellets. The ^{1}H, ^{31}P, and ^{19}F NMR spectra were taken on a Varian Unity-300 spectrometer (300, 121.42, and 287.2 MHz, respectively). The ^{13}C and ^{13}C–{^{1}H} NMR spectra were measured on a Bruker MSL-400 spectrometer (100.6 MHz). The ^{1}H, ^{13}C, ^{13}C–{^{1}H}, 2D COSY, 2D HSQC, and 2D HMBC NMR spectra of **X** were recorded on a Bruker Avance-600 spectrometer (^{1}H 600 MHz and ^{13}C 150.9 MHz) in DMSO-d_6 at 50°C against the residual proton or carbon signals of the solvent. The ^{31}P NMR spectra were recorded against external H_3PO_4. The ^{19}F NMR spectra were recorded in $CDCl_3$ (unless otherwise indicated) and in acetone-d_6; the internal reference was C_6F_6, and the chemical shifts were then recalculated to $CFCl_3$. The electron impact mass spectra were measured on a TRACE MS Finnigan MAT apparatus at ionizing electron energy of 70 eV; the ion source temperature was 200°C.

The single crystal X-ray diffraction studies of the compounds were carried out on Enraf-Nonius CAD-4 automatic four-circle diffractometers at 20°C, ω/2θ

Table 4. Parameters of the ^{1}H (600 MHz), ^{13}C, and ^{13}C–{^{1}H} (150.9 MHz, $CDCl_3$) NMR spectra and results of 2D COSY, 2D HCQC, and 2D HMBC experiments for **X**

Atom	δ, ppm (*J*, Hz)	Cross peaks in 2D COSY
H^3	6.70 d ($^2J_{PCH}$ 3.5)	–
H^6	8.72 br.s	–
H^7	8.24 d ($^3J_{H^8H}$ 78.2)	H^8
H^8	7.65 br.d.d ($^3J_{H^7H^8}$ 8.2, $^3J_{H^9H}$ 87.0)	H^7, H^9
H^9	7.69 br.d.d ($^3J_{H^{10}H^9}$ 8.2, $^3J_{H^8H^9}$ 7.0)	H^8, H^{10}
H^{10}	7.89 br.d ($^3J_{H^8H^{10}}$ 8.2)	H^9
H^{11}	7.39 br.s	H^m
H^o	7.80 br.d.d ($^3J_{PCCH^o}$ 12.6, $^3J_{H^mH^o}$ 8.0)	H^m
H^m	7.51 m	H^o, H^p
H^p	7.71 br.t ($^3J_{H^mH^p}$ 7.2)	H^m

