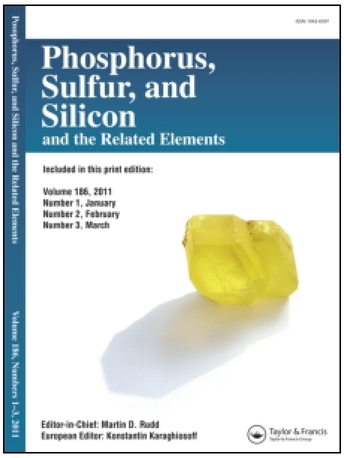

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Alexey I. Polosukhin[a]; Andrey Yu. Kovalevsky[a]; Andrey V. Korostylev[a]; Vadim A. Davankov[a]; Konstantin N. Gavrilov[b]
[a] Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia [b] Department of Chemistry, Ryazan State Pedagogic University, Ryazan, Russia

To cite this Article Polosukhin, Alexey I. , Kovalevsky, Andrey Yu. , Korostylev, Andrey V. , Davankov, Vadim A. and Gavrilov, Konstantin N.(2000) '(3R,8R)-5-HY DRO-3,8-DIETHY L-1,6-DIOXA-4,9-DIAZA-5-PHOSPHASPIRO[4.4]NONANE. SYNTHESIS, STRUCTURAL AND SPECTROSCOPIC PROPERTIES', Phosphorus, Sulfur, and Silicon and the Related Elements, 159: 1, 69 — 77

To link to this Article: DOI: 10.1080/10426500008043651

URL: http://dx.doi.org/10.1080/10426500008043651

Phosphorus, Sulfur, and Silicon, 2000, Vol. 159, pp. 69-77
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(3R,8R)-5-HYDRO-3,8-DIETHYL-1,6-DIOXA-4,9-DIAZA-5-PHOSPHASPIRO[4.4]NONANE. SYNTHESIS, STRUCTURAL AND SPECTROSCOPIC PROPERTIES

ALEXEY I. POLOSUKHIN[a], ANDREY YU. KOVALEVSKY[a], ANDREY V. KOROSTYLEV[a], VADIM A. DAVANKOV[a] and KONSTANTIN N. GAVRILOV[b]*

[a]*Institute of Organoelement Compounds, Russian Academy of Sciences, 28, Vavilova Str., Moscow, 117813, Russia and* [b]*Department of Chemistry, Ryazan State Pedagogic University, 46, Svoboda str., Ryazan, 390000, Russia*

(Received July 29, 1999)

(3R,8R)-5-Hydro-3,8-diethyl-1,6-dioxa-4,9-diaza-5-spiro[4.4]nonane (**1**) was prepared by the reaction of (R)-2-aminobutanol-1 with $P(NEt_2)_3$. A mixture of diastereoisomers with different phosphorus center configurations was obtained. Compound **1** was studied by the following set of methods: NMR ^{31}P, ^{13}C, ^{15}N, IR spectroscopy, mass-spectrometry, ultra-cenrifugation and single crystal X-ray diffraction analysis. The phosphorus atom is a slightly distorted trigonal bipyramid with the two oxygen atoms in apical positions and the nitrogen atoms in equatorial positions.

Keywords: crystal structure; hydrophosphorane; chirality; ^{31}P NMR; ^{13}C NMR; ^{15}N NMR

INTRODUCTION

Oxazahydrospirophosphoranes (OAHSP) as a special class of organophosphorus compounds have been known for a long time. The interest to study these compounds arises from stereochemical parameters of the phosphorus atom and their capability to react by opening one of the two oxazaphospholidine rings[1]. The latter becomes apparent when the phosphorus atom is coordinated with transition metal atoms. Of special interest are optically

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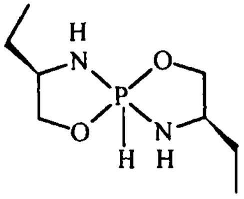
* Corresponding author. Fax: +7 (095) 135–64–71. E-mail: chem@ttc.ryazan.ru.

active OAHSP obtained by one-pot synthesis from chiral β-aminoalkohols. As a result of their coordination, metallocomplexes, having chiral centers of equal configuration in the structure of the metallocycle and the peripheral phosphorus cycle, are obtained. The last fact is very perspective both for coordination chemistry and metallocomplex asymmetric catalysis[1].

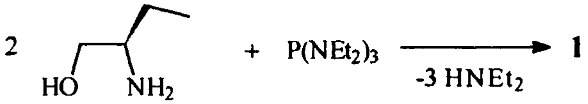
This paper is aimed at the synthesis and structural characterization of (3R,8R)-5-hydro-3,8-diethyl-1,6-dioxa-4,9-diaza-5-spiro[4.4]nonane (**1**) by a wide range of physico-chemical methods.



