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To the 100th Anniversary of A.N. Pudovik

Synthesis and Conformational Analysis of Phosphine Selenides

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Abstract—Methods of preparation of complex phosphine selenide via the original Trofimov–Gusarova reaction are described. The results of the products conformational analysis by means of a set of physical methods (IR spectroscopy, dipole moments, and quantum chemical calculation) are presented.

Keywords: phosphine selenide, the Trofimov–Gusarova reaction, polarity, conformational analysis, quantum chemical calculation

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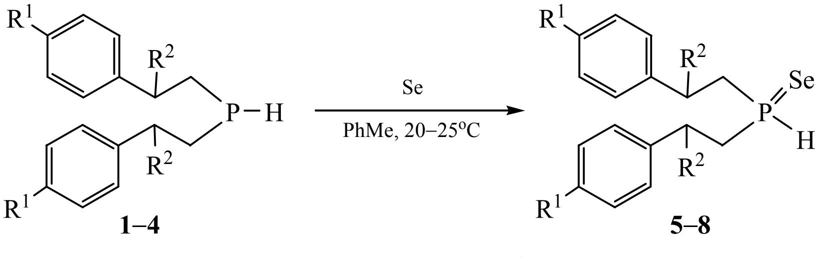
1. Synthesis of secondary and tertiary phosphine selenides based on the Trofimov–Gusarova reaction. Secondary and tertiary phosphine selenides are attractive as ligands for design of multipurpose metal complexes [1–4], precursors of physiologically active compounds [5–9], building blocks of organophosphorus compounds [10–15], intermediates of elemental selenium preparation, and convenient models to study the physicochemical properties of complex molecules [19–24]. Conventional methods of phosphine selenides synthesis utilizing aggressive phosphorus halides and organometallic compounds are inconvenient, multistage, and environmentally unfriendly. However, these compounds have been successfully prepared [25–30] via the Trofimov–Gusarova reaction (direct phosphorylation of electrophiles with elemental phosphorus or the phosphine generated therefrom in the presence of strong bases) [31–35].

1.1. Synthesis of secondary phosphine selenides from red phosphorus, styrenes, and elemental selenium. The synthesis of target secondary phosphine selenides is based on oxidation of the corresponding secondary phosphines **1–4** with elemental selenium. The reaction occurs under mild conditions (ambient temperature, 0.5–1.5 h, toluene, argon), the yield of secondary phosphine selenides **5–8** is practically quantitative [19, 36, 37] (Scheme 1).

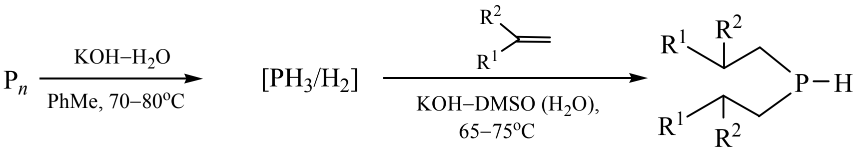
The original method of preparation of the starting secondary phosphines has been elaborated based on

Scheme 1.



$R^1 = R^2 = H$ (**1**, **5**); $R^1 = H$, $R^2 = Me$ (**2**, **6**); $R^1 = 4\text{-}^t\text{Bu-}C_6H_4$, $R^2 = H$ (**3**, **7**); $R^1 = 4\text{-Cl-}C_6H_4$, $R^2 = H$ (**4**, **8**).

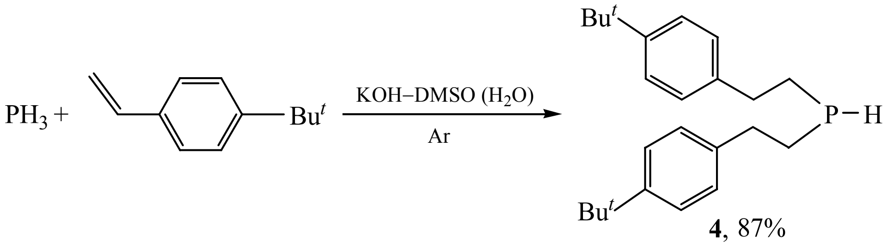
Scheme 2.



1–3

R^1 = Ph, R^2 = H (**1**, 79%); R^1 = Ph, R^2 = Me (**2**, 63%); R^1 = 4-ClC_6H_4, R^2 = H (3, 67%).

Scheme 3.



4, 87%

Scheme 4.

2, 54%

nucleophilic addition of phosphine to weakly electrophilic styrenes in the presence of a superbasic KOH–DMSO system [36–39]. Phosphine and hydrogen have been generated in ~1 : 1 ratio from red phosphorus and potassium hydroxide in a water–toluene medium [36]. In order to achieve the proper chemical selectivity of the reaction and to stop it at the stage of the secondary phosphines formation, the styrene substrate should be slowly introduced in a heated KOH–DMSO (H_2O) suspension, phosphine being vigorously passed through the mixture.

The following conditions have been suggested for the synthesis of secondary phosphines **1**–**3**: 60–75°C, 3 h, ratio of alkene : KOH : H_2O [1 : 3 : 6.8 for **1** [38], 1 : 5.2 : 2.8 for **2** [37] or 1 : 2.8 : 6.2 for **3** [39] in DMSO. The yield of the secondary phosphines has been 79 (**1**), 63 (**2**), and 67% (**3**) (Scheme 2).