Atom	δ_C, ppm (*H*, Hz) (in parentheses, signal shape in ^{13}C–{^{1}H} NMR spectrum	Cross peaks in 2D HSQ	Cross peaks in 2D HMBC
C^3	80.07 d.d (d) ($^1J_{PC^3}$ 94.8, $^1J_{HC^3}$ 151.1)	H^3	–
C^5	164.93 d.d.d (s) ($^3J_{HC^3OC^5}$ 5.3, $^3J_{HC^6CC^5}$ 3.7, $^4J_{HC^{11}CCC^5}$ 1.7)	–	H^3, H^6, H^{11}
C^{5a}	120.84 br.d (s) ($^3J_{HC^{11}CC^{5a}}$ 6.0)	–	H^6, H^{11}
C^6	136.40 d.d (s) ($^1J_{HC^6}$ 166.6, $^3J_{HC^7CC^6}$ 5.0)	H^6	H^7
C^{6a}	130.97 d.d.d (s) ($^3J_{HC^8CC^{6a}}$ 8.4–8.6, $^3J_{HC^{10}CC^{6a}}$ 8.4–8.6, $^3J_{HC^{11}CC^{6a}}$ 8.4–8.6)	–	H^8, H^{10}, H^{11}
C^7	129.66 br.d.d.d (s) ($^1J_{HC^7}$ 162.8, $^3J_{HC^9CC^7}$ 8.3–8.4, $^3J_{HC^6CC^7}$ 5.7)	H^7	H^6, H^9
C^8	127.61 d.d (s) ($^1J_{HC^8}$ 163.4, $^3J_{HC^{10}CC^8}$ 8.1)	H^8	H^{10}
C^9	130.37 d.d (s) ($^1J_{HC^9}$ 162.1, $^3J_{HC^7CC^9}$ 8.4)	H^9	$H^{7'}$
C^{10}	127.92 br.d.d.d (s) ($^1J_{HC^{10}}$ 162.6, $^3J_{HC^8CC^{10}}$ 7.6–7.7, $^3J_{HC^{11}CC^{10}}$ 5.0)	H^{10}	H^8, $H^{11'}$
C^{10a}	136.24 br.d.d.d (s) ($^3J_{HC^9CC^{10a}}$ 6.8–7.1, $^3J_{HC^7CC^{10a}}$ 6.8–7.1, $^3J_{HC^6CC^{10a}}$ 6.8–7.1)	–	H^6, H^7, $H^{9'}$
C^{11}	120.16 d.d.d (d) ($^1J_{HC^{11}}$ 164.7, $^3J_{POCC^{11}}$ *4.5,* $^3J_{HC^{10}CC^{11}}$ 4.5)	H^{11}	$H^{10'}$
C^{11a}	143.85 d.d.d (d) ($^3J_{HC^6CC^{11a}}$ 9.9–10.0, $^2J_{POC^{11a}}$ 9.6, $^2J_{HC^{11}C^{11a}}$ 5.0)	–	H^6, $H^{11'}$
C^i	128.04 br.d.t (d) ($^1J_{PC^i}$ *130.9,* $^3J_{HC^mCC^i}$ *7.7)*	–	$H^{m'}$
C^o	132.17 br.d.d.d.d (d) ($^3J_{HC^o}$ 163.8, $^2J_{PCC^o}$ 10.4, $^3J_{HC^{o'}CC^o}$ 7.2, $^3J_{HC^pCC^o}$ 7.2)	H^o	$H^{o'}$, $H^{p'}$
C^m	129.12 d.d.d.d (d) ($^1J_{HC^m}$ 163.4, $^3J_{PCCC^m}$ 15.0, $^3J_{HC^{m'}CC^m}$ 7.2, $^2J_{HCC^m}$ 1.5)	H^m	$H^{m'}$
C^p	134.62 d.t.d (d) ($^2J_{HC^p}$ 161.3, $^3J_{HC^oCC^p}$ 7.5, $^4J_{PCCCC^p}$ 2.7)	H^p	H^o
CCl	94.38 d.d (d) ($^2J_{PC^3C}$ 6.6, $^2J_{HC^3C}$ 6.5)	–	H^3

scanning; the scanning rate was varied within 1–16.4 deg min^{-1} for θ; no decrease in the intensity of reference reflections was observed. The structures were decoded by the direct method using the SIR program [23] and refined first in the isotropic and then in the anisotropic approximation using the MoLEN program package [24]. The coordinates of hydrogen atoms were refined isotropically for **IV** and **VIII**, and for **IX** they were calculated with fixed positional and thermal parameters. Analysis of intermolecular contacts, including hydrogen bonds, in crystals was carried out using PLATON program [24]. The unit cell parameters, details of experiments, and results of structure refinement are given in Table 5.

Synthesis of hydroxynaphthoic acid bis(*O*-trimethylsilyl) derivatives. To a solution of 0.054 mol of appropriate hydroxynaphthoic acid in 20 ml of benzene at 18–20°C, 15 ml of triethylamine and 0.14 mol of trimethylchlorosilane (2.5-fold excess) were added. The reaction mixture was heated for 8 h at 80°C, cooled, and the precipitate of triethylammonium chloride was filtered off. The solvent was removed in a vacuum (50 mm Hg). The residue, a

Table 5. Unit cell parameters, experimental details, and results of structure refinement for **V, VIII, and IX**

Parameter	V	VIII	IX
Color, habit	Yellow, prismatic		Colorless, prismatic
Formula	$C_{15}H_9F_6O_5P$	$C_{14}H_8F_6O_3$	$C_{14}H_{10}Cl_3O_5P$
Molecular weight	414.20	338.21	395.57
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$		$P2_1/n$
Unit cell parameters, Å	a 13.270(2)	a 6.966(7)	a 9.691(1)
	b 8.246(2)	b 19.010(5)	b 19.346(4)
	c 15.199(5)	c 9.846(2)	c 9.690(2)
	β 107.22(1)°	β 91.20(6)°	β 113.70(2)°
V, Å^3	1588.6	1303.57	1663.45
Z	4	4	4
d, g cm^{-3} (calc)	1.73	1.72	1.58
Absorption coefficient, cm^{-1}	0.258	1.167	6.231
F(000)	832	680	800
Radiation (λ, Å)	MoK_α, λ 0.71073		CuK_α, λ 1.53184
Range of θ	θ ≤ 24.66	θ ≤ 22.76	θ ≤ 73.83
Range of Miller indices	–15 ≤ h ≤ 11,	–7 ≤ h ≤ 6,	–12 ≤ h ≤ 0,
	0 ≤ k 9,	–20 ≤ k 18,	0 ≤ k 24,
	–17 ≤ l 16	–10 ≤ l 10	–16 ≤ l ≤ 11
Number of measured reflections	3862	4462	3139
Number of observed unique reflections with $I > 3\sigma(I)$	1693	1384	1703
Absorption corrections	None		Empirical 0
Final divergence factors	R 0.036,	R 0.043,	R 0.065,
	R_W 0.044	R_W 0.045	R_W 0.073
Fit parameters	1.291	1.276	2.107
Number of refined parameters	237	793	335
	280	240	208