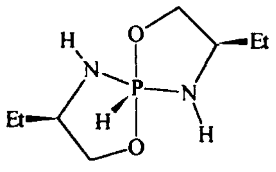
1

RESULTS AND DISCUSSION

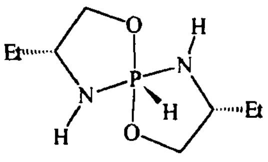
Earlier the synthesis of **1** was reported[2]. However, a detailed analysis of ^{31}P NMR spectra allows to make the conclusion that the phosphorane concerned was obtained with the use of 2-aminobutanol-1 of inadequate enantiomeric purity. Unlike the reported synthesis, we made the phosphorylation of optically pure (R)-2-aminobutanol-1, according to the following scheme:



The reaction product was characterized by ^{31}P, ^{13}C, ^{15}N NMR spectroscopy (See Table **1**). As was anticipated [3–5], a mixture of diastereoisomers **1′** and **1″** with different phosphorus center configurations was obtained.



1'



1''

TABLE I ^{31}P, ^{13}C, ^{15}N NMR data for compound 1

Diastereo-isomer	*$^{31}P\{^1H\}$ NMR ($CDCl_3$), δ_P, ppm,($^1J_{P-H}$, Hz)*	*$^{15}N\{^1H\}$ NMR (heptane), δ_N, ppm, ($^1J_{N-P}$, Hz)*	*$^{13}C\{^1H\}$ NMR ($CDCl_3$), δ_C, ppm (J, Hz)*			
			$POCH_2$	*PNCH ($^2J_{C-P}$)*	*CH_2 ($^3J_{C-P}$)*	*CH_3*
1'	55.4	-320.0	64.4	51.3	28.8	10.0
	(738.0)	(30.5)		(11.1)	(4.6)	
1''	57.0	-320.5	64.5	51.4	28.6	9.9
	(741.0)	(30.5)		(11.0)	(7.9)	

^{31}P and ^{15}N NMR spectra show that the diastereoisomers ratio at 25°C is equal to 3:7 and it can be changed by temperature variation [3]. Examples of investigation of this chemical class of compounds by ^{15}N NMR spectroscopy are rare, but the data obtained using this method allow to study the behavior of the nitrogen center in the course of reactions of OAHSP under openning of one of the heterocycles [2]. In the IR spectrum of **1** determined in CCl_4 the following absorption bands were observed: 3476 cm^{-1}, characteristic of N-H bond and a broad band at 2360 cm^{-1}, characteristic of P-H bond. The fragmentation of **1** under the mass-spectral experiment conditions (electron impact) has much in common with the fragmentation of various amines [6]. In particular, the peak of the molecular ion has a small intensity, m/z (1,%): 206 (4), $[M]^+$. The most intensive ions are formed as the result of α-break: 58 (100) $[EtCHNH_2]^+$ and β-break: 72 (63) $[CH_2CH(Et)NH_2]^+$. In addition, there are fragment ions characteristic for OAHSP: 191 (12) $[M - CH_3]^+$, 136 (17) $[H_2NCH(Et)CH_2OPOH]^+$, 120 (10) $[H_2NCH(Et)CH_2OPH]^+$.

Single crystal X-ray diffraction analysis has been carried out and the stucture of this isomer identified as 1''. In the crystal, the crystallographic

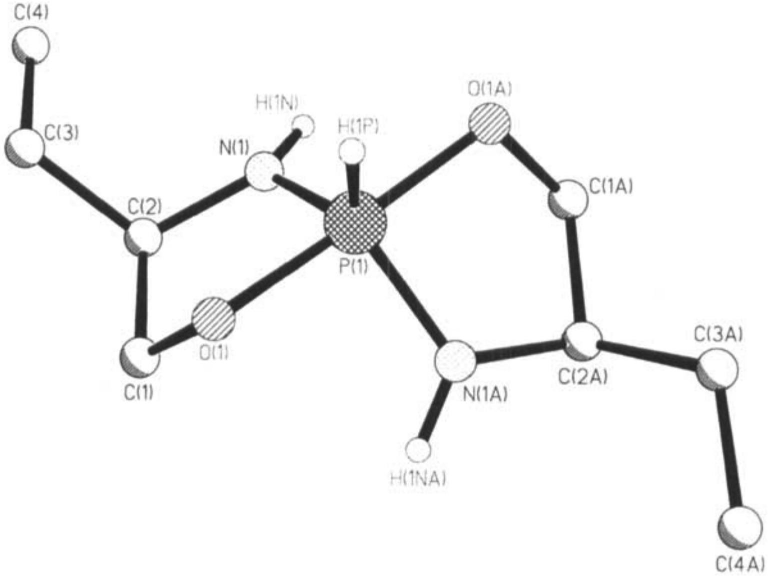


FIGURE 1 A perspective view of **1**. Only H-atoms of phosphorus and nitrogens are shown for clarity

