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Benzaldehyde *N*,*N*-Dimethylhydrazone in the Reaction with 4-Oxo-2-pentafluorophenoxy-5,6-benzo-1,3,2-dioxaphosphorinane. Preparation and Spatial Structure of 4-Dimethylamino-2,5-dioxo-2-pentafluorophenoxy-3-phenyldihydro-6,7-benzo-1,4,2-oxazaphosphepine

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Abstract — Benzaldehyde *N*,*N*-dimethylhydrazone with 4-oxo-2-pentafluorophenoxy-5,6-benzo-1,3,2-dioxaphosphorinane is capable to yield with high stereoselectivity a product of the phosphorus heterocycle expansion: unstable to hydrolysis 4-dimethylamino-2,5-dioxo-2-pentafluorophenoxy-3-phenyldihydro-6,7-benzo-1,4,2-oxazaphosphepine. The configuration of the prevailing isomer of the latter was determined by X-ray diffraction study.

Reactions of 2-R-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinanes (mixed cyclic anhydrides of salicylic and phosphorous acids, or salicyl phosphites) with compounds containing activated heteroatomic multiple bonds is a promising approach to preparation of functionally-substituted seven-membered heterocycles, 6,7-benzo-1,3,2- and 6,7-benzo-1,4,2-diheterophosphepines. Actually, as we demonstrated before, the reaction of salicyl phosphites with activated ketones and aldehydes, and also with *N*-methylbenzalimine occurred with high regio and stereoselectivity affording in fairly good yields the corresponding phosphepine derivatives [1–8]. It seemed promising to extend this approach to the other types compounds containing C=N bonds, e.g. hydrazones. The compounds possess an electrophilic site, the carbon atom of the C=N bond, and two nucleophilic sites, amine and imine nitrogen atoms. Therefore they are capable to behave as electrophile or nucleophile toward the salicyl phosphites. It should be noted that depending on the character of the substituents attached to the carbon and the amine nitrogen the order of basicity and consequently of nucleophilicity of the nitrogens in the hydrazone moiety can vary [9]. We showed formerly that the *N*-methylbenzalimine unlike benzaldehyde that contained a more polarized multiple bond readily reacted with the salicyl phosphites possessing an exocyclic acceptor substituent at the phosphorus atom. The salicyl phosphites with a donor substituent at the phosphorus atom did not react with the *N*-methylbenzalimine under similar conditions [8]. Basing on these fact it was presumed that occurred a nucleophilic attack of imine on the electrophilic carbon in the salicyl phosphite.

In order to test the presumable capability of the imine bond in hydrazones to insert into a dioxaphosphorinane ring we studied for the first time the reaction of 2-methoxy-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (**Ia**) and 4-oxo-2-pentafluorophenoxy-5,6-benzo-1,3,2-dioxaphosphorinane (**Ib**) with the easily available benzaldehyde *N*,*N*-dimethylhydrazone (**II**) which did not contain any N–H bonds that also could cleave the anhydride fragment P^{III}–O–C(O) (preliminary communication see [10]).

Phosphite **Ia** does not show any signs of reacting with hydrazone **II** at least within 6 months, whereas compound **Ib** in this period reacts with hydrazone **II** in dichloromethane solution to afford lemon-yellow adduct of 1 : 1 composition giving a signal in the ^{31}P NMR spectrum at δ_P 22.3 ppm corresponding to a phosphonate structure. In the ^{31}P NMR spectrum of the filtrate after separation of the precipitate alongside the signal at δ_P 22.3 ppm is observed also a weak peak at δ_P 21.9 ppm that we believe to belong to the second stereoisomer. This isomer was not isolated for its quantity was too small. A similar pattern of the process was observed in the reaction of fluoroalkoxy-

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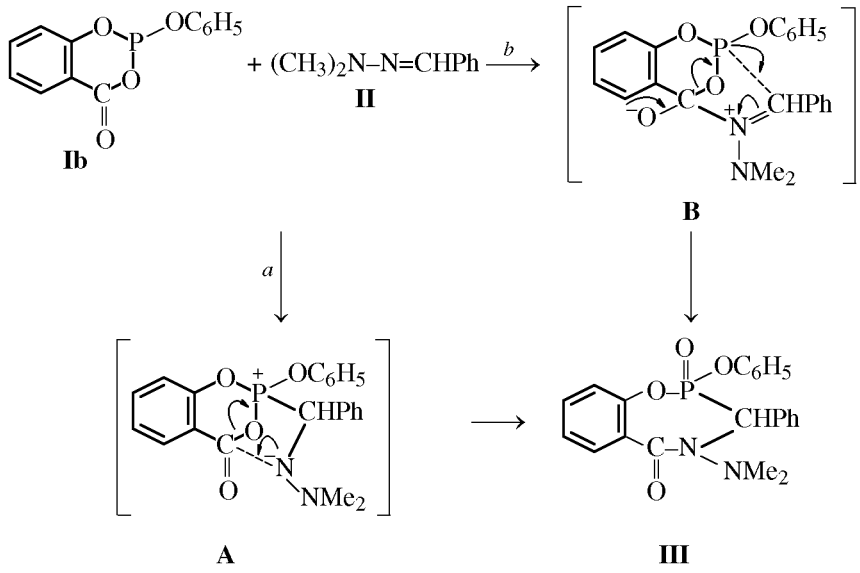
salicyl phosphites with *N*-methylbenzalimine [8]. In the IR spectrum of the crystalline product is present a strong absorption band at 1662 cm^{-1} belonging to the amide carbonyl group. In the ^1H NMR spectrum of the major isomer appears a proton signal (δ 5.85 ppm, d, $^2J_{PCH}$ 10.9 Hz) indicating the presence of a fragment P(O)–CH–N. In keeping with these findings the structure of 4-dimethylamino-2,5-dioxo-2-pentafluorophenoxy-3-phenyldihydro-6,7-benzo-1,4,2-oxazaphosphepine (**III**) was assigned to the product. Thus it may be concluded that the reaction of compounds **Ib** and **II** occurs with high regio and stereoselectivity ensuring the prevailing formation of 1,4,2-oxazaphosphepine **III**.