4-*tert*-Butylstyrene has been less reactive towards hydrophosphination than unsubstituted styrene. The reaction has been performed at 70°C using the ratio alkene : KOH : H_2O (1 : 3 : 1.6) in DMSO. The conversion of *tetr*-butylstyrene under the said conditions has been as low as 75%. The process is chemically selective, and the yield of the secondary phosphine **4** is 87% (accounting for the conversion of *tert*-butylstyrene) [36] (Scheme 3).

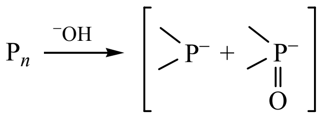
Using α-methylstyrene as an example, it has been demonstrated that secondary phosphine selenide can be prepared from phosphine, styrene, and elemental selenium without isolation of the intermediate secondary phosphine from the reaction mixture [40].

The synthesis of the secondary phosphine **2** via activation of red phosphorus under combined action of a strong base and microwave irradiation (200 W, 15 min) has been reported as well. The approach has allowed for direct phosphorylation of α-methylstyrene in the P_n–KOH–DMSO(H_2O) system affording the secondary phosphine **2** in 54% yield [37] (Scheme 4).

The reaction does not occur in the absence of KOH, the fact evidencing the nucleophilic mechanism of the process that can be expressed by the Schemes 5, 6.

The first stage consists in the generation of phosphide and phosphinite anions from red phos-

Scheme 5.



phorus under the action of the superbase and microwave irradiation.

Phosphide anions further react with α-methylstyrene in a superbasic KOH–DMSO system forming sequentially the primary and the secondary phosphines (Scheme 6).

1.2. Synthesis of tris(2-pyridyl)phosphine selenide from 2-bromopyridine, elemental phosphorus, and elemental selenium. Oxidation of tris(2-pyridyl)phosphine **9** with elemental selenium under mild conditions (ambient temperature, 0.5 h, toluene, argon) has resulted in quantitative formation of tris(2-pyridyl)phosphine selenide **10** (Scheme 7).

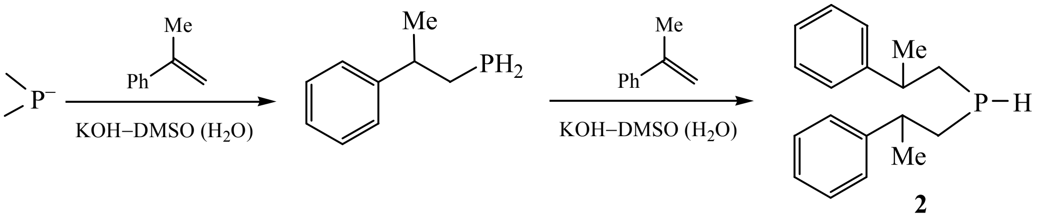
The starting tertiary phosphine **9** has been synthesized via direct phosphorylation of 2-bromopyridine with elemental (red or white) phosphorus via the Trofimov–Gusarova reaction [41–43] in a KOH–DMSO (H_2O) system at heating (100°C and 3 h in the case of red phosphorus, 75°C and 3 h in the case of white phosphorus; argon). The phosphine yield is 62 (red phosphorus) and 50% (white phosphorus) [41, 42]. The activation with microwave irradiation (300 W) has decreased the duration of the red phosphorus reaction with 2-bromopyridine down to 20 min [43] (Scheme 8).

The described reaction occurs likely via initial splitting of elemental phosphorus by weakly solvated hydroxide ions yielding phosphorus-centered anions. Interaction of the latter with 2-bromopyridine via aromatic nucleophilic substitution mechanism leads to the formation of tris(2-pyridyl)phosphine (Scheme 9).

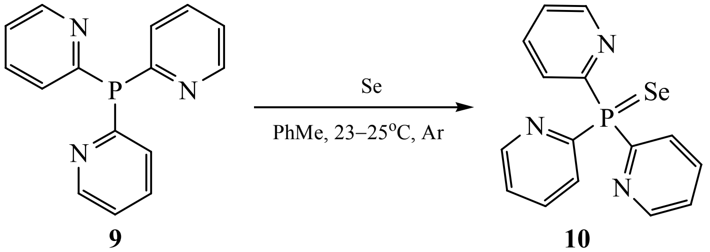
This is the first example of formation of the C_{sp^2}–P bond directly from elemental phosphorus and hetarylhalide.

Hence, the Trofimov–Gusarova reaction is a convenient approach towards synthesis of organophos-

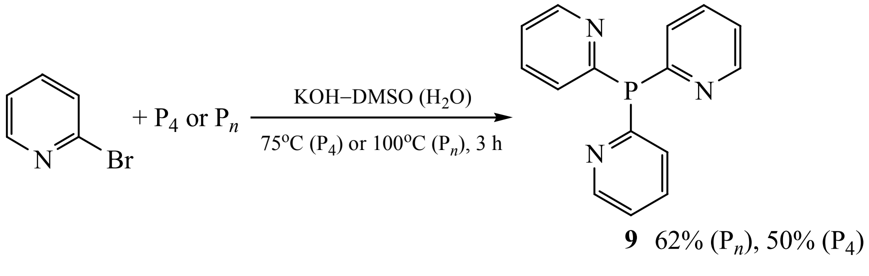
Scheme 6.



