

Conference paper

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Polarity and structure of derivatives of bis(2-phenylethyl)selenophosphinic acid

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Abstract: Conformational analysis of derivatives of bis(2-phenylethyl)selenophosphinic acid was carried out by the method of dipole moments and density functional theory calculations. The conformations of the examined compounds fit into the overall conformational picture for the PIV compounds: these derivatives exist as conformational equilibrium of non-eclipsed *gauche* and *trans* forms with propeller arrangement of the substituents relative to the P=Se bond. We stipulate that the eclipsed *cis* orientation of substituent may be caused by the formation of H-contact.

Keywords: conformational analysis; DFT calculations; dipole moments; ICPC-21; phosphine selenides; phosphinoselenoates.

Introduction

Phosphinochalcogenoic esters, thioesters, and amides have attracted considerable attention due to their applications as drug intermediates [1–4], ligands for the design of metal complexes [5–7], flame retardants for polymeric materials [8], as well as building blocks in organic and elementoorganic synthesis [9–13]. Thioselenophosphinic *S*-esters and amides are of particular interest as promising selenium sources for the preparation of metal selenide thin films [14] and selenium-containing nanoparticles [15].

The oxidative transition-metal free cross-coupling reaction between secondary phosphine selenides and various phenols, thiols or amines using the carbon tetrachloride/triethylamine system under mild conditions resulted in previously unknown phosphinochalcogenoic *O*-esters, *S*-esters, and amides in high yields [15–17]. The starting secondary phosphine selenides were prepared via the Trofimov-Gusarova reaction (a halogen-free method from red phosphorus, styrenes and elemental selenium) [18–22].

Previously, we have carried out the conformational analysis of some secondary bis(2-phenylethyl)- and bis(2-phenylpropyl)phosphine arylalkylphosphine selenides [23, 24] and tris(2-pyridyl)phosphine selenide [25]. The data on synthesis, polarity, and conformational analysis using a complex of physical methods (IR spectroscopy, dipole moments, and quantum chemical calculation) of these compounds are presented in [26].

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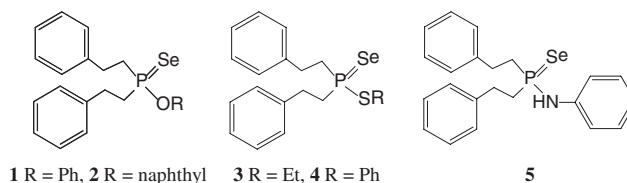
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Results and discussion

In this study, we have determined previously unknown polarities of *O*-phenyl diphenethylphosphinosele-noate **1**, *O*-(naphthalen-1-yl) diphenethylphosphinosele-noate **2**, *S*-ethyl diphenethylphosphinosele-nothioate **3**, *S*-phenyl diphenethylphosphinosele-nothioate **4**, and *P,P*-diphenethyl-*N*-phenylphosphinosele-noic amide **5**, carried out quantum chemical calculations of the dipole moments of their possible conformers, and calculated polarities of these conformers according to the vector-additive scheme.



For determining the experimental values of the dipole moments, we used the second Debye method based on the measurement of the dielectric constant of the dilute solutions of the polar substance in a nonpolar solvent. The experimental dipole moments of **1–5** are listed in Table 1, their values are sufficiently high and are typical for the polarities of the compounds of tetra-coordinated phosphorus (2.5–5.0 Debye) [27].