Taking into account the features of the electronic structure of the original hydrazone **II**, its notably lower reactivity toward phosphite **Ib** as compared to *N*-methylbenzalimine [8], and the data on the effect of the substituent character in the phosphorus fragment, of the two possible routes of phosphepine **III** formation (*a*, *b*) the second one should be preferred. The first path assumes primary attack of phosphorus atom on the multiple bond N=C (route *a*) resulting in bipolar ion **A**; the subsequent intramolecular attack of the *N*-anion within the structure **A** on the carbon atom of the carbonyl group affords the final product **III**. Alternative path presumes a nucleophilic attack of imine nitrogen of compound **II** on the carbon of the carbonyl group in phosphite **Ib** (route *b*) providing an intermediate **B** with tetrahedral carbon atom stabilized by formation of a P–C bond, of phosphoryl and carbonyl groups.



It is also interesting that in the reaction of alkylsalicyl phosphites with hexafluoroacetonimine whose reactive center is activated by acceptor substituents [11] the phosphites behave as nucleophiles, and salicyl phosphite **Ia** reacts notably faster than analogous fluoroalkyl-containing salicyl phosphites. In the reaction with hydrazone **II** the higher reactivity of pentafluorophenyl phosphite Ib than that of methyl phosphite **Ia** is more likely to correspond to the nucleophilic attack of hydrazone on the carbonyl group of phosphite **Ib**, i.e. route *b*. It should be also noted that the tertiary amines do not form acylium salts with salicyl phosphites (usually in the synthesis of the latter is applied an excess triethylamine). Therefore one more reaction pathway assuming primary nucleophilic attack of amine nitrogen from hydrazone **II** on the carbonyl group in the phosphite is hardly probable. The pathway *b* with the primary attack of the imine nitrogen is also thermodynamically favorable since it results in formation of the most feasible reaction product, phosphonate **III**.

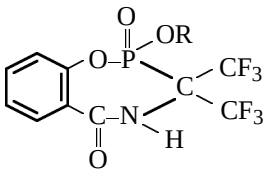
The configuration of the isolated prevailing diastereomer of phosphepine **III** was established by means of X-ray diffraction analysis. In Tables 1–4 are given the main geometrical parameters, and on Fig. 1 is presented the spatial structure of the molecule of phosphepine **III** in a crystal.

Table 1. Coordinates of atoms in the structure of phosphepine **III**, equivalent isotropic temperature factors of nonhydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i, j)$ (Å^2), and isotropic temperature factors of hydrogen atoms B_{iso} (Å^2)

Atom	*x*	*y*	*z*	*B* or B_{iso}	Atom	*x*	*y*	*z*	*B* or B_{iso}
P^2	0.2378	0.16779(5)	0.0884	3.74(1)	C^{17}	0.0913(6)	0.1513(2)	0.2705(2)	4.76(8)
F^{13}	0.0267(5)	0.3000(1)	0.1604(1)	7.23(6)	C^{18}	0.5114(6)	0.0588(2)	0.1247(2)	3.79(6)
F^{14}	–0.3138(5)	0.3113(1)	0.2406(2)	8.31(7)	C^{19}	0.3371(6)	0.0180(2)	0.1326(2)	5.07(8)
F^{15}	–0.3888(4)	0.2164(2)	0.3398(2)	8.26(7)	C^{20}	0.3783(8)	–0.0372(2)	0.1811(2)	6.21(9)
F^{16}	–0.1251(5)	0.1099(2)	0.3591(2)	8.24(7)	C^{21}	0.5838(9)	–0.0493(2)	0.2208(2)	6.3(1)
F^{17}	0.2202(5)	0.0988(1)	0.2802(1)	6.85(6)	C^{22}	0.7559(8)	–0.0091(2)	0.2113(3)	6.8(1)
O^1	0.2560(4)	0.2299(1)	0.0367(1)	4.48(5)	C^{23}	0.7184(7)	0.0451(2)	0.1643(2)	5.05(8)
O^2	0.0196(4)	0.1391(1)	0.0709(1)	4.66(5)	C^{25}	0.1885(9)	0.0558(3)	–0.0953(3)	7.7(1)
O^5	0.5537(5)	0.1446(1)	–0.1220(1)	5.51(6)	C^{26}	0.560(1)	0.0074(2)	–0.0572(3)	7.3(1)
O^{12}	0.2975(4)	0.1933(1)	0.1766(1)	4.42(5)	H^3	0.595(4)	0.149(2)	0.088(2)	3.2(6)
N^4	0.4680(4)	0.1106(1)	–0.0080(1)	3.71(5)	H^8	0.408(4)	0.342(1)	0.062(2)	3.0(6)
N^{24}	0.3851(5)	0.0489(1)	–0.0359(2)	4.92(7)	H^9	0.718(7)	0.391(2)	0.031(3)	7(1)
C^3	0.4794(5)	0.1208(2)	0.0761(2)	3.44(6)	H^{10}	0.953(8)	0.338(3)	–0.042(3)	9(1)
C^5	0.5353(6)	0.1565(2)	–0.0554(2)	4.03(7)	H^{11}	0.857(5)	0.219(2)	–0.076(2)	4.6(7)
C^6	0.5839(6)	0.2239(2)	–0.0233(2)	3.84(6)	H^{19}	0.192(5)	0.030(2)	0.105(2)	4.0(7)
C^7	0.4517(5)	0.2578(2)	0.0198(2)	4.02(7)	H^{20}	0.262(7)	–0.057(2)	0.194(2)	7(1)
C^8	0.4950(7)	0.3220(2)	0.0413(2)	5.37(9)	H^{21}	0.58(1)	–0.092(3)	0.256(3)	11(2)
C^9	0.6759(7)	0.3530(2)	0.0190(3)	6.3(1)	H^{22}	0.926(9)	–0.024(3)	0.247(3)	11(2)
C^{10}	0.8081(7)	0.3203(2)	–0.0243(2)	5.50(9)	H^{23}	0.840(9)	0.060(3)	0.155(3)	10(1)
C^{11}	0.7635(6)	0.2572(2)	–0.0454(2)	4.55(7)	H^{251}	0.124(7)	0.013(2)	–0.105(3)	7(1)
C^{12}	0.1278(6)	0.1996(2)	0.2193(2)	4.14(7)	H^{252}	0.206(8)	0.097(3)	–0.137(3)	10(1)
C^{13}	–0.0075(6)	0.2532(2)	0.2101(2)	4.87(8)	H^{253}	0.04(1)	0.071(3)	–0.073(3)	11(2)
C^{14}	–0.1820(7)	0.2593(2)	0.2506(2)	5.72(9)	H^{261}	0.502(6)	–0.037(2)	–0.065(2)	6.0(9)
C^{15}	–0.2179(6)	0.2112(2)	0.3005(2)	5.41(9)	H^{262}	0.618(7)	0.031(2)	–0.105(3)	8(1)
C^{16}	–0.0844(7)	0.1573(2)	0.3108(2)	5.48(9)	H^{263}	0.68(1)	–0.013(4)	–0.003(4)	13(2)