viscous colorless oil consisting of bis(*O*-trimethylsilyl) derivative of the corresponding hydroxynaphthoic acid, was dried in a vacuum (0.1 mm Hg) and used without additional purification. 2-Trimethylsiloxycarbonyl-3-trimethylsiloxynaphthalene, yield 98%; 2-trimethylsiloxycarbonyl-1-trimethylsiloxynaphthalene, yield 96%.

Synthesis of 2-methoxynaphtho[2,3-*d*]-1,3,2-dioxaphosphorin-4-one I. To 2.15 g of di-(*O*-trimethylsilyl) derivative of 2-hydroxy-3-naphthoic acid, 9.1 g of methyl phosphorodichloridite was added dropwise in an argon flow. The reaction mixture slightly warmed up (to 25–30°C). The resulting mixture was kept for 30 min at 20°C and then at 50–60°C in a vacuum (100 mm Hg) to completely distill off trimethylchlorosilane (30–40 min). A bright yellow viscous oil consisting of compound **I** was obtained; it was used without additional purification (δ_P 124.5 ppm). Found, %: C 53.19; H 4.27; P 14.03. $C_{12}H_9O_4P$. Calculated, %: C 53.57; H 4.02; P 13.84.

2-Phenylnaphtho[2,3-*d*]-1,3,2-dioxaphosphorin-4-one **II** (δ_P 158.4 ppm) and 2-ethoxynaphtho[1,2-*d*]-1,3,2-dioxaphosphorin-4-one **III** (δ_P 124.8 ppm), light brown viscous oils, were prepared similarly. Consistent analytical data were obtained.

2-Methoxy-2,5-dioxo-4,4-bis(trifluoromethyl)-naphtho[2,3-*d*]-1,3,2λ^5-dioxaphosphepin IV. Hexafluoroacetone (9 g) was passed through a solution of 12.82 g of phosphite **I** in 20 ml of anhydrous methylene chloride in an argon flow with cooling to –40°C (until the weight gain of the reaction mixture reached 9 g). Then the reaction mixture was allowed to stand for 6 h. The precipitate of dioxaphosphepin **IV** was filtered off and dried in a vacuum; yield 69%, mp 137–138°C. IR spectrum, ν, cm^{-1}: 1709 (C=O), 1645, 1602 ($C_{12}H_6$), 1570, 1500, 1354, 1340, 1315, 1290, 1278 (P=O), 1228, 1170, 1130, 1085, 1042, 1015, 988, 963, 930, 915, 892, 860, 800, 760, 722, 685, 615. ^{31}P NMR spectrum, δ_P, ppm ($CDCl_3$): –10.0 q ($^3J_{POCH}$ 12.0 Hz). ^{19}F NMR spectrum, δ_F,