Scheme 7.



Scheme 8.



phorus compounds (first of all, organic phosphines and phosphine chalcogenides) based on direct phosphorylation of electrophiles (electrophilic alkenes, acetylenes, and organylhalides) with elemental phosphorus (or the generated phosphine) in the presence of superbases.

2.1. Conformational analysis of secondary arylphosphine selenides. Comprehensive conformational analysis of complex polyfunctional organic compounds (in particular, organophosphorus compounds with several axes of internal rotation) has been rarely reported in the literature; at the best, mutual spatial arrangement of the molecule fragments has been discussed. Detailed conformational analysis can be assessed by the study of the molecules structure in solution taking advantage of complementary physical methods; such approach was used in this work.

In view of the scarce data on the structure of compounds containing P=Se bonds, we performed conformational analysis of phosphine selenides **5**–**8** using the method of dipole moments and quantum chemical calculations [DFT B3PW91/6-31G(d) and B3PW91/6-311++G(3df,3pd)] [20–23, 44] as well as IR spectroscopy of compound **6** in different states of matter [20].

Experimental dipole moments of compounds **5**–**8** were determined in solutions of benzene and dioxane (Table 1). Polarity of the selenides **5**–**8** was typical of compounds containing tetracoordinate phosphorus atom, 2.5–5.0 D [45].

In order to base the experimental values of dipole moments, we calculated all possible conformers of phosphine selenides **5**–**8** using the density functional theory method DFT B3PW91/6-31G(d).

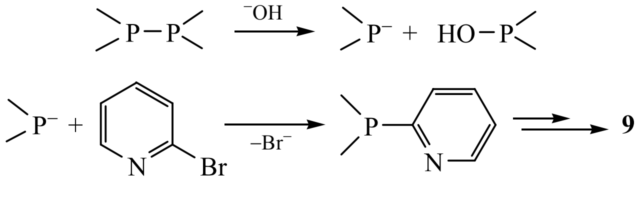
The values of relative energy and dipole moments (theoretical as well as calculated via the vector-additive scheme) of the possible conformers of compound **5** (Fig. 1) are collected in Table 2. The lowest energy corresponded to the symmetric conformer **5a** with the Se=P–C_{sp^3}–C_{sp^3} dihedral angles of 47° and –47° (the g^+ and g^- orientation of the P=Se and C_{sp^3}–C_{sp^3} bonds, respectively) [20, 21, 44]. Such mutual orientation of the bonds is typical of the most of the tetracoordinate phosphorus compounds [49]. Conformers **5b** and **5c** exhibited similar energy values. Neither theoretical nor calculated values of dipole moment of the possible conformers of phosphine selenide **5** coincided with the experimental data, even though a series of model compounds with different surroundings of the phosphorus atom and the reported polarity were considered to determine the dipole moment of the P=Se bond (Table 2). It should be noted that the use of the conformationally uniform rigid bicyclic selenophosphate [47] as the model compound was less appropriate, since that molecule contained no P–C bonds. Even with the lowest dipole moment of the P=Se bond (2.50 D) [47] used for the calculation, the theoretical and calculated dipole moments of all the conformers of compound **5** were lower than the experimental value. This fact deserves further investigation involving the extended range of the phosphorus compounds containing the P=Se bond. Accounting for the close values of energy of conformers **5a**–**5e**, they likely contributed almost equally to the conformational equilibrium.

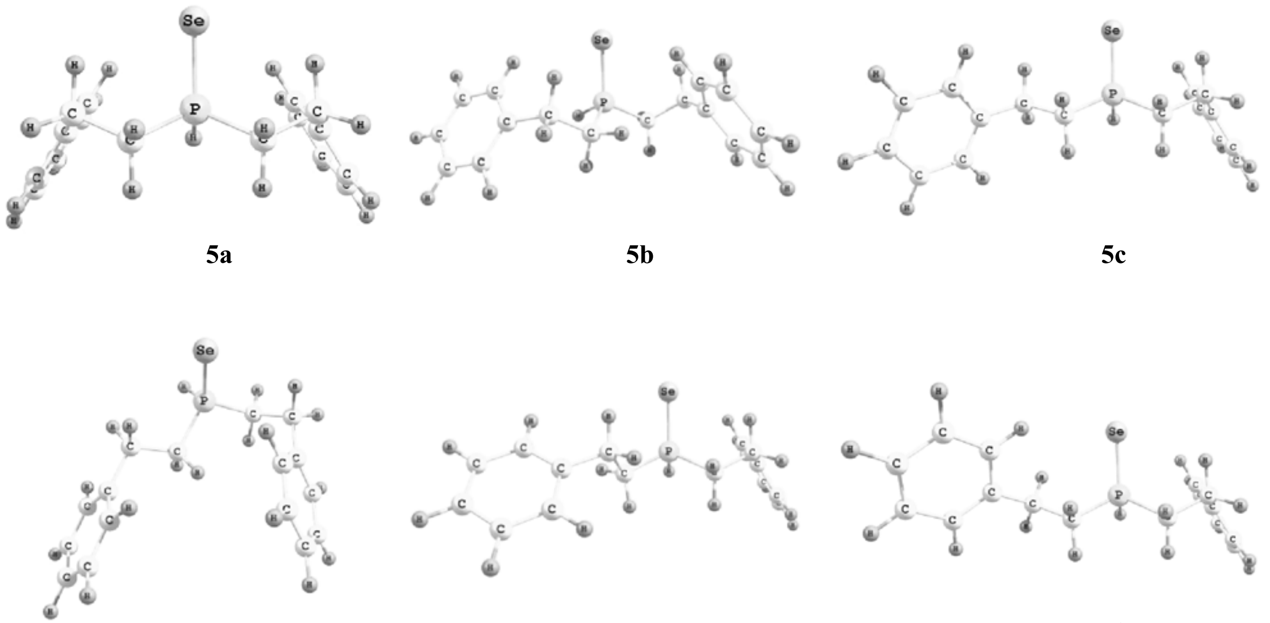
Table 1. Experimental dipole moments of compounds **5**–**8**