As seen from Fig. 1 in the molecule of the isolated diastereomer of phosphepine **III** the phenyl and pentafluorophenoxy groups are located in trans-position with respect to P–C bond [configuration S_PS_C (R_PR_C)].

The conformation of the seven-membered heterocycle in molecule **III** is the distorted (asymmetrical) *boat*, similar to that in the related structures previously studied by us: 2-RO-2,5-dioxo-3,3-bis(trifluoromethyl)-1,2-dihydro-6,7-benzo-1,4,2-oxazaphosphepines (**IV, V**).



IV, V

R = Me (**IV**), $CH_2CF_2CHF_2$ (**V**).

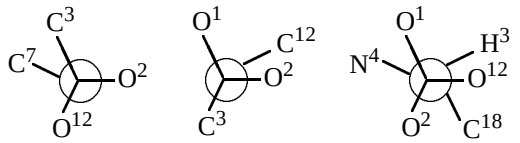
Conformation of the seven-membered heterocycle in these molecules is determined mainly by the presence in the heterocyclic part of a planar fragment $O^1C^7C^6C^5$ fused with benzene substituent [the corresponding torsion angle is equal to 0.0(6)°]. The other atoms of the heterocycle in phosphepine **III** molecule deviate from this plane [P^2 by –1.1537(3), C^3 by –1.925(3) and N^4 by –0.851(2) Å] to the same side but by different distances. Thus arises a conformation of distorted *boat*. The phosphoryl group and the phenyl substituent at C^3 atom take a pseudoequatorial position, and aryloxy group and dimethylamino group attached to N^4 atom are in pseudoaxial position. Analogous pseudoaxial position of an alkoxy substituent due to anomeric effect is also observed in the molecules we have previously studied: in 3-methyl-2,5-dioxo-2-(2,2,3,3-tetrafluoropropoxy)-3-trifluoromethyl-6,7-benzo-1,4,2-dioxaphosphepine [6] and in 2-methoxy-2,5-dioxo-3-trichloromethyl-6,7-benzo-1,4,2-dioxaphosphepine [7] whereas in oxazaphos-

Table 2. Bond lengths (*d*, Å) in the structure of phosphepine **III**

Bond	*d*	Bond	*d*
P^2–O^1	1.574(2)	C^7–C^8	1.377(5)
P^2–O^2	1.443(2)	C^8–C^9	1.384(6)
P^2–O^{12}	1.618(2)	C^8–H^8	0.80(3)
P^2–C^3	1.801(3)	C^9–C^{10}	1.368(6)
F^{13}–C^{13}	1.333(5)	C^9–H^9	0.83(5)
F^{14}–C^{14}	1.328(5)	C^{10}–C^{11}	1.357(5)
F^{15}–C^{15}	1.343(5)	C^{10}–H^{10}	1.05(5)
F^{16}–C^{16}	1.335(5)	C^{11}–H^{11}	1.14(3)
F^{17}–C^{17}	1.326(5)	C^{12}–C^{13}	1.365(5)
O^1–C^7	1.398(4)	C^{12}–C^{17}	1.375(5)
O^5–C^5	1.217(4)	C^{13}–C^{14}	1.376(6)
O^{12}–C^{12}	1.378(4)	C^{14}–C^{15}	1.358(6)
N^4–N^{24}	1.416(4)	C^{15}–C^{16}	1.364(6)
N^4–C^3	1.481(4)	C^{16}–C^{17}	1.381(6)
N^4–C^5	1.359(4)	C^{18}–C^{19}	1.376(5)
N^{24}–C^{25}	1.465(5)	C^{18}–C^{23}	1.370(5)
N^{24}–C^{26}	1.455(6)	C^{19}–C^{20}	1.412(5)
C^3–C^{18}	1.522(4)	C^{19}–H^{19}	0.97(3)
C^3–H^3	0.92(3)	C^{20}–C^{21}	1.356(6)
C^5–C^6	1.498(5)	C^{20}–H^{20}	0.87(4)
C^6–C^7	1.378(5)	C^{21}–C^{22}	1.364(7)
C^6–C^{11}	1.397(5)	C^{21}–H^{21}	1.07(6)
C^{22}–C^{23}	1.378(6)	C^{25}–H^{253}	1.08(7)
C^{22}–H^{22}	1.17(5)	C^{26}–H^{261}	0.97(4)
C^{23}–H^{23}	0.84(6)	C^{26}–H^{262}	1.07(5)
C^{25}–H^{251}	0.96(4)	C^{26}–H^{263}	1.18(6)
C^{25}–H^{252}	1.14(6)		

phenes **IV**, **V** the alkoxy substituents are in pseudo-equatorial position because of steric hindrances from two trifluoromethyl groups in position 3.