twofold axis lies along the P-H bond of the molecule (See Figure **1**). The geometry of **1** agrees well with related compounds studied ealier [3,7,8]. The phosphorus atom is a slightly distorted trigonal bipyramid with the two oxygen atoms in apical positions and the nitrogen atoms in equatorial positions. This conclusion arises from the O-P-O and N-P-N bond angles which are 175.7(2)° and 121.8(1)°, respectively. The five-membered ring of **1** has a distorted envelope conformation (atoms C(1) and C(2) are displaced from the plane of the atoms of the ring by 0.68 and 0.27Å, respectively). The displacement of the C(2) atom results from the non-planar configuration of the nitrogen atom N(1) (the sum of its bond angles is 357(3)°) what is probably caused by the formation of weak intermolecular N-H...O hydrogen bonds H(1N)...O(1)′ (0.5+x, 0.5+y, z) (H...O distance is 2.27Å, N-H...O angle is 168.4°).

The ethyl groups occupy an equatorial position in the ring, being in a *-ap* conformation with respect to C-C bond (torsion angle C(1)-C(2)-C(3)-C(4) of −177.1(2)°). The experiment quality allowed the

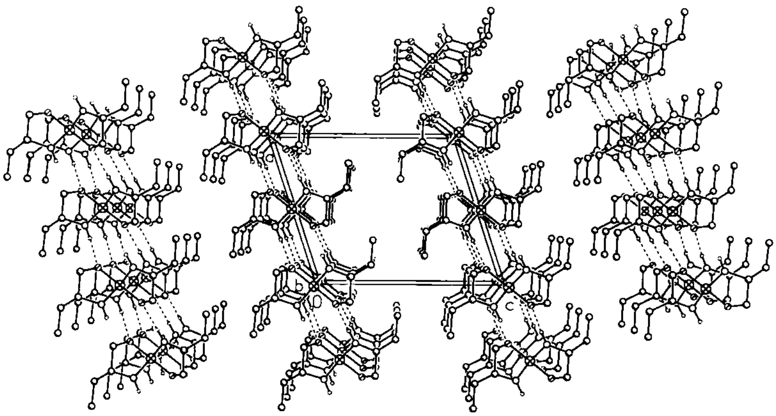


FIGURE 2 A view of crystal packing of **1**. The projection along the crystallographic axis ***b*** is shown

H atoms positions to be refined. But it should be noted that the P-H distance (1.24(5)Å) appeared to be somewhat shorter than that presented in the earlier studies [3, 7] (1.47–1.49Å). This fact can be probably explained by the lower quality of the related structures refinement in the investigations mentioned above.

In the crystal, molecules of **1** form stacks along the crystallographic axis ***b***. The molecules of different stacks are connected by H-bonds referred above (See Figure **2**).

The size of OAHSP molecule was estimated by diffusion method in heptane solution. It was found that the molecule of **1** can be inscribed in a sphere of 9.6Å in diameter. This stands in a good agreement with the experimental X-ray diffraction data (10.6Å).

EXPERIMENTAL

Solvents were purified according to published procedures [9]. Infrared spectra were recorded on a Specord M80 spectrophotometer. ^{13}C NMR: Bruker AC 200 (50.3 MHz) with Me_4Si as internal standard; ^{31}P NMR: Bruker AMX 400 (162.0 MHz), 85% H_3PO_4 as external standard. ^{15}N

NMR: Bruker AC 200 (20.27 MHz), saturated NH_4NO_3 water solution as external standard (with $\delta[NO_3]^- = 0$). Mass spectrum was recorded on a Kratos MS 890 spectrometer. Sedimentation analyses were performed on a MOM-3180 analytical ultracentrifuge according to published techniques [10–12]. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow).

The crystals of compound **1** were obtained by slow evaporation of its solution in heptane. Crystallographic data for compound **1** are given in Table **2**.