Compound	Solvent	μ_{exp}, D
5	Benzene	2.65
	Dioxane	3.25
6	Benzene	4.16
	Dioxane	4.68
7	Benzene	3.94
	Dioxane	4.63
8	Benzene	3.78
	Dioxane	3.69

X-ray diffraction analysis of phosphine selenide **5** [19] showed that the **5e** form with the *gauche*-orientation of the P=Se and C_{sp^3}–C_{sp^3} bonds (Fig. 2a) exists in crystal. The crystal packing of the compound

Scheme 9.





5a **5b** **5c**

5d **5e** **5f**

Fig. 1. Possible conformers of compound **5** according to the B3PW91/6-31G(d) simulation.

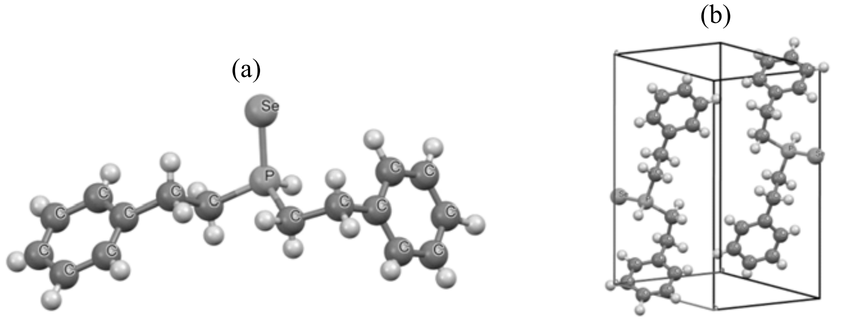


Fig. 2. Geometry of compound **5** molecule (a) in the crystal according to the X-ray diffraction data [19] and (b) crystal packing of phosphine selenide **5** [19].

(Fig. 2b) showed no π-stacking interactions between the parallel benzene rings.

Since the experimental and theoretical values of dipole moments of compound **5** were different, we calculated the theoretical dipole moments of the preffered in energy conformer **5a** using a variety of quantum chemical methods and basis sets (Table 3). In general, the values determined using different non-empirical methods were fairly close. Hence, we failed to understand the deviation from experimental of the theoretical dipole moments of phosphine selenide **5** conformers.

IR spectral data (KBr) for phosphine selenides **5** and **6** have been reported in [19, 40]. An absorption band of medium intensity at 440 to 600 cm^{-1} has been generally assigned to the P=Se bond stretching vibrations. Comparative analysis of IR spectra of compound **6** [20] recorded in different states of the specimen (crystal, melt, and solution in CCl_4 or CH_2Cl_2) showed that the number of the bands was the same for solid and liquid samples (Fig. 3) evidencing the presence of a single major conformer in all states or the identity of the spectra of the rotamers in the 400–1600 cm^{-1} range. It should be noted that the position of the band assigned to the P=Se bond vibration (440 cm^{-1}) [19] in IR spectra of compound **6** was the same irrespectively of the state of the specimen (Fig. 3). That vibration was observed as a strong band with a maximum at 442 cm^{-1} in Raman spectrum of compound **6** (Fig. 4).

According to the DFT B3PW91/6-31G(d) quantum chemical simulation, twelve conformers were possible for phosphine selenide **6**, the **6a**-*RR*, **6a**-*RS*, **6a**-*SR*, and

Table 2. Relative energy and dipole moments (theoretical and calculated using the vector-additive scheme) of compound **5** conformers

Conformer	ΔE, kJ/mol	μ_{theor}, D	m(P=>Se), D (model compound)			
			4.00 [45] ($Et_3P=Se$)	3.73 [46] ($Ph_3P=Se$)	3.00 [47] ($EtCl_2P=Se$)	2.50 [48] [$MeC(CH_2O)_3P=Se$]
			μ_{calc}, D			
5a	0.0	4.36	4.64	4.38	3.67	3.20
5b	1.0	4.33	4.80	4.53	3.81	3.31
5c	5.7	4.42	4.66	4.39	3.67	3.18
5d	7.0	4.41	4.74	4.47	3.75	3.26
5e	7.5	4.38	4.73	4.46	3.74	3.25
5f	10.3	4.34	4.88	4.61	3.89	3.39

6a-*SS* forms being the most favorable (Table 4 and Fig. 5) [21, 23, 44]. These were non-symmetrical structures showing the Se=P–C_{sp^3}–C_{sp^3} dihedral angles of 40–60° (*gauche*-orientation of the P=Se and C_{sp^3}–C_{sp^3} bonds); the **6b**-*RR*, **6b**–**6d**-*SR* conformers were close in energy as well.