ppm: –72.54 and –72.65 (A_3B_3 system, $^4J_{FF}$ 9.0 Hz). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 8.29 br (H^6), 7.96 d.m (H^7, $^3J_{H^8H^7}$ 8.3, $^4J_{H^9H^7}$ 1.3 Hz), 7.58 d.d.d (H^8, $^3J_{H^9H^8}$ 6.9, $^3J_{H^7H^8}$ 8.3, $^4J_{H^{10}H^8}$ 1.3 Hz), 7.68 d.d.d (H^9, $^3J_{H^8H^9}$ 6.9, $^3J_{H^{10}H^9}$ 8.3, $^4J_{H^7H^9}$ 1.3 Hz), 7.85 d.m (H^{10}, $^3J_{H^9H^{10}}$ 8.3, $^4J_{H^8H^{10}}$ 1.3 Hz), 7.66 br.d (H^{11}, $^4J_{POCCH}$11 2.1 Hz). ^{13}C NMR spectrum, δ_C, ppm (DMSO-d_6, 50°C) (here and hereinafter, the signal shape in the ^{13}C–{^{1}H} NMR spectrum is given in parentheses): 83.40 sept.d (sept.d) (C^4, $^2J_{FCC^4}$ 30.4, $^2J_{POC^2}$ 6.7 Hz), 186.13 br.d (s) (C^5, $^3J_{HC^6CC^5}$ 4.7 Hz), 126.87 br.d (br.s) (C^{5a}, $^3J_{HC^{11}CC^{5a}}$ 5.0 Hz), 134.39 d.d (s) (C^6, $^1J_{HC^6}$ 165.5, $^3J_{HC^7CC^6}$ 4.8 Hz), 130.61 d.d.d (s) (C^{6a}, $^3J_{HC^{11}CC^{6a}}$ 6.5–6.7, $^3J_{HC^{10}CC^{6a}}$ 6.5–6.7, $^3J_{HC^8CC^{6a}}$ 6.5–6.7 Hz), 129.59 d.d.d (s) (C^7, $^1J_{HC^7}$ 161.9, $^3J_{HC^9CC^7}$ 6.8–7.0, $^3J_{HC^6CC^7}$ 5.8–6.0 Hz), 127.46 d.d (s) (C^{10}, $^1J_{HC^{10}}$ 163.6, $^3J_{HC^{11}CC^{10}}$ 7.8–8.0, $^3J_{HC^8CC^{10}}$ 7.8–8.0 Hz), 136.64 br.d.d.d (s) (C^{10a}, $^3J_{HC^9CC^{10a}}$ 6.7–7.1, $^3J_{HC^7CC^{10a}}$ 6.7–7.1, $^3J_{HC^6CC^{10a}}$ 6.7–7.1 Hz), 118.83 d.d.d (d) (C^{11}, $^1J_{HC^{11}}$ 165.0, $^3J_{POCC^{11}}$ 7.6, $^3J_{HC^{10}CC^{11}}$ 4.6 Hz), 143.25 d.d.d (d) (C^{11a}, $^2J_{POC^{11a}}$ 7.5, $^3J_{HC^6CC^{11a}}$ 8.0, $^2J_{HC^{11}C^{11a}}$ 4.0 Hz), 56.54 q.d (d) (C^{12}, $^1J_{HC^{12}}$ 150.6, $^2J_{POC^{12}}$ 5.9 Hz), 119.81 br.q.d (br.q.d) (CF_3, $^1J_{FC^{13}}$ 285.8, $^3J_{POCC^{13}}$ 7.6 Hz). Mass spectrum, *m/z* (relative intensity, % max), ion: 414 (36.3), $[M]^{+\cdot}$ (here and in hereinafter, the peaks of ions containing the most abundant isotope are given, namely: ^{12}C, ^{1}H, ^{16}O, ^{14}N, ^{31}P, ^{35}Cl), 395 (4.6) $[M - F]^+$, 386 (30.6), 267 (5.4), 235 (21.8), 172 (36.7), 171 (16.7), 170 (100.1), 143 (10.6), 142 (84.9), 126 (3.1), 114 (45.3), 81 (17.6), 69 (27.4), 57 (14.4), 47 (2.2), 43 (12.9), 41 (11.1). Found, %: C 43.30; H 2.01. $C_{15}H_9F_6O_5P$. Calculated, %: C 43.48; H 2.17.