The phosphorus atom in molecule **III** has a common distorted tetrahedral coordination (Table 3); conformation along the bonds P^2–O^1, P^2–O^{12}, and P^2–C^3 is shown below on the Newman projections.



P^2–O^1 P^2–O^{12} P^2–C^3

Therewith the conformation along the endocyclic P–O bond is favorable for hyperconjugation interaction of the lone pair of O^1 atom with the antibonding orbital of the exocyclic P^2–O^{12} bond (anomeric effect). Presumably the observed elongation of the exocyclic P–O bond compared to the endocyclic one [1.618(2) and 1.574(2) Å respectively] is due to this interaction. As it is also observed the increase in the bond angle $O^1P^2O^{12}$ [105.4(1)°] compared to angles $O^1P^2C^3$ and $O^{12}P^2C^3$ [103.0(1) and 102.9(1)°] in agreement with expected alterations in the geometrical parameters caused by the anomeric effect. Along the P^2–C^3 bond is realized the preferred twist conformation, and the length of the bond [1.801(3) Å] corresponds to the statistical average for the bond lengths of P^{IV}–C(sp^3) [1.800(15) Å] [12]. Note that the conformation existing along the exocyclic P^2–O^{12} bond is favorable for the reversed anomeric effect, n–σ^*, the interaction of the lone electron pair of the O^{12} atom with the antibonding orbital of the P^2–O^1 bond (see the Newman projections). Apparently these effects determine the sp^2-hybridization of the O^1 and O^{12} atoms (Table 3).

The conformation of the pentafluorophenoxy group at the phosphorus atom along the $O^{12}C^{12}$ bond is common for the compounds of pentavalent four-coordinate phosphorus atom excluding the conjugation in this moiety: the angle $\varphi(P^2O^{12}C^{12}C^{13})$ is equal to –79.9(4)°. Presumably this conformation of the aryloxy groups in the phosphorus compounds depends on the above mentioned hyperconjugation interactions of the lone electron pair of oxygen with the antibonding orbitals of the phosphorus bonds preventing the conjugation with the aromatic system.

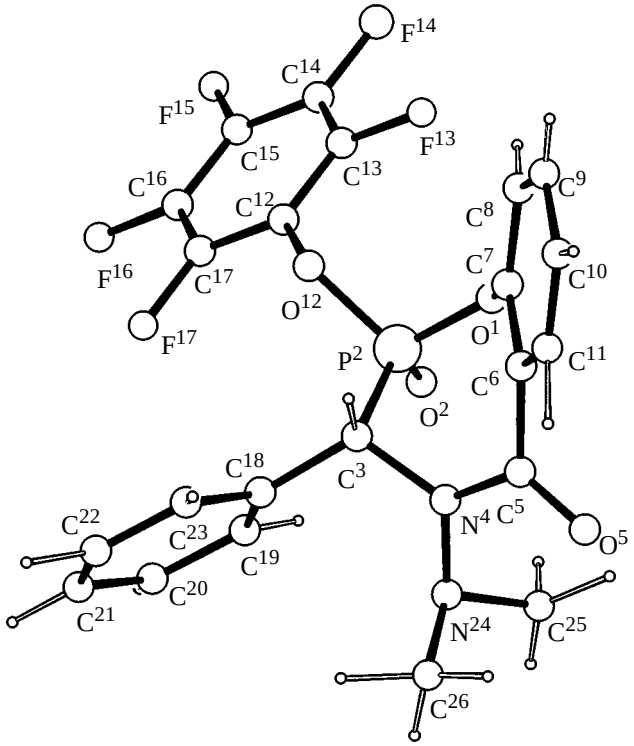


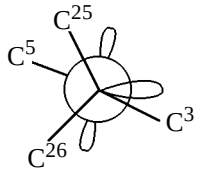
Fig. 1. Spatial arrangement of phosphepine **III** molecule in a crystal.