Dipole moments of the possible conformers of compound **6** were calculated using the P=Se bond polarity values given in Table 4. As expected, the bicyclic selenophosphate was not a suitable model compound. The obtained results coincided fairly well with the experiment (Table 4). Similarly to the case of compound **5**, the equilibrium of the coexisting conformers close in the energy could not be excluded for compound **6**. That was a reason for the no changes in IR spectra of compounds **5** and **6** depending on the state of the specimen (crystal, melt, or solution) [20]: evidently, the spectral parameters of the conformers in equilibrium were close.

The simple 6-31G(d) and the extended 6-311++G(3df,3pd) basis sets were used in the quantum chemical calculation of the possible conformers of bis[(4-*tert*-butylphenyl)ethyl]phosphine selenide **7** and bis[(4-chlorophenyl)ethyl]phosphine selenide **8** [22]. The resulting most probable conformers are shown in Fig. 6.

In the case of the phosphine selenide **8**, the B3PW91/6-31G(d) results showed that the lowest energy corresponded to the symmetrical **8a** conformer, however, the simulation in the extended basis set evidenced the preference for conformer **8b** (Table 5). The dipole moment of the conformer **8b** determined in both sets was in better agreement with the experiment than the values for conformer **8a**; hence, the conformer **8b** was likely the preferred one. The dipole moments of the conformers calculated via the vector-additive scheme disagreed with both the theoretical and the experimental data. Probably, conformers **8a**–**8c** existed in the conformational equilibrium, since their relative energies were close.

Similarly, in the case of the phosphine selenide **7** the simulation using different basis sets predicted the energy preference for different conformers, even though the simulated dipole moments were close. Accounting for the slight energy difference between the conformers (4 kJ/mol as determined in the extended basis set), the equilibrium of three conformers of compound **7** in the solution could be expected.

Hence, the dipole moment measurement, IR spectroscopy, and quantum chemical calculation showed

Table 3. Dipole moments (μ_{theor}) of the favorable by energy conformer **5a** (ΔE = 0.0 kJ mol^{-1}) determined via various quantum chemical methods

Calculation method	μ_{theor}, D
PM3	5.35
HF/6-31G(d)	5.04
HF/6-311++G(3df,3pd)	5.17
B3PW91/6-31G(d)	4.36
B3PW91/6-311++G(3df,3pd)	4.36
B3PW91/cc-pVTZ	4.46
MP2/6-31G (d)	4.93

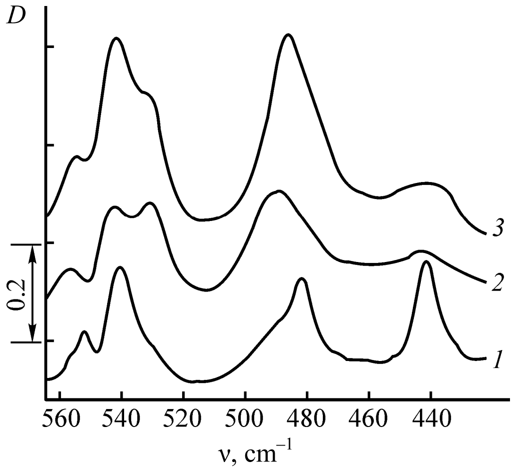


Fig. 3. IR spectra of compound **6** in the crystal (*1*), the melt (*2*), and the solution in CH_2Cl_2 (*3*).

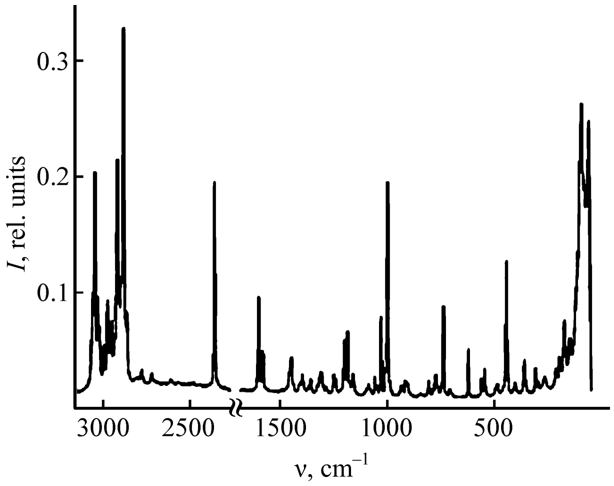


Fig. 4. Raman spectrum of compound **6** in the crystal.