In the calculations of dipole moments according to the vector-additive scheme (Table 2) we used the theoretical geometric parameters and the following bonds moments: $m(\text{P} \rightarrow \text{Se}) = 4.00$ D, calculated from $\mu_{\text{exp}} \text{Et}_3\text{P} = \text{Se}$ [27]; $m(\text{P} \rightarrow \text{N}) = 0.31$ D, calculated from $\mu_{\text{exp}} (\text{Me}_2\text{N})_3\text{P}$ [27]; $m(\text{O} \rightarrow \text{P}) = 0.51$ D, calculated from $\mu_{\text{exp}} \text{MeC}(\text{CH}_2\text{O})_3\text{P} = \text{O}$ [27]; $m(\text{S} \rightarrow \text{P}) = 0.80$ D, calculated from μ_{exp} 2-methyl-1,3,2-dithiaphosphinane 2-sulfide [27]; $m(\text{C}_{\text{sp}^3} \rightarrow \text{P}) = 0.55$ D, calculated from $\mu_{\text{exp}} \text{Me}_3\text{P}$ [27]; $m(\text{C}_{\text{sp}^3} \rightarrow \text{C}_{\text{sp}^2}) = 0.75$ D, calculated from $\mu_{\text{exp}} \text{C}_6\text{H}_5\text{CH}_3$ [28]; $m(\text{CPh} \rightarrow \text{N}) = 1.73$ D, calculated from $\mu_{\text{exp}} \text{C}_6\text{H}_5\text{NH}_2$ [28]; $m(\text{H} \rightarrow \text{N}) = 1.31$ D, calculated from $\mu_{\text{exp}} \text{C}_6\text{H}_5\text{NH}_2$ [28]; $m(\text{C}_{\text{Ph}} \rightarrow \text{O}) = 0.37$ D, calculated from $\mu_{\text{exp}} \text{C}_6\text{H}_5\text{OH}$ [28]; $m(\text{C}_{\text{Ph}} \rightarrow \text{S}) = 0.30$ D, calculated from $\mu_{\text{exp}} \text{C}_6\text{H}_5\text{SH}$ [28]; $m(\text{C}_{\text{sp}^3} \rightarrow \text{S}) = 1.14$ D, calculated from $\mu_{\text{exp}} (\text{CH}_3)_2\text{S}$ [28]; $m(\text{C}_{\text{naphthyl}} \rightarrow \text{O}) = 0.33$ D, calculated from $\mu_{\text{exp}} \alpha$ -naphthol [28].

We identified the possible conformations of isolated molecules of **1–5** using the method of density functional theory – B3PW91, and broadened basis 6-311++G(df,p), calculated their theoretical polarities and relative energies, and compared theoretical results with experimental data. According to the data of the theoretical calculations for each of the compounds **1–5**, three energetically possible conformers were found (relative energy of preferred conformers is not more than $5.1 \text{ kJ} \cdot \text{mol}^{-1}$), which arise as a result of internal rotation about to the $\text{P}-\text{C}_{\text{sp}^3}$, $\text{P}-\text{O}$, $\text{P}-\text{S}$ or $\text{P}-\text{N}$ bonds.

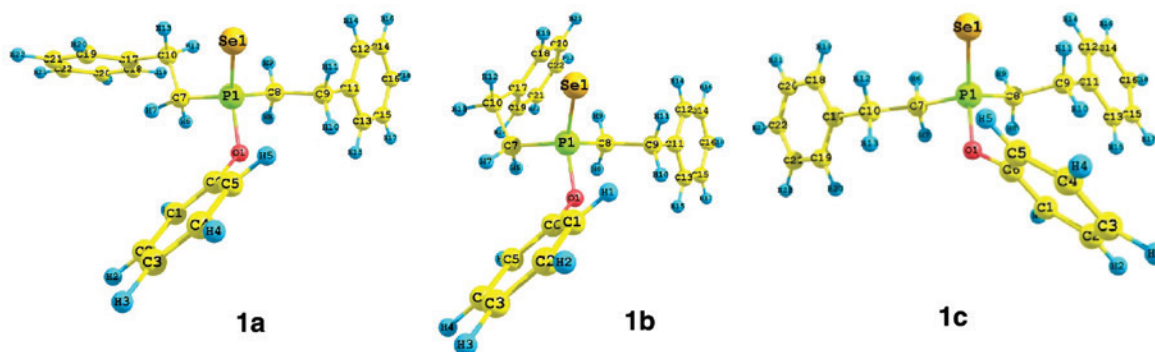
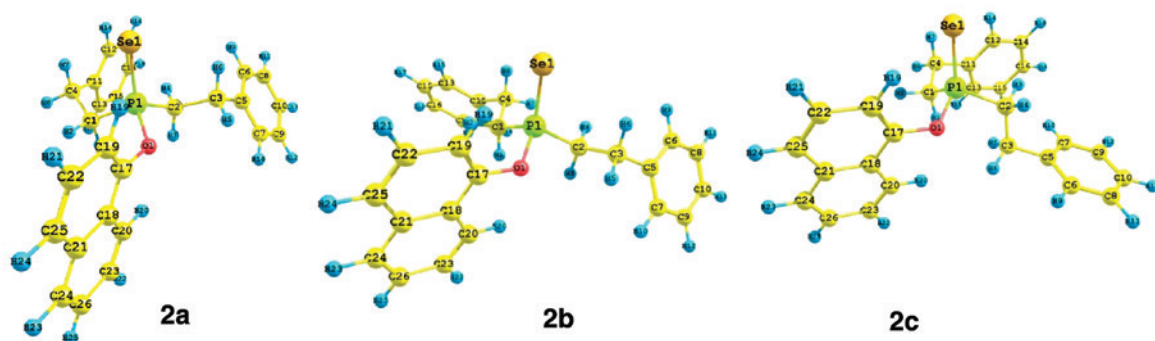
The possible conformers of **1–5** are shown in Fig. 1–3, 5 and 6, while their relative energy values, theoretical and calculated according to vector-additive scheme dipole moments are listed in Table 2. The percentage of possible conformers (n , %) was found using values of calculated according vector-additive scheme dipole moments of these forms:

Table 1: Coefficients in the calculation equations, orientation polarizabilities, and experimental dipole moments of **1–5**.

Compound	Solvent	α	γ	$P_{\text{or}}, \text{cm}^3$	$\mu_{\text{exp}}, \text{D}$
1	Benzene	5.430	0.300	399.046	4.40
	Dioxane	6.670	0.398	426.824	4.55
2	Benzene	4.925	0.296	403.660	4.42
	Dioxane	5.040	0.580	276.766	3.64
3	Benzene	3.333	0.287	218.515	3.25
	Dioxane	5.040	0.580	276.766	3.64
4	Benzene	4.979	0.299	378.169	4.28
	Dioxane	5.731	0.512	367.768	4.22
5	Benzene	6.028	0.314	443.434	4.63
	Dioxane	7.317	0.488	463.277	4.74

Table 2: Relative energies, theoretical and calculated according to vector-additive scheme dipole moments, and percentage of conformers of 1–5.

	ΔE , kJ·mol ⁻¹	μ_{theor} , D	μ_{calc} , D	n , %
1a	0.0	3.32	4.10	11
1b	0.8	3.34	4.48	76
1c	1.9	3.38	4.18	13
2a	0.0	3.75	4.56	30
2b	0.1	3.78	4.20	42
2c	4.4	3.66	4.58	28
3a	0.0	2.50	3.65	46
3b	3.1	2.52	3.50	43
3c	3.6	2.75	4.11	11
4a	0.0	2.98	4.22	41
4b	1.3	3.00	4.55	13
4c	1.3	2.36	4.21	40
5a	0.0	3.83	4.76	31
5b	0.4	4.20	4.40	43
5c	5.1	4.38	4.84	26

**Fig. 1:** The possible conformers of 1 according to DFT B3PW91/6-311++G(df,p) method.**Fig. 2:** The possible conformers of 2 according to DFT B3PW91/6-311++G(df,p) method.

In each of three conformers **1a–c** (Fig. 1, Table 2) with the symmetrical structure, the phosphorus atom has a pyramid coordination, and substituents at the phosphorus atom are arranged like a propeller relative to the P=Se group. Most energetically advantageous conformer is **1a** with *gauche, gauche, gauche*-orientation of the substituents (Csp³–Csp³ and P–O bonds) relative to the P=Se bond (dihedral angles Se=P–C7–C10 54°, Se=P–C8–C9 56°, Se=P–O–C6 48°). Phenyl rings are located *trans* relative to the P–C_{sp³} bonds (dihedral angles