Table 3. Bond angles (ω, deg) in molecule of phosphepine **III**

Angle	ω	Angle	ω
$O^1P^2O^2$	110.7(1)	$N^4C^5C^6$	117.6(3)
$O^1P^2O^{12}$	105.4(1)	$C^5C^6C^7$	124.8(3)
$O^1P^2C^3$	103.0(1)	$C^5C^6C^{11}$	117.4(3)
$O^2P^2O^{12}$	113.2(1)	$C^7C^6C^{11}$	117.5(3)
$O^2P^2C^3$	120.2(1)	$O^1C^7C^6$	120.4(3)
$O^{12}P^2C^3$	102.9(1)	$O^1C^7C^8$	117.5(3)
$P^2O^1C^7$	126.4(2)	$C^6C^7C^8$	121.8(3)
$P^2O^{12}C^{12}$	118.5(2)	$C^7C^8C^9$	119.0(4)
$N^{24}N^4C^3$	115.3(2)	$C^7C^8H^8$	119(2)
$N^{24}N^4C^5$	121.9(2)	$C^9C^8H^8$	121(2)
$C^3N^4C^5$	122.9(3)	$C^8C^9C^{10}$	120.1(4)
$N^4N^{24}C^{25}$	111.5(3)	$C^8C^9H^9$	125(3)
$N^4N^{24}C^{26}$	111.8(3)	$C^{10}C^9H^9$	115(3)
$C^{25}N^{24}C^{26}$	115.1(3)	$C^9C^{10}C^{11}$	120.4(4)
$P^2C^3N^4$	106.6(2)	$C^9C^{10}H^{10}$	127(3)
$P^2C^3C^{18}$	114.2(2)	$C^{11}C^{10}H^{10}$	113(3)
$P^2C^3H^3$	105(2)	$C^6C^{11}C^{10}$	121.3(4)
$N^4C^3C^{18}$	115.0(2)	$C^6C^{11}H^{11}$	106(2)
$N^4C^3H^3$	103(2)	$C^{10}C^{11}H^{11}$	133(2)
$C^{18}C^3H^3$	112(2)	$O^{12}C^{12}C^{13}$	120.2(3)
$O^5C^5N^4$	122.3(3)	$O^{12}C^{12}C^{17}$	120.2(3)
$O^5C^5C^6$	120.1(3)	$C^{13}C^{12}C^{17}$	119.6(3)
$F^{13}C^{13}C^{12}$	119.8(3)	$C^{19}C^{20}H^{20}$	116(3)
$F^{13}C^{13}C^{14}$	119.2(4)	$C^{21}C^{20}H^{20}$	121(3)
$C^{12}C^{13}C^{14}$	121.0(4)	$C^{20}C^{21}C^{22}$	119.6(4)
$F^{14}C^{14}C^{13}$	120.5(4)	$C^{20}C^{21}H^{21}$	111(3)
$F^{14}C^{14}C^{15}$	120.4(4)	$C^{22}C^{21}H^{21}$	130(3)
$C^{13}C^{14}C^{15}$	119.1(4)	$C^{21}C^{22}C^{23}$	120.0(4)
$F^{15}C^{15}C^{14}$	119.5(4)	$C^{21}C^{22}H^{22}$	114(3)
$F^{15}C^{15}C^{16}$	119.5(4)	$C^{23}C^{22}H^{22}$	126(3)
$C^{14}C^{15}C^{16}$	120.9(4)	$C^{18}C^{23}C^{22}$	121.3(4)
$F^{16}C^{16}C^{15}$	120.1(4)	$C^{18}C^{23}H^{23}$	127(3)
$F^{16}C^{16}C^{17}$	120.0(4)	$C^{22}C^{23}H^{23}$	110(4)
$C^{15}C^{16}C^{17}$	119.9(4)	$N^{24}C^{25}H^{251}$	108(2)
$F^{17}C^{17}C^{12}$	120.6(3)	$N^{24}C^{25}H^{252}$	112(2)
$F^{17}C^{17}C^{16}$	119.9(3)	$N^{24}C^{25}H^{253}$	114(3)
$C^{12}C^{17}C^{16}$	119.5(4)	$H^{251}C^{25}H^{252}$	130(4)
$C^3C^{18}C^{19}$	121.9(3)	$H^{251}C^{25}H^{253}$	89(4)
$C^3C^{18}C^{23}$	118.7(3)	$H^{252}C^{25}H^{253}$	101(4)
$C^{19}C^{18}C^{23}$	119.4(3)	$N^{24}C^{26}H^{261}$	108(2)
$C^{18}C^{19}C^{20}$	118.6(3)	$N^{24}C^{26}H^{262}$	106(3)
$C^{18}C^{19}H^{19}$	118(2)	$N^{24}C^{26}H^{263}$	113(3)
$C^{20}C^{19}H^{19}$	124(2)	$H^{261}C^{26}H^{262}$	118(3)
$C^{19}C^{20}C^{21}$	121.1(4)	$H^{261}C^{26}H^{263}$	88(4)
$H^{262}C^{26}H^{263}$	122(4)		

Similar to the structure studied before, in the molecule of compound **III** the fragments of the structure are considerably turned along the C^5–C^6 bond [$\varphi(O^5C^5C^6C^{11})$ –39.0(5)°]. As a result the oxygen atom of the carbonyl group deviates from the base plane of the heterocycle to the opposite side from the atoms P^2, C^3, N^4. This deviation of the oxygen from the ($O^1C^6C^7C^5$) plane precludes the conjugation of the C^5=O^5 with the fused benzene ring. It is interesting to note that here the deviation of the O^5 atom of the carbonyl group from the plane $O^1C^7C^6C^5$ is even greater than analogous deviation of this group from the plane in the related molecules **IV**, **V** [by –32.9(20) and –29.2(3)° respectively] and is the maximal in the series of 1,3,2- and 1,4,2-dioxaphosphepines we have studied [5–7, 11]. This may be due to greater delocalization in the electronic system of the amide fragment O^5=C^5–N^4 in molecule **III** than in the ester fragments of molecules **IV** and **V**. The fragment $O^5C^5N^4N^{24}$ is virtually planar [the corresponding torsion angle φ is equal to –9.1(5)°], and the O^5 atom is located symmetrically with respect to the methyl groups of the dimethylamine moiety. The N^4 atom is in planar-trigonal coordination (the sum of bond angles at the nitrogen is 360°), therefore the conjugation of its lone electron pair with the C=O bond is favored. The length of bond N^4–C^5 [1.359(4) Å] is considerably shorter than that of the unconjugated bond N–C(sp^2) (1.452 Å) [12,13]. Presumably the energy gain from conjugation in the amide fragment significantly weakens the conjugation of the π-bond C^5=O^5 with the fused benzene ring, and this permits the turn of the C^5=O^5 group along the C^5–C^6 bond to such notable angle.

The nitrogen atom of dimethylamino group has trigonal-pyramidal coordination (sum of the bond angles is here 338.4°), and along the N^{24}–N^4 bond is realized the sterically preferred conformation with virtually orthogonal lone electron pairs of the nitrogen atoms (φ_{NN} –83°).



N^{24}–N^4

A similar turn along the N–N bond is observed both in unsubstituted hydrazine and 1,1-dimethylhydrazine [14, 15] and in more complicated hydrazine derivatives, e.g., in 1,2-diacyl-1-arylhydrazines [16]. The degree of pyramidal character of the nitrogen in the dimethylamino group calculated in keeping with data from [17] amounts to 0.545. The length of the N–N bond in the molecule of compound **III** [1.416(4) Å] is in agreement with the statistical mean