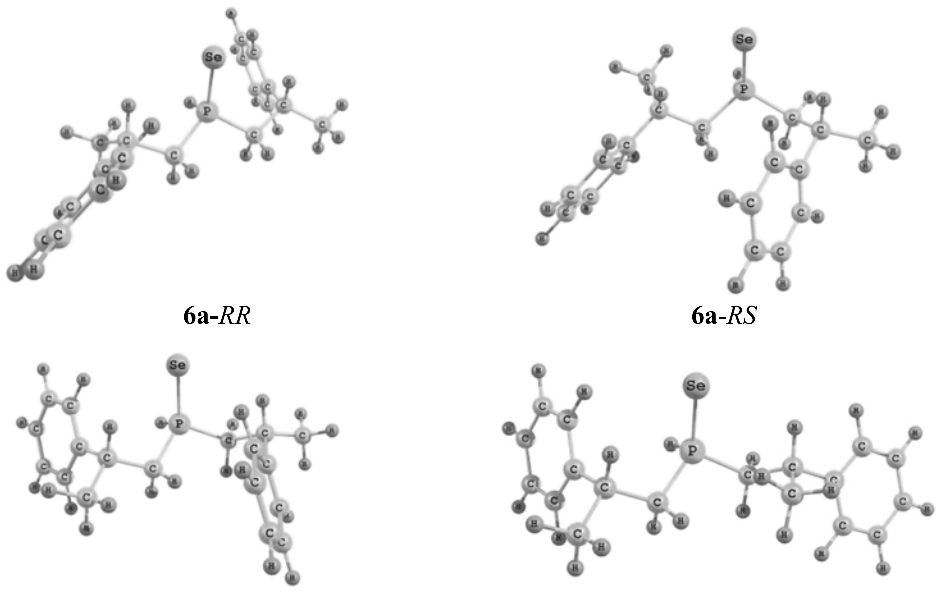
that compounds **5**–**8** in the solution were mixtures of several conformers close in energy; the *gauche*-orientation of the P=Se and C_{sp^3}–C_{sp^3} bonds exists in all the coexisting conformations, typical of the rotation around the P–C_{sp^3} bond in the compounds containing tri- and tetracoordinate phosphorus atom [49].

2.2. Conformational analysis of tris(2-pyridyl)-phosphine and tris(2-pyridyl)phosphine selenide. Tris(2-pyridyl)phosphine and its chalcogenides have been used as convenient models in the study of conformational behavior of organic compounds of tri- and tetracoordinate phosphorus [24]. The earlier undefined polarities of tris(2-pyridyl)phosphine **9** and tris(2-pyridyl)phosphine selenide **10** have been determined, quantum chemical calculation of the dipole moments of the possible conformers of these compounds has been performed, and their polarity has been calculated using the vector-additive scheme [24].

Figures 7 and 8 display the values of relative energy and experimental as well as theoretical dipole

Table 4. Relative energy and dipole moments (theoretical and calculated using the vector-additive scheme) of compound **6** conformers

Conformer	Δ*E*, kJ/mol	μ_{theor}, D	*m*(P=>Se), D (model compound)			
			4.00 [45] ($Et_3P=Se$)	3.73 [46] ($Ph_3P=Se$)	3.00 [47] ($EtCl_2P=Se$)	2.50 [48] [$MeC(CH_2O)_3P=Se$]
			μ_{calc}, D			
6a-*RR*	0.0	4.22	4.56	4.29	3.57	3.07
6b-*RR*	1.9	4.14	4.63	4.36	3.63	3.13
6c-*RR*	7.6	4.24	4.68	4.41	3.68	3.18
6a-*SS*	0.0	4.19	4.58	4.32	3.59	3.09
6b-*SS*	13.0	4.29	4.77	4.50	3.78	3.28
6a-*RS*	0.0	4.19	4.57	4.30	3.58	3.08
6b-*RS*	8.0	4.22	4.61	4.34	3.62	3.12
6a-*SR*	0.0	4.13	4.73	4.46	3.74	3.25
6b-*SR*	3.1	4.23	4.86	4.59	3.87	3.37
6c-*SR*	5.5	4.23	4.93	4.66	3.94	3.45
6d-*SR*	2.2	4.31	4.16	3.90	3.19	2.70
6e-*SR*	6.3	5.22	4.56	4.29	3.58	3.09



6a-*RR* **6a**-*RS*

6a-*SS* **6a**-*SR*

Fig. 5. Preferred conformers of compound **6** according to the B3PW91/6-31G(d) calculation.