1-(2-Hydroxynaphth-1-yl)-2-hydroxy-2-trifluoromethyl-3,3,3-trifluoropropan-1-one V. A mixture of 5.65 g of dioxaphosphepin **V** and 30 ml of a 1 : 1 mixture of ethanol and water was heated for 6 h at 90–100°C. The cooled solution was extracted with ether (3 × 30 ml), and the extract was dried over $MgSO_4$ and concentrated in a vacuum (12 mm Hg). The residue (compound **V**) was a bright yellow oil; yield 70%. IR spectrum, ν, cm^{-1}: 3000–3400 v.br (OH), 1715–1740 (C=O), 1640, 1605 ($C=C_{arom}$), 1500, 1450–1470, 1390–1410, 1335, 1320, 1285, 1220–1250, 1170, 1155, 1130, 1095, 1046, 970, 680, 845, 790–810, 756, 690. ^{19}F NMR spectrum, δ_F, ppm: –74.62 (br.s). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm ($CDCl_3$): 119.30 d.d (s) (C^4, $^1J_{HC^4}$ 164.2, $^3J_{HC^5CC^4}$ 3.3 Hz), 167.18 br.d.d (s) (C^3, $^3J_{HC^1CC^3}$ 8.1, $^2J_{HC^4C^3}$ 2.6 Hz), 110.72 br.d (s) (C^2, $^3J_{HC^4CC^2}$ 9.6 Hz), 132.23 d.d (s) (C^1, $^1J_{HC^1}$ 161.5, $^3J_{HC^8CC^1}$ 8.4 Hz), 124.94 br.m (s) (C^{8a}, $^3J_{HCCC^{8a}}$ 5.5, $^3J_{HCCC^{8a}}$ 6.2, $^3J_{HCCC^{8a}}$ 7.0 Hz), 127.38 d.d.d (s) (C^8, $^1J_{HC^8}$ 161.9, $^3J_{HC^1CC^8}$ 5.2, $^3J_{HC^6CC^8}$ 6.0 Hz), 125.31 d.d (s) (C^7, $^1J_{HC^7}$ 164.4, $^3J_{HC^5CC^7}$ 6.3 Hz), 126.62 d.d (s) (C^6, $^1J_{HC^6}$ 162.4, $^3J_{HC^8CC^6}$ 6.7 Hz), 123.79 br.d.m (br.s) (C^5, $^1J_{HC^5}$ 164.2 Hz), 138.16 m (s) (C^{4a}), 189.35 br.d (s) (C^9, $^1J_{HC^1CC^9}$ 2.7 Hz), 81.75 sept (sept) (C^{10}, $^2J_{FCC^{10}}$ 31.0 Hz), 121.36 q (q) (CF_3, $^1J_{FC}$ 287.9 Hz).

2,3-Dihydro-3,3-bis(trifluoromethyl)naphtho-[2,3-*b*]furan-3-one VI. Naphthofuranone **VI** was obtained by high-temperature distillation of compound **V** (120°C, 0.02 mm Hg) in 67% yield as yellow crystals, mp 110°C. IR spectrum, KBr pellet, ν, cm^{-1}: 1979 w, 1919 w, 1863 w, 1756 s (C=O), 1636 s, 1615 m, 1591, 1510, 1465, 1391, 1348, 1284, 1232, 1179, 1154, 1133, 1094, 1063, 1018, 914, 905, 872, 837, 764, 746, 696, 657, 623, 606, 563, 550, 538, 521. ^{1}H NMR spectrum, δ, ppm (acetone-d_6): 8.69 br.s (H^4), 8.22 d.m (H^5, $^3J_{H^6H^5}$ 8.3–8.4, $^4J_{H^7H^5}$ 1.3 Hz), 7.62 d.d.d (H^6, $^3J_{H^7H^6}$ 6.9, $^3J_{H^5H^6}$ 8.3–8.4, $^4J_{H^8H^6}$ 1.3 Hz), 7.79 d.d.d (H^7, $^3J_{H^6H^7}$ 6.9, $^3J_{H^8H^7}$ 8.4, $^4J_{H^5H^7}$ 1.3 Hz), 8.05 d.m (H^8, $^3J_{H^7H^8}$ 8.4, $^4J_{H^6H^8}$ 1.3 Hz), 7.92 br.s (H^9). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 8.37 br.s (H^4), 7.94 d.m (H^5, $^3J_{H^6H^5}$ 8.4, $^4J_{H^7H^5}$ 1.3 Hz), 7.46 d.d.d (H^6, $^3J_{H^7H^6}$ 7.0, $^3J_{H^5H^6}$ 8.4, $^4J_{H^8H^6}$ 1.3 Hz), 7.63 d.d.d (H^7, $^3J_{H^6H^7}$ 7.0, $^3J_{H^8H^7}$ 8.4, $^4J_{H^5H^7}$ 1.3 Hz), 7.82 d.m (H^8, $^3J_{H^7H^8}$ 8.4, $^4J_{H^6H^8}$ 1.3 Hz), 7.57 br.s (H^9). ^{19}F NMR spectrum, δ_F, ppm: –75.18 (s) ($CDCl_3$), –73.63 br.s (acetone-d_6). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm ($CDCl_3$): 82.22 sept (sept) (C^2, $^2J_{FCC^2}$ 31.7 Hz), 185.74 br.d (s) (C^3, $^3J_{HC^4CC^3}$ 3.0 Hz), 118.66 d.d (s) (C^{3a}, $^3J_{HC^9CC^{3a}}$ 5.1, $^2J_{HC^4C^{3a}}$ 1.8 Hz), 131.17 d.d (s) (C^4, $^1J_{HC^4}$ 163.4, $^3J_{HC^5CC^4}$ 8.7 Hz), 130.20 m (s) (C^{4a}), 131.05 d.d.d (s) (C^5, $^1J_{HC^5}$ 161.1, $^3J_{HC^7CC^5}$ 7.2, $^3J_{HC^4CC^5}$ 5.5 Hz), 126.25 d.d (s) (C^6, $^1J_{HC^6}$ 163.0, $^3J_{HC^8CC^6}$ 8.5 Hz), 128.32 d.d (s) (C^7, $^1J_{HC^7}$ 166.8, $^3J_{HC^5CC^7}$ 4.8 Hz), 127.81 d.d.d (s) (C^8, $^1J_{HC^8}$ 163.4, $^3J_{HC^6CC^8}$ 6.3, $^3J_{HC^9CC^8}$ 5.1 Hz), 139.77 br.m (s) (C^{8a}, $^3J_{HCCC^{8a}}$ 6.8–7.0, $^3J_{HCCC^8}$ 6.8–7.0, $^3J_{HCCC^8}$ 7.4 Hz), 108.73 d.d (s) (C^9, $^1J_{HC^9}$ 166.7, $^3J_{HC^8CC^9}$ 4.7 Hz), 164.11 d.d (s) (C^{9a}, $^3J_{HC^4CC^{9a}}$ 8.8–9.0, $^2J_{HC^9C^{9a}}$ 3.8–3.9 Hz), 119.96 q.m (q.m) (CF_3, $^1J_{FC}$ 286.0, $^3J_{FCCC}$ 1.5 Hz). Mass spectrum, *m/z* (relative intensity, % max), ion: 320 (78.8)