Table 4. Torsion angles (φ, deg) in phosphepine **III** molecule

Angle	φ	Angle	φ
$O^2P^2O^1C^7$	–158.82(0.24)	$C^5N^4C^3H^3$	–28.12(1.93)
$O^{12}P^2O^1C^7$	78.49(0.26)	$N^{24}N^4C^5O^5$	–9.06(0.50)
$C^3P^2O^1C^7$	–29.07(0.27)	$N^{24}N^4C^5C^6$	169.92(0.29)
$O^1P^2O^{12}C^{12}$	106.49(0.24)	$C^3N^4C^5O^5$	169.83(0.31)
$O^2P^2O^{12}C^{12}$	–14.60(0.28)	$C^3N^4C^5C^6$	–11.20(0.45)
$C^3P^2O^{12}C^{12}$	–145.87(0.24)	$N^4N^{24}C^{25}H^{251}$	–169.57(2.74)
$O^1P^2C^3N^4$	–55.45(0.22)	$N^4N^{24}C^{25}H^{252}$	41.45(2.93)
$O^1P^2C^3C^{18}$	176.35(0.21)	$N^4N^{24}C^{25}H^{253}$	–72.74(3.37)
$O^1P^2C^3H^3$	53.68(1.84)	$C^{26}N^{24}C^{25}H^{251}$	61.72(2.76)
$O^2P^2C^3N^4$	68.20(0.24)	$C^{26}N^{24}C^{25}H^{252}$	–87.27(2.93)
$O^2P^2C^3C^{18}$	–59.99(0.26)	$C^{26}N^{24}C^{25}H^{253}$	158.54(3.36)
$O^2P^2C^3H^3$	177.33(1.83)	$N^4N^{24}C^{26}H^{261}$	167.97(2.29)
$O^{12}P^2C^3N^4$	–164.91(0.19)	$N^4N^{24}C^{26}H^{262}$	–64.59(2.66)
$O^{12}P^2C^3C^{18}$	66.89(0.23)	$N^4N^{24}C^{26}H^{263}$	72.28(3.65)
$O^{12}P^2C^3H^3$	–55.78(1.84)	$C^{25}N^{24}C^{26}H^{261}$	–63.45(2.32)
$P^2O^1C^7C^6$	65.49(0.37)	$C^{25}N^{24}C^{26}H^{262}$	63.99(2.67)
$P^2O^1C^7C^8$	–120.49(0.31)	$C^{25}N^{24}C^{26}H^{263}$	–159.14(3.64)
$P^2O^{12}C^{12}C^{13}$	–79.87(0.37)	$P^2C^3C^{18}C^{19}$	42.91(0.38)
$P^2O^{12}C^{12}C^{17}$	99.02(0.33)	$P^2C^3C^{18}C^{23}$	–134.18(0.28)
$C^3N^4N^{24}C^{25}$	121.62(0.32)	$N^4C^3C^{18}C^{19}$	–80.87(0.39)
$C^3N^4N^{24}C^{26}$	–107.96(0.32)	$N^4C^3C^{18}C^{23}$	102.04(0.34)
$C^5N^4N^{24}C^{25}$	–59.42(0.42)	$H^3C^3C^{18}C^{19}$	161.43(1.93)
$C^5N^4N^{24}C^{26}$	71.00(0.39)	$H^3C^3C^{18}C^{23}$	–15.65(1.95)
$N^{24}N^4C^3P^2$	–99.28(0.26)	$O^5C^5C^6C^7$	134.01(0.36)
$N^{24}N^4C^3C^{18}$	28.43(0.38)	$O^5C^5C^6C^{11}$	–38.98(0.47)
$N^{24}N^4C^3H^3$	150.83(1.91)	$N^4C^5C^6C^7$	–44.99(0.46)
$C^5N^4C^3P^2$	81.77(0.32)	$N^4C^5C^6C^{11}$	142.02(0.32)
$C^5N^4C^3C^{18}$	–150.52(0.30)	$C^5C^6C^7O^1$	0.03(0.61)

for the N–N bonds with one nitrogen in trigonal-planar, the other in pyramidal coordination [1.420(15) Å] [12].

The aromatic fragments in compound **III** molecule are of common geometry. A short intramolecular contact of N^{24} atom with the benzene ring $C^{18–23}$ should be noted: the distance $C^{18}\cdots N^{24}$ is 2.808(5) Å, the nitrogen atom deviates from the plane of the ring by 2.15(2) Å. Therewith the lone electron pair of the nitrogen is directed to the ring (Fig.1). The bond angle $N^{24}N^4C^3$ [115.3(2)°] is smaller than the $N^{24}N^4C^5$ angle [121.9(2)°]. Apparently in the molecule of compound **III** occurs an attractive interaction of the $n–\pi^*$-type between the exocyclic nitrogen atom and the phenyl substituent at the C^3 atom.

The packing of compound **III** molecules in a crystal is determined by van der Waals contacts, weak hydrogen bonds of C–H···O type, and π–π interactions between the parallel benzene rings C^6–C^{11} and that of pentafluorophenoxy group (dihedral angle between their planes 11°, the distance between the centroids 4.14 Å, the distance between the planes 3.28, the angle between the normal to the plane and the line connecting the centroids 27.7°; Fig. 2). The parameters of the hydrogen bonds are as follows: C^{21}–H···$O^{5'}$ (*x*, –*y*, 1/2 + *z*), C^{21}–H 1.07(6), $C^{21}\cdots O^{5'}$ 3.405(4), $H\cdots O^{5'}$ 2.43(5) Å, angle C^{21}–H···$O^{5'}$ 152(4)°; C^{23}–H···$O^{2''}$ (1 + *x*, *y*, *z*), C^{23}–H 0.84(6), $C^{23}\cdots O^{2''}$ 3.271(5), $H\cdots O^{2''}$ 2.55(6) Å, angle C^{23}–H···$O^{2''}$ 145(4)°. In compound **III** molecule is observed a short contact C^{19}–H···O^2 interpreted by PLATON routine as an intramolecular hydrogen bond with the following parameters: C^{19}–H 0.97(3), $C^{19}\cdots O^2$ 3.219(5), $H\cdots O^2$ 2.50(3) Å, angle C^{19}–H···O^2 131(2)°.