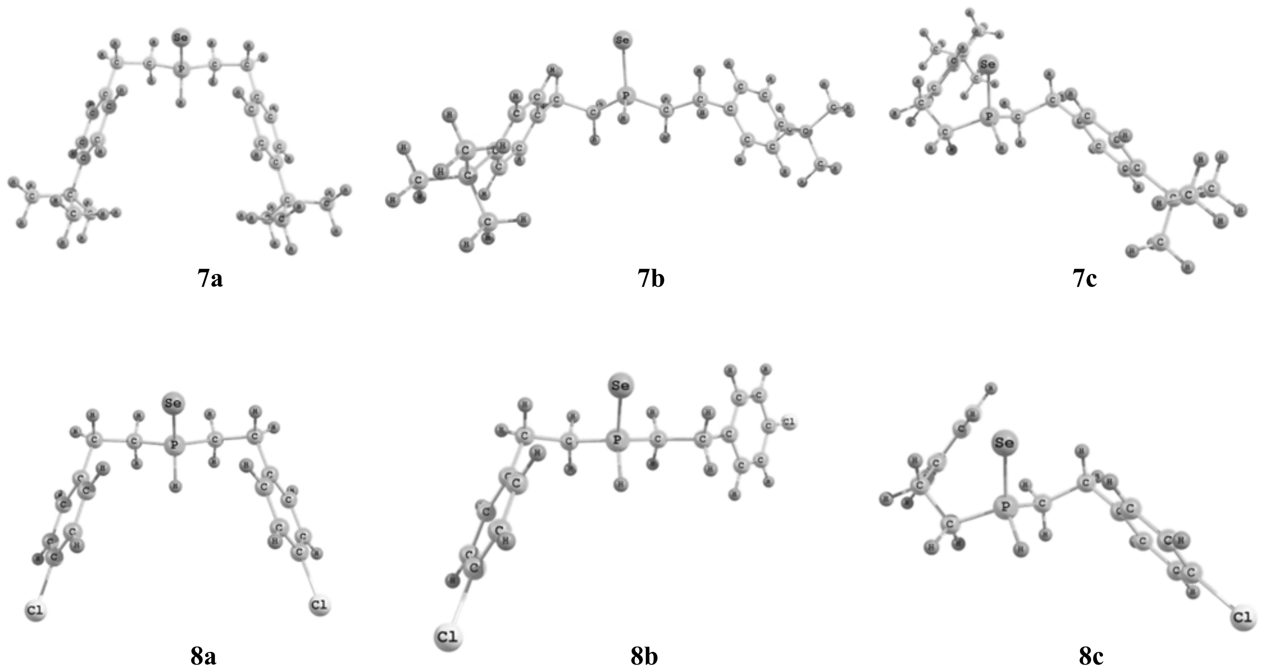
moments of the possible conformers of compounds **9** and **10**. The experimental dipole moment of compound **9** was unexpectedly high (4.16 D); dipole moments of the trivalent phosphorus compounds typically do not exceed 3 D [45]. ^{31}P NMR spectrum of phosphine **9** registered under similar conditions (dioxane, δ_P = –1.44 ppm) was practically identical to that reported in the literature (–1.98 ppm) [42]; thus, the compound did not undergo any transformations under the experimental conditions. Further studies confirmed that tris(2-pyridyl)phosphine was in fact very polar.

According to the calculation data, tris(2-pyridyl)phosphine **9** and its selenide **10** have the pyramidal structure, the pyridyl rings being located in the propeller shape with respect to the P=Y fragment (Y = lone-electron pair or Se atom).

In the case of the unsubstituted phosphine **9** (Fig. 7), two conformations corresponded to the energy minimum: **9a** with the nitrogen atoms of all the three pyridyl rings being directed towards the P=Y fragment and **9b** with only two pyridyl nitrogen atoms directed towards P=Y. The *cis*-Y–P–C_{sp2}–N dihedral angles were of 50°–60°, corresponding to the *gauche,gauche, -gauche*-orientation of the pyridyl rings rotating around the P–C_{sp2} (cycle) bond. The proportion between the theoretical and experimental dipole moments evidenced the conformational equilibrium of the **9a** and **9b** forms in solution. According to the X-ray diffraction data [50], weak intermolecular C–H···N interactions were operative in compound **9**, likely responsible for its high polarity in comparison with the other trivalent phosphorus compounds [45]. The low dielectric constant (and, thus, dipole moment) values

Table 5. Relative energy and dipole moments (theoretical and calculated using the vector-additive scheme) of compounds **7** and **8** conformers

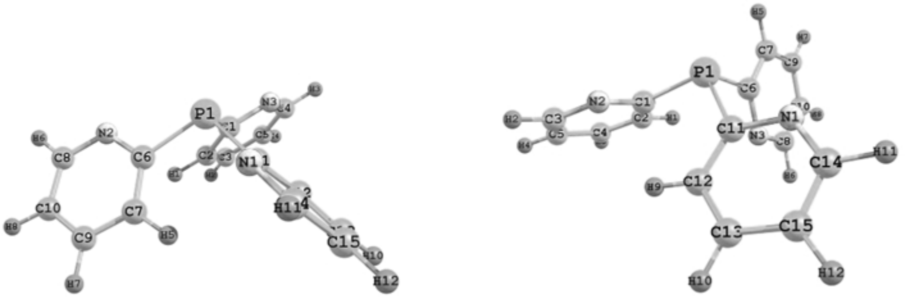
Conformer	B3PW91/6-31G(d)		B3PW91/6-311++G(3df,3pd)		μ_{calc}, D
	Δ*E*, kJ/mol	μ_{theor}, D	Δ*E*, kJ/mol	μ_{theor}, D	
7a	0.00	4.40	0.92	4.63	4.90
7b	5.65	4.57	0.00	4.69	4.91
7c	0.96	4.38	4.14	4.65	4.85
8a	0.00	5.69	0.35	5.02	5.79
8b	6.42	3.71	0.00	3.51	4.28
8c	0.72	4.25	3.51	3.79	4.71



7a **7b** **7c**

8a **8b** **8c**

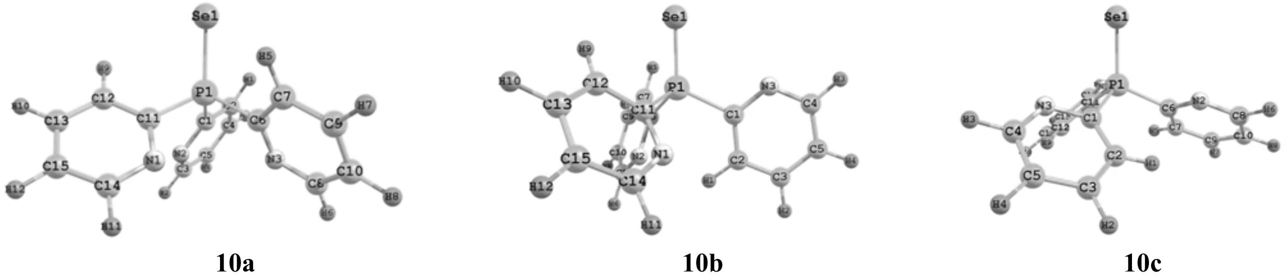
Fig. 6. Possible conformers of compounds **7** and **8** according to the B3PW91/6-311++G(3df,3pd) simulation.