TABLE II Crystallographic data for compound **1**

Compound	*1*
Empirical formula	$C_8H_{19}N_2O_2P$
Color, habit	colorless, parallelepipeds
Formula weight	206.22
Crystal system	Monoclinic
Space group,	C2
Z	2
Temperature, K	293(2)
	a= 9.806(5)
Cell parameters (Å), deg.	b= 4.943(2)
	c= 11.685(6)
	β= 108.32(2)
Volume (Å^3)	537.6(4)
D_{calc}, g•cm^{-3}	1.274
μ, mm^{-1}	0.230
F(000)	224
Collected reflections	1348
Independent reflections	1288
R_{int}	0.019
Diffractometer	Siemens P3/PC
$2\theta_{max}$. deg.	70
Refined reflections	1257
Reflections with F>4σ(F)	1046
R_1 (obs.)	0.043
wR2 (all data)	0.102
S (all data)	1.049

The structure was solved by direct method using SHELXTL PLUS 5 program package [13]. Positions of hydrogen atoms were located from the difference map of electron density. All H-atoms were refined in isotropic approximation. The atomic coordinates for compounds **1** are listed in Table **3**, bond lengths and angles are given in Table **4**.

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$) for **1**

Atom	*x*	*y*	*z*	*U(eq)*
P(1)	5000	220	0	31(1)
O(1)	3871(1)	91(5)	844(1)	41(1)
N(1)	6185(2)	1850(4)	1115(1)	37(1)
C(1)	4080(2)	2394(5)	1615(2)	45(1)
C(2)	5701(2)	2874(4)	2091(2)	38(1)
C(3)	6436(3)	1482(7)	3288(2)	51(1)
C(4)	8027(3)	2069(9)	3790(3)	68(1)
H(1P)	5000	−2292(112)	0	59(12)
H(1N)	7012(33)	2556(78)	1009(25)	56(8)
H(1A)	3770(31)	2042(78)	2119(31)	60(9)
H(1B)	3643(40)	4070(90)	1125(33)	72
H (2)	5871(27)	4644(59)	2244(23)	40(7)
H(3A)	6323(42)	−329(90)	3263(34)	72(12)
H(3B)	5993(30)	1982(70)	3804(24)	51(8)
H(4A)	8009(48)	4044(120)	3895(38)	102(16)
H(4B)	8638(45)	1720(118)	3149(37)	94(12)
H(4C)	8391(34)	942(74)	4547(25)	60(9)

TABLE IV Bond lengths [Å] and angles [°] for **1**

P(1)-N(1)	1.656(2)	O(1)-C(1)	1.426(3)
P(1)-N(1)#1	1.656(2)	N(1)-C(2)	1.457(2)
P(1)-O(1)#1	1.700(1)	C(1)-C(2)	1.529(3)
P(1)-O(1)	1.700(1)	C(2)-C(3)	1.521(3)
P(1)-H(1P)	1.24(6)		
N(1)-P(1)-N(1)#1	121.8(1)	C(2)-N(1)-P(1)	117.7(1)
N(1)-P(1)-O(1)#1	92.89(8)	O(1)-C(1)-C(2)	106.3(2)

N(1)#1-P(1)-O(1)#1	89.21(8)	N(1)-C(2)-C(3)	112.7(2)
N(1)-P(1)-O(1)	89.21(8)	N(1)-C(2)-C(1)	102.6(2)
N(1)#1-P(1)-O(1)	92.89(8)	C(3)-C(2)-C(1)	113.7(2)
O(1)#1-P(1)-O(1)	175.7(2)	C(4)-C(3)-C(2)	113.8(2)
C(1)-O(1)-P(1)	110.2(1)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z

(3R,8R)-5-Hydro-3,8-diethyl-1,6-dioxa-4,9-diaza-5-phosphaspiro[4.4] nonane (1)

Ligand **1** known earlier [2] has been synthesized according to the following technique: a mixture of $P(NEt_2)_3$ (0.02 mole, 4.94 g) and (R)-2-aminobutanol-1 (0.04 mole, 3.56 g) was stirred at 120°C for 1.5 hour. Then the mixture was vacuumed (10 mm Hg, 100°C) for 0.5 hour to remove $HNEt_2$. The product was purified by recrystallization from hexane and sublimation in vacuum (1mm Hg) at 70–75°C. Colorless crystals. Yield: 90%, mp 72–75°C. Anal. Calc. for $C_8H_{19}N_2O_2P$: C, 46.59; H, 9.29; N, 13.58; P, 15.05. Found: C, 46.35; H, 9.43; N, 13.60; P, 15.20%

Acknowledgements

This work was supported by the Scientific Training Centers of Chemistry of Organometallic Compounds (grant 234, the Federal Target Program "Integration"), of Biomedical Chemistry (project No. K0559, the Federal Target Program "Integration"). The authors acknowledge the Russian Fund for Basic Research for the help (Grant N 97–03–33783a and 96–15–97367).

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