An interesting feature of phosphepine **III** is its instability against hydrolysis. Already during dissolution in acetone or DMF if the air moisture is not excluded compound **III** hydrolyzis to afford pyrophosphonate **VII**. This compound readily precipitates

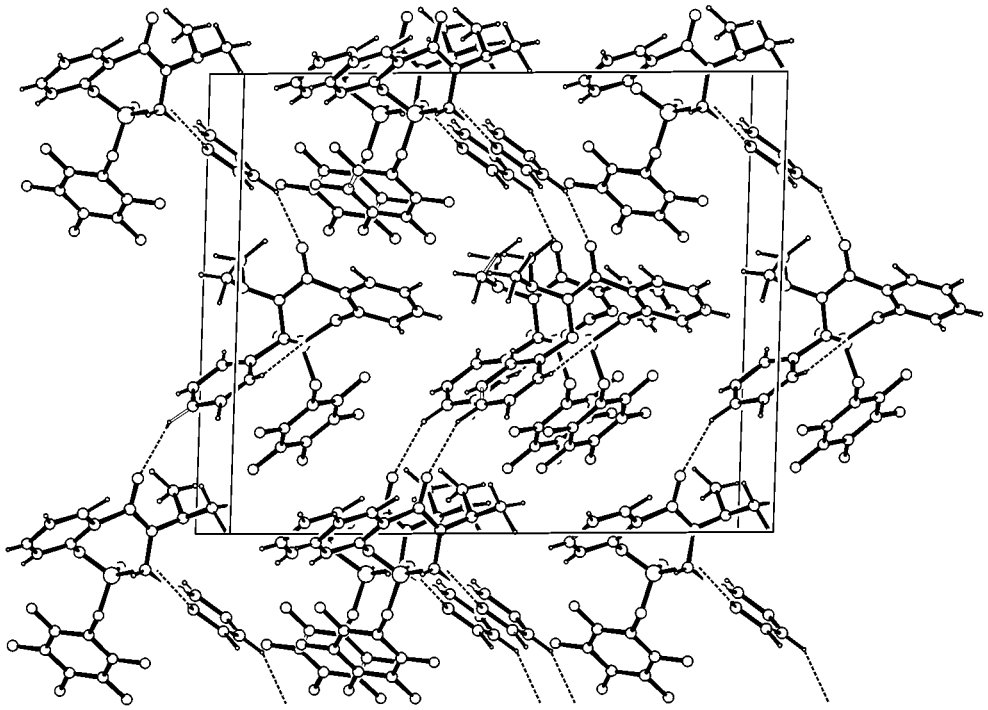
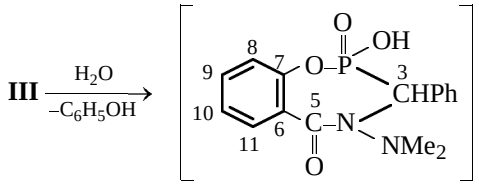
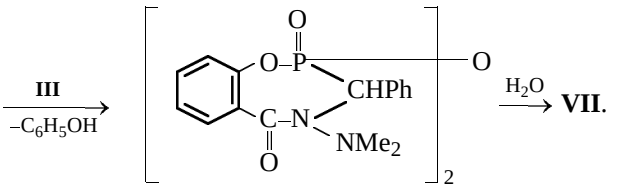


Fig. 2. Hydrogen bonds system in phosphepine **III** crystal.

even from DMF. In the IR spectrum of the crystalline specimen are lacking the absorption bands of OH groups or of any internal salts with the hydrazide part, and in the ^{19}F NMR spectrum are no fluorine signals. These facts are consistent with the easy cleavage of the pentafluorophenol from molecule **III** effected by water, and with fast reaction of the intermediately formed acid **VI** with initial phosphepine **III** to yield compound **VII**.



VI



However in DMF or DMSO in the presence of water traces compound **VII** can slowly hydrolyze to acid **VI**. Thus after two recrystallizations and subsequent dissolution in a moist DMF compound **VII** lost the ability to crystallize and transformed into a glass-like substance. The ^{13}C NMR spectrum of the latter is presented in Table 5. First interesting fact consists in the presence in the upfield region of a distinct doublet (δ_C 59.0 ppm) from the carbon atom of the fragment P(O)–C^{3}H that evidences the existence of a single isomer. It is clear since the phosphorus atom in the course of hydrolysis becomes achiral. An additional proof of pyrophosphonate **VII** hydrolysis is the lack of additional spin-spin coupling that should have appeared along the chain P–O–P–C^3. The signal from carbons of the dimethylamino group in the ^{13}C NMR spectrum is very broad [$\Delta_{1/2}(\delta_C)$ ~80–90 Hz] probably due to the exchange of proton between the nitrogen of the dimethylamino group and the oxygen attached to phosphorus. Finally, it should be noted, that in the IR spectrum of hydrolysis product **VI** appear strong bands in 2800–3100 cm^{-1} region that also indicate the presence of a hydroxy group linked to phosphorus.

EXPERIMENTAL

IR spectra were recorded on Specord M-80 spectrophotometer from mulls in mineral oil.

NMR spectra were registered on instruments Bruker MSL-400 (^{13}C, ^{13}C–{^1H}, 100.6 MHz; ^{31}P–{^1H}, 162.0 MHz), Bruker WM-250 (^1H, 250 MHz), Varian Unity-300 (^{19}F, 282.16 MHz), Varian Gemini

200 (^{1}H, 200 MHz) related to internal references HMDS or C_6F_6, and external reference H_3PO_4; the fluorine chemical shifts were recalculated with respect to $CFCl_3$.

X-ray analysis of compound III. Crystals monoclinic. At 20°C *a* 6.103(2), *b* 20.422(8), *c* 17.552(5) Å; β 99.21(3)°, *V* 2159(1) Å^3, *Z* 4, d_{calc} 1.53 g/cm^3, space group C_c. Unit cell parameters and intensities of 2332 reflections (1790 among them with $I \geq 3\sigma$) were measured on an automatic four-circle diffractometer Enraf-Nonius CAD-4 at 20°C ((λMoK_α-irradiation, graphite monochromator, ω/2θ-scanning, $\theta \leq 29°$). In the course of the recording was no intensity decrease observed for three control reflections.