9a
μ_{theor} = 5.61 D, Δ*E* = 0.0 kJ/mol

9b
μ_{theor} = 3.82 D, Δ*E* = 1.8 kJ/mol

Fig. 7. Possible conformers of compound **9** (μ_{exp} = 4.16 D, dioxan).



10a
μ_{theor} = 3.64 D, Δ*E* = 0.0 kJ/mol

10b
μ_{theor} = 5.85 D, Δ*E* = 9.1 kJ/mol

10c
μ_{theor} = 8.60 D, Δ*E* = 26.3 kJ/mol

Fig. 8. Possible conformers of compound **10** (μ_{exp} = 4.19 D, dioxane).

are typical of compounds with the intramolecular hydrogen bonding [51].

In the case of tris(2-pyridyl)phosphine selenide **10**, the **10a** form with the nitrogen atoms of all the pyridyl rings directed oppositely with respect to the P=Se group (the *trans,trans,trans*-orientation of the pyridyl cycles with respect to the P=Se bond) was the most favorable conformation (Fig. 8). The **10b** conformer had the *trans,trans,cis*-orientation of the pyridyl rings with respect to the P=Se bond. The **10c** conformer with the highest relative energy showed the *gauche,gauche,gauche*-orientation of the pyridyl rings with respect to the P=Se bond (Fig. 8). Comparative analysis of the theoretical and experimental dipole moments of compound **10** evidenced the predominant presence of the **10a** conformer in the solution, the **10b** conformer being the minor component.

It should be noted that tris(2-pyridyl)phosphine oxide and tris(2-pyridyl)phosphine sulfide existed in the form of the predominant conformer (the pyridyl rings in *gauche*- or *trans*-orientation with respect to the P=O or P=S bond) in the equilibrium with the second minor form in the solution [24].

The *m*(Het→P) group moment of 3.41 D was determined using the unsubstituted phosphine **9** as the model compound. If primary pyridylphosphine ($\mu_{\text{theor}} =$ 2.83 D) or secondary bispyridylphosphine ($\mu_{\text{theor}} =$ 3.26 D) were used as the model compounds, the *m*(Het→P) group moment was of 5.31 and 3.54 D, respectively. The closeness of the first and the third mentioned dipole moment values was remarkable. However, the vector-additive calculation of dipole moment of the phosphine selenide **10** using those values did not afford the dipole moment coinciding with the experimental data. All the calculated dipole moments were significantly higher (by at least 2 D) than the experimental value. It should be noted that the vector-additive dipole moment value was independent of the direction of the nitrogen atoms of the heterocycles with respect to the P=Y fragment [24].

Hence, the method of dipole moments and quantum chemical calculations revealed that the preferred conformations of tris(2-pyridyl)phosphine and its selenide (*gauche* and *trans* forms with the propeller-like orientation of the pyridyl rings with respect to the P=Y fragment) were in line with the general conformational behavior of tri- and tetra-coordinate phosphorus compounds containing alkyl or thioalkyl substituents.

EXPERIMENTAL

Experimental dipole moments of compounds **5–9** in solution of benzene or dioxane were determined using the Debye II method [20–24]. The vector-additive calculation of the dipole moments of compounds **5–9** was performed using the geometry parameters derived from the quantum chemical calculation as well as the dipole moments of the bonds and groups given in [45, 52, 53].

The quantum chemical calculations were performed as follows. First, the fast search for the possible conforma-tions of the studied compounds was carried out applying the DFT B3PW91/6-31G(d) method, and then the refining calculation was run in the extended 6-311++G(df,p) basis set. However, in certain cases the B3PW91/6-311++G(df,p) and the B3PW91/6-31G(d) calculations evidenced the different conformations corresponding to the energy minimum. In those cases, modern wB97XD DFT method was used, including the exchange functional accounting for the dispersion intramolecular interactions [54]. When combined with the extended basis set, the latter method gave better agreement of the calculated data with the experimental ones; however, it was more time-consuming.

In the case of the B3PW91 method, the dipole moment values were practically independent of the applied basis set, including the set of the Slater functions. Dipole moments determined using the semi-empirical PM3 method were somewhat higher than in the cases of the non-empirical methods. The dipole moments determined by the different non-empirical methods were generally close.

Quantum chemical calculations were performed using GAUSSIAN 09 software [55], with full geometry optimization. The correspondence of the found stationary points to the energy minimum in all cases was confirmed by the calculation of the second derivatives of the energy over the atomic coordinates; all equilibrium structures corresponding to the stationary points of the potential energy minimum had only positive frequencies.

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