$[M]^{+\cdot}$, 301 (5.8) $[M - F]^+$, 251 (30.1) $[M - CF_3]^+$, 201 (1.5), 154 (39.9), 126 (100.0), 63 (31.5). Found, %: C 52.30; H 2.01. $C_{14}H_6O_2P$. Calculated, %: C 52.50; H 1.88.

2-Ethoxy-2,5-dioxo-4,4-bis(trifluoromethyl)-naphtho[1,2-*d*]-1,3,2λ^5-dioxaphosphepin VII. Compound **VII** was prepared from hexafluoroacetone and phosphite **III** similarly to **IV**. Light brown viscous liquid, yield 95%. ^{31}P NMR spectrum, δ_P, ppm (CH_2Cl_2): 13.3 t ($^3J_{POCH}$ 9.2 Hz). ^{19}F NMR spectrum, δ_F, ppm: –72.10 and –72.34 (A_3B_3 system, $^4J_{FF}$ 9.3 Hz). ^{1}H NMR spectrum, δ, ppm (acetone-d_6): 1.68 t.d (CH_3, $^3J_{HH}$ 7.0, $^4J_{POCCH}$ 1.2 Hz), 4.75 d.q (OCH_2, $^3J_{POCH}$ 9.4, $^3J_{HH}$ 7.0 Hz), 8.03 d (H^6, $^3J_{H^7H^6}$ 9.2 Hz), 7.91–7.96 m (H^7, H^9, H^{10}), 8.15 br.d.d (H^8, $^3J_{H^7H^8}$ 7.0, $^4J_{H^{10}H^8}$ 2.1 Hz), 8.55 d.m (H^{11}, $^3J_{H^{10}H^{11}}$ 7.0, $^4J_{H^9H^{11}}$ 2.5 Hz). Found, %: C 45.20; H 2.41. $C_{16}H_{11}F_6O_5P$. Calculated, %: C 44.86; H 2.57.