The structure was solved by the direct method along SIR software [14] and was refined first in isotropic and then in anisotropic approximation. All the hydrogen atoms were revealed from electron density difference series and refined in isotropic approximation at the final stage. The final values of divergence factors are *R* 0.033, R_W 0.041 from 1721 independent reflections with $F^2 \geq 3\sigma$. All calculations were carried out with the use of program package MolEN [15] on the computer Alpha Station 200. The analysis of intermolecular contacts in the crystal was performed along PLATON routine [20].

Reaction of 4-oxo-2-pentafluorophenoxy-5,6-benzo-1,3,2-dioxaphosphorinane (Ib) with benzaldehyde *N,N*-dimethylhydrazone (II). At long (over 6 month) storage of a reaction mixture containing 5.1 g of phosphorinane Ib, 2.2.g of hydrazone **II**, and 25 ml of CH_2Cl_2 was obtained a precipitate of large lemon-yellow crystals, 4-dimethylamino-2,5-dioxo-2-pentafluorophenoxy-3-phenyldihydro-6,7-benzo-1,4,2-oxazaphosphepine (**III**). Yield 67%, mp 164–166°C. IR spectrum, ν, cm^{-1}: 1662 [C(O)N], 1615 (C=C$_{arom}$), 1528 (C_6F_5), 1480, 1332, 1315, 1287 (P=O), 1260, 1218, 1149, 1102, 1050, 1032, 1010, 970, 830, 785, 760, 706. NMR spectrum ^{31}P–{^{1}H} (DMF-d_7): δ_P 22.3 ppm. ^{1}H NMR spectrum (400 MHz, acetone-d_6–DMSO, 2 : 1), δ, ppm (*J*, Hz): 7.86 br.d (H$_o$, H^{11}, $^3J_{HH}$ 7.8–8.1), 7.78 br.d.d (H^9, $^3J_{HH}$ 7.8–8.1), 7.57 br.d.d (H^{10}, $^3J_{HH}$ 7.8–8.1), 7.50 br. m (H$_p$), 7.45 br. m (H$_m$), 7.42 br.d (H^8, $^3J_{HH}$ 7.8–8.1), 5.85 d (PCH, $^2J_{PCH}$ 10.9). ^{19}F NMR spectrum (DMF-d_7), δ_F, ppm (*J*, Hz): –159.81 t (F$_p$, $^3J_{F_pCCF_m}$ 21.4), –152.61 br.d (F$_o$, $^3J_{F_oCCF_m}$ 20.0), –162.01 br.d.d (F$_m$, $^3J_{F_pCCF_m}$ 21.4, $^3J_{F_oCCF_m}$ 20.0). Found, %: C 53.18; H 3.44. $C_{22}H_{16}F_5N_2O_4P$. Calculated, %: C 53.01; H 3.21.

On recrystallization of compound **III** from DMF in contact with air moisture were obtained colorless fine crystals of 2-(4-dimethylamino-2,5-dioxo-3-phenyldihydro-6,7-benzo-1,4,2-oxazaphosphepin-2-yloxy)-4-dimethylamino-2,5-dioxo-3-phenyldihydro-6,7-benzo-1,4,2-oxazaphosphepine (**VII**). Yield 81%, mp 200–201°C. IR spectrum, ν, cm^{-1}: 1650, 1600, 1345, 1300, 1280 sh, 1205, 1150, 1100, 986, 970, 965, 950, 777, 760, 750, 695, 586, 538. ^{31}P NMR spectrum (DMF): δ_P 14.4 ppm Found, %: C 59.87; H 5.08; P 9.47. $C_{32}H_{32}N_4O_7P_2$. Calculated, %: C 59.44; H 4.95; P 9.59.

Table 5. ^{31}P and ^{13}C NMR spectra of compound **VI** (DMF-d_7) (the same numbering of carbon atoms as in Fig. 1)

Atom	δ, ppm	*J*, Hz
P^2	13.50 d	13.3 (PCH^3)
C^3	59.0 d (br.d.d)	142.8 (PC^3), 141.0 (HC^3)
C^5	166.62 s (br.s)	–
C^6	128.33 br.s (br.m)	–
C^7	148.75 d (br.m)	8.0 (POC^7)
C^8	121.08 d (br.d.d.d)	163.7 (HC^8), 7.5 (HC^{10}CC^8), 2.7 (POCC^8)
C^9	131.40 s (d.d)	161.6 (HC^9), 8.3 (HC^{11}CC^9)
C^{10}	123.28 s (br.d. m)	162.8 (HC^{10})
C^{11}	128.57 s (br.d.d)	161.0 (HC^{11}), 7.2 (HC^{9}CC^{11})
C^{18}	132.08 br.s (br.m)	–
C^{19}	130.71 d (br.d.m)	160.6 (HC^{13}), 7.6 (PCCC^{13})
C^{20}	126.23 s (d.d)	162.3 (HC^{14}), 5.0 (HCCC^{14})
C^{21}	126.53 s (br.d.m)	162.0 (HC^{15})

A short heating of compound **VII** in aqueous DMF to 100°C followed by removing DMF in a vacuum afforded glass-like 2-hydroxy-4-dimethylamino-2,5-dioxo-3-phenyldihydro-6,7-benzo-1,4,2-oxazaphosphepine (**VI**). ^{1}H NMR spectrum (250 MHz, DMSO + 30% acetone-d_6), δ, ppm (*J*, Hz): 4.96 d (PCH, $^2J_{PCH}$ 13.3); 7.65 and 7.34 2 m (C_6H_5, H^{10}, H^{11}), 7.57 br.d.d (H^9, $^3J_{HCCH}$ 7.4–7.8), 7.17 br.d (H^8, $^3J_{HCCH}$ 8.3). ^{1}H NMR spectrum (200 MHz, DMSO + 30% ethanol-d_6), δ, ppm (*J*, Hz): 5.07 d (PCH, $^2J_{PCH}$ 13.4).

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