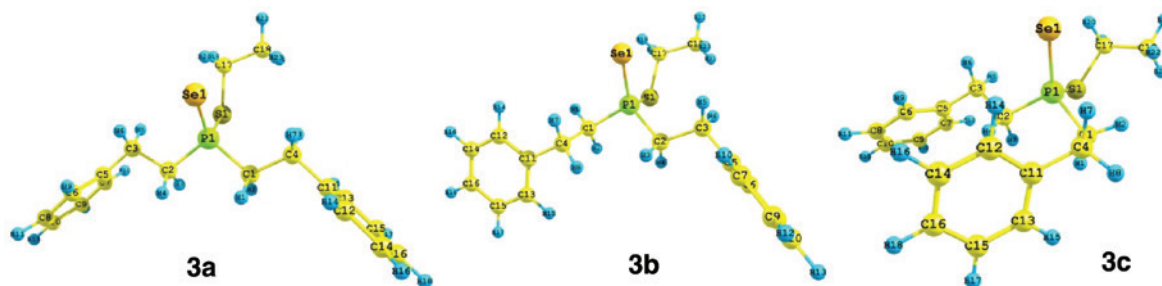


Fig. 3: The possible conformers of **3** according to DFT B3PW91/6-311++G(df,p) method.

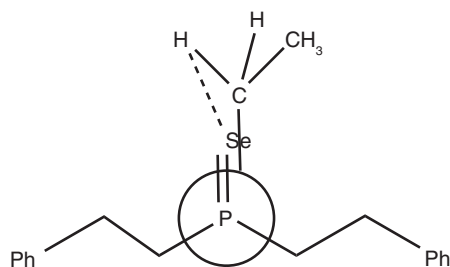


Fig. 4: Intramolecular hydrogen interaction $P=Se \cdots H-C_{sp^3}$ in molecule **3** (Newman's projection).

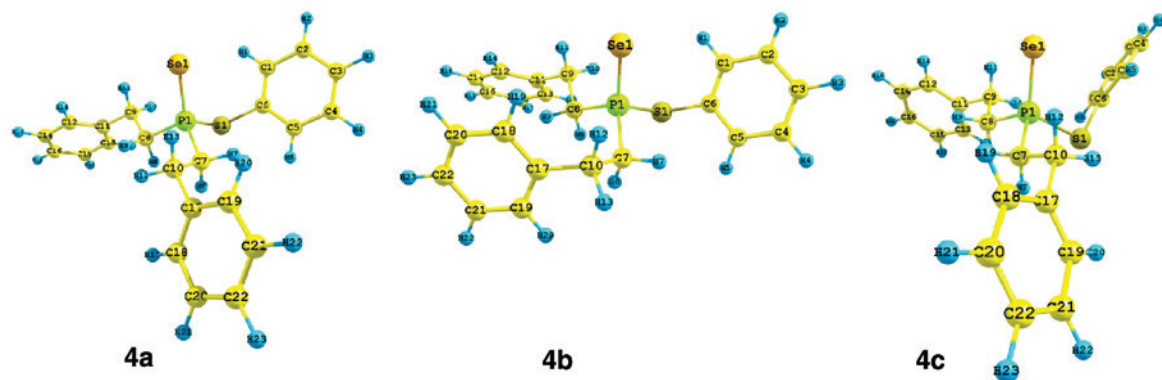


Fig. 5: The possible conformers of **4** according to DFT B3PW91/6-311++G(df,p) method.

$P-C7-C10-C17$ 176° , $P-C8-C9-C11$ 176°). In conformers **1b** and **1c** the substituents at the phosphorus atom are *gauche, gauche, gauche*-oriented as well, and the value of the angles are slightly differed from **1a** (**1b**: dihedral angles $Se=P-C7-C10$ 46° , $Se=P-C8-C9$ 55° , $Se=P-O-C6$ 48° ; **1c**: dihedral angles $Se=P-C7-C10$ 58° , $Se=P-C8-C9$ 47° , $Se=P-O-C6$ 54°), phenyl rings are located *gauche* and *trans* in **1b**, and *trans* in **1c** relative to the $P-C_{sp^3}$ bonds (**1b**: dihedral angles $P-C7-C10-C17$ 70° , $P-C8-C9-C11$ 179° ; **1c**: dihedral angles $P-C7-C10-C17$ 177° , $P-C8-C9-C11$ 175°).