1-(1-Hydroxynaphth-2-yl)-2-hydroxy-2-trifluoromethyl-3,3,3-trifluoropropan-1-one VIII. Hydrolysis of 1,3,2λ^5-dioxaphosphepin **VII** was carried out in an acid medium (H_2O, C_2H_5OH, HCl, 1 : 1 : 0.3) similarly to the hydrolysis of **IV**. Naphthyl ketone **VIII** as yellow crystals was obtained in 76% yield, mp 82–86°C. IR spectrum, ν, cm^{-1}: 3360 (OH), 1640 (C=O), 1610, 1580, 1550, 1510, 1422, 1320, 1280, 1240, 1220, 1170, 1165, 1120, 1080, 1035, 970, 945, 890, 820, 800, 770, 755, 722, 701, 652, 637, 605, 580, 550, 535. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 8.02 (H^3, *B* part of *ABX* system, $^3J_{H^4H^3}$ 8.2 Hz), 7.99 m (H^4, *A* part of *ABX* system, $^3J_{H^3H^4}$ 8.2, $^4J_{H^5H^4}$ 1.2 Hz), 8.79 d.m (H^5, $^3J_{H^6H^5}$ 8.4, $^4J_{H^4H^5}$ 1.2, $^4J_{H^7H^5}$ 1.2, $^5J_{H^8H^5}$ 1.0 Hz), 7.85 d.d.d (H^6, $^3J_{H^5H^6}$ 8.4, $^3J_{H^7H^6}$ 6.0, $^4J_{H^8H^6}$ 2.1 Hz), 8.02 m (H^7, $^3J_{H^6H^7}$ 6.0 Hz), 8.34 br.d (H^8, $^3J_{H^7H^8}$ 8.6–9.0 Hz), 5.85 br.s (OH), 13.60 br.s (OH). ^{19}F NMR spectrum, δ_F, ppm: –75.89 br.s. ^{13}C NMR spectrum, δ_C, ppm ($CDCl_3$): 166.89 m (s) (C^1, $^3J_{H^3CC^1}$ 7.9-8.0, $^3J_{HC^8CC^1}$ 3.7–3.8 Hz), 110.35 d.d (s) (C^2, $^3J_{HC^4CC^2}$ 8.8, $^3J_{H^3C^2}$ 1.7 Hz), 123.43 br.d.m (br.m) (C^3, $^1J_{HC^3}$ 164.5 Hz), 137.84 m (s) (C^{4a}), 127.07 d.d.d (s) (C^5, $^1J_{HC^5}$ 161.3, $^3J_{HC^7CC^5}$ 7.0, $^1J_{HC^4CC^5}$ 5.3 Hz), 126.32 d.d (s) (C^6, $^1J_{HC^6}$ 161.5, $^3J_{HC^8CC^6}$ 7.0, $^2J_{HCC^6}$ 1.1 Hz), 125.00 d.d (s) (C^7, $^1J_{HC^7}$ 164.8, $^3J_{HC^5CC^7}$ 5.6, $^2J_{HCC^7}$ 1.5 Hz), 131.94 d.d (s) (C^8, $^1J_{HC^8}$ 161.2, $^3J_{HC^6CC^8}$ 8.8 Hz), 122.42 d.d.d (s) (C^{8a}, $^3J_{HCCC^{8a}}$ 7.7–8.0, $^3J_{HCCC^{8a}}$ 6.2–6.3, $^3J_{HCCC^{8a}}$ 6.2–6.3 Hz), 188.92 br.m (br.s) (C^9), 81.39 sept (sept) (C^{10}, $^2J_{FCC^{10}}$ 31.2 Hz), 121.03 br.q.q (br.q.q) (CF_3, $^1J_{FC}$ 287.5, $^3J_{FCCC}$ 2.3 Hz). Mass spectrum, *m/z* (relative intensity, % max), ion: 338 (78.8) $[M]^{+\cdot}$, 277 (1.5), 249 (3.2), 216 (1.8), 171 (100.0), 144 (30.1), 143 (25.2), 115 (50.9), 69 (11.7). Found, %: C 45.20; H 2.41. $C_{14}H_8F_6O_3$. Calculated, %: C 49.70; H 2.37.