Theoretical and calculated using additive scheme dipole moments of conformers **1a–c** are in agreement with the experimental data (Table 2). Relative energies as well as theoretical and calculated dipole moments of all three conformers **1a–c** are very close to each other, which indicates the conformational equilibrium in **1**. Comparison of the polarity data (Table 2) shows that in the conformational equilibrium of compound **1** the prevailed form is conformer **1b** (76%); conformers **1a** and **1c** are almost equally present in the equilibrium.

Exchange of phenoxyl substituent for a bulkier naphthyl fragment in **2** does not lead to the significant changes in the arrangement of substituents at the phosphorus atom. For phosphinoselenoate **2**, there are

three energetically preferable conformers (Fig. 2, Table 2). Conformers **2a** and **2b** are almost equal in relative energy. In both conformers, substituents at the phosphorus atom which has pyramidal structure are symmetrically arranged *gauche, gauche, gauche* (mutual orientation of the $C_{sp^3}-C_{sp^3}$ and P–O bonds relative to the P=Se bond; **2a**: dihedral angles Se=P–C1–C4 45°, Se=P–C2–C3 57°, Se=P–O–C17 66°; **2b**: dihedral angles Se=P–C1–C4 53°, Se=P–C2–C3 58°, Se=P–O–C17 65°).

The phenyl rings of the phenylethyl fragments are located *gauche* or *trans* relative to the $C_{sp^3}-C_{sp^3}$ bonds (**2a**: dihedral angles P–C1–C4–C11 71°, P–C2–C3–C5 –178°; **2b**: dihedral angles P–C1–C4–C11 176°, P–C2–C3–C5 176°). In conformer **2c**, one of the phenylethyl fragments is oriented *trans*, and second phenylethyl as well as the phenoxy group are oriented *gauche* relative to the P=Se bond (dihedral angles Se=P–C1–C4 46°, Se=P–C2–C3 178°, Se=P–O–C17 59°), the phenyl rings maintain *gauche* and *trans* positions relative to the $C_{sp^3}-C_{sp^3}$ bonds (dihedral angles P–C1–C4–C11 73°, P–C2–C3–C5 176°).

Comparison of the values of theoretical, calculated and experimental dipole moments of **2a**, **2b**, and **2c** conformers also supports conformational equilibrium in solution of **2**, however, while in **1** one conformer predominates, in **2** the percentages of **2a**, **2b**, and **2c** forms are practically equal.

In phosphinoselenothioate **3**, oxygen-containing fragment at the phosphorus atom replaced by the thioethyl group. The minimum of relative energy corresponds to the conformer **3a**, and two other preferred conformers **3b** and **3c** have higher energies by 3.1 and 3.6 kJ mol⁻¹ respectively (Fig. 3, Table 2). In conformer **3a** the symmetrically arranged phenylethyl substituents have *gauche* orientation relative to the P=Se bond (dihedral angles Se=P–C1–C4 –55°, Se=P–C2–C3 54°), while the thioethyl group is in eclipsed *cis* position (dihedral angle Se=P–S–C17 is only 4°). The phenyl rings of the phenylethyl fragments are *trans* arranged relative to the $C_{sp^3}-C_{sp^3}$ bonds (dihedral angles P–C1–C4–C11 178°, P–C2–C3–C5 –179°). In less symmetrical conformers **3b** and **3c**, the arrangement of substituents at the phosphorus atom remains (**3b**: dihedral angles Se=P–C1–C4 –59°, Se=P–C2–C3 –55°, Se=P–S–C17 4°; **3c**: dihedral angles Se=P–C1–C4 45°, Se=P–C2–C3 49°, Se=P–S–C17 22°, which corresponds to the *gauche, gauche, cis*-orientation of the $C_{sp^3}-C_{sp^3}$ and S– C_{sp^3} bonds relative to the P=Se group). In phenylethyl fragments of **3b** aromatic rings are *trans* arranged relative to the $C_{sp^3}-C_{sp^3}$ bonds (dihedral angles P–C1–C4–C11 174°, P–C2–C3–C5 177°), and in **3c** – *gauche* and *trans* (dihedral angles P–C1–C4–C11 71°, P–C2–C3–C5 179°).