2-Methoxy-2,5-dioxo-3-(trichloromethyl)naphtho[2,3-*e*]-1,4,2λ^5-dioxaphosphepin IX. A mixture of 6.97 g of phosphite **I** and 4.43 g of chloral in 10 ml of methylene chloride was allowed to stand for 2 months. The crystals formed were filtered off, washed with ether, and dried in a vacuum to obtain 78% of compound **IX**, mp 192–194°C. IR spectrum, ν, cm^{-1}: 1759, 1640, 1605, 1509, 1345, 1303, 1290, 1255, 1240, 1201, 1170, 1145, 1095, 1042, 962, 942, 900, 860, 821, 785, 775, 750, 720, 650, 615, 590, 542, 485, 442. ^{31}P–{^{1}H} NMR spectrum, δ_P, ppm ($CDCl_3$): 13.0 (s). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 4.08 d.d (OCH_3, $^3J_{POCH}$ 11.4 Hz), 5.78 d (H^3, $^2J_{PCH}$ 5.9 Hz), 8.54 br.s (H^6), 8.17 br.d (H^7, $^3J_{H^8H^7}$ 8.2 Hz), 7.77 d.d.d (H^8, $^3J_{H^7H^8}$ 8.2, $^3J_{H^9H^8}$ 7.0, $^4J_{H^{10}H^8}$ 1.2 Hz), 7.68 br.d.d.d (H^9, $^3J_{H^{10}H^9}$ 8.2, $^3J_{H^8H^9}$ 7.0, $^4J_{H^7H^9}$ 1.0 Hz), 8.05 br.d.m (H^{10}, $^3J_{H^9H^{10}}$ 8.2 Hz), 7.99 br.d (H^{11}, $^4J_{POCCH^{11}}$ 2.2 Hz). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm (DMSO-d_6, 50°C): 80.04 d.d (d) (C^3, $^1J_{PC^3}$ 159.1, $^1J_{HC^3}$ 152.0 Hz), 164.16 d.d (s) (C^5, $^3J_{HC^3OC^5}$ 3.7, $^3J_{HC^6CC^5}$ 3.7 Hz), 120.45 br.d (s) (C^{5a}, $^3J_{HC^{11}CC^{5a}}$ 5.0 Hz), 135.32 br.d.d (s) (C^6, $^1J_{HC^6}$ 165.5, $^3J_{HC^7CC^6}$ 4.5 Hz), 130.75 br.m (s) (C^{6a}) 130.03 br.d.d (s) (C^9, $^1J_{HC^9}$ 160.0, $^3J_{HC^7CC^9}$ 8.7 Hz), 127.42 br.d.d (s) (C^8, $^1J_{HC^8}$ 162.7, $^3J_{HC^{10}CC^8}$ 7.5 Hz), 129.29 br.d.m (s) (C^7, $^1J_{HC^7}$ 161.4, $^3J_{HC^9CC^7}$ 8.1 Hz), 127.60 br.d.d.d (s) (C^{10}, $^1J_{HC^{10}}$ 162.2, $^3J_{HC^8CC^{10}}$ 7.2, $^3J_{HC^{11}CC^{10}}$ 4.2 Hz), 136.17 m (s) (C^{10a}), 119.71 br.d.m (d) (C^{11}, $^1J_{HC^{11}}$ 161.3, $^3J_{POCC^{11}}$ 4.1, $^3J_{HC^{10}CC^{11}}$ 4.7 Hz), 143.26 d.d.d (d) (C^{11a}, $^2J_{POC^{11a}}$ 9.5, $^3J_{HC^6CC^{11a}}$ 10.0, $^2J_{HC^{11}C^{11a}}$ 4.5 Hz), 93.54 d.d (d) (CCl_3, $^2J_{PCC}$ 7.9, $^2J_{HC^3C}$ 5.6 Hz), 54.45 q.d (d) (CH_3, $^1J_{HC}$ 151.0, $^2J_{POC}$ 7.5 Hz). Mass spectrum, *m/z* (relative intensity, % max), ion: 398 (4.8), 396 (13.7), 198 (14.4) $[M]^{+\cdot}$, 359 (4.1) $[M - Cl]^+$, 277 (6.5) $[M - CCl_3]^+$, 248 (30.2), 217 (7.5), 171 (54.8), 170 (100.0), 143 (12.1), 142 (76.3), 97 (26.8), 69 (25.3), 57 (27.5), 47 (6.3), 43 (35.0), 41 (12.1). Found, %: C 42.30; H 2.21. $C_{14}H_{10}Cl_3O_5P$. Calculated, %: C 42.48; H 2.53.

2-Phenyl-2,5-dioxo-3-(trichloromethyl)naphtho-[2,3-*e*]-1,4,2λ^5-dioxaphosphepin X. To a solution of 7.93 g of dioxaphosphorin-4-one **II** in 10 ml of methylene chloride, 3.97 g of chloral was added. The reaction mixture slightly warmed up, compound **X**

partially precipitated. The reaction mixture was allowed to stand for 2 days, and the precipitate was filtered off, washed with ether, and dried in a vacuum (12 mm Hg). Yield of phosphepin **X** 85%, mp 192–193°C. $^{31}P-\{^1H\}$ NMR spectrum, δ_P, ppm (DMSO): 31.5 (s). IR spectrum, ν, cm^{-1}: 1740 (C=O), 1641, 1602, 1562, 1505, 1415, 1380, 1275 sh, 1260, 1235, 1205, 1170, 1145, 1122, 1075, 1060, 970, 932, 910, 893, 875, 842, 810, 772, 755, 732, 697. Found, %: C 51.30; H 2.21. $C_{19}H_{12}Cl_3O_4P$. Calculated, %: C 51.64; H 2.72.

X-ray diffraction data for compounds **IV**, **VIII**, and **IX** are deposited in Cambridge Structural Database, CCDC nos. 616981–616983, respectively.

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