In all three conformers **3a–c** eclipsed orientation of the P=Se and S– C_{sp^3} bonds of the thioethyl fragment (Fig. 4) is favorable for the formation of intramolecular hydrogen interaction P=Se···H– C_{sp^3} (Se···H distance in **3a** – 2.76 Å, **3b** – 2.76 Å, **3c** – 2.81 Å) [29]. These H-contacts define the lower value of polarity of phosphine selenide **3** in comparison with the compounds **1**, **2**, **4**, and **5** (Table 1), since it is well known that compounds with an intramolecular hydrogen bond are usually characterized by low values of dielectric permittivity and, accordingly, dipole moments [30].

Furthermore, analysis of the experimental frequencies of the stretching vibrations of the P=Se bond in **1–5** shows lowest value of ν P=Se 527 cm⁻¹ for the phosphinoselenothioate **3** [15] (ν P=Se 583 cm⁻¹ for **1** [16]; ν P=Se 587 cm⁻¹ for **2** [16]; ν P=Se 574 cm⁻¹ for **4** [15]; and ν P=Se 577 cm⁻¹ for **5** [17]), which also supports to the existence of intramolecular P=Se···H– C_{sp^3} contact.

The values of theoretical, calculated according to additive scheme, and experimental dipole moments are in good agreement (Table 2). Based on a comparison of the polarities of **3a–c** conformers, we believe that in solution phosphinoselenothioate **3** exists as conformational equilibrium, in which **3a** and **3b** forms are equally probable, and the conformer **3c** is minor.

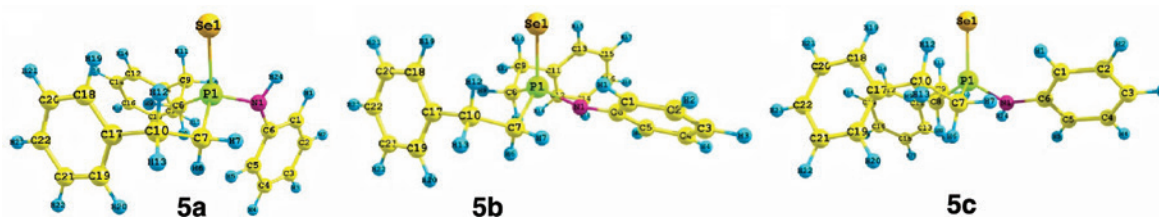


Fig. 6: The possible conformers of **5** according to DFT B3PW91/6-311++G(df,p) method.

Replacement of ethyl radical for a phenyl in **4** leads to a change of this substituent orientation (Fig. 5, Table 2). In conformer **4a**, substituents at the phosphorus atom are arranged symmetrically in the form of a propeller, and have *gauche, gauche, gauche*-orientation of the P–C_{sp³} bonds relative to the P=Se bond (dihedral angles Se=P–C7–C10 53°, Se=P–C8–C9 51°, Se=P–S–C6 51°), the phenyl rings under the rotation about the C_{sp³}–C_{sp³} bonds occupy *trans* position relative to the P–C_{sp³} bonds (dihedral angles P–C7–C10–C17 –176°, P–C8–C9–C11 –177°). Energies of conformers **4b** and **4c** are close to that of **4a**, the substituents at the phosphorus atom are arranged *gauche, gauche, gauche* (**4b**: dihedral angles Se=P–C7–C10 45°, Se=P–C8–C9 49°, Se=P–S–C6 50°; **4c**: dihedral angles Se=P–C7–C10 –50°, Se=P–C8–C9 56°, Se=P–S–C6 –31°), the phenyl rings are *trans*-oriented relative to the P–C_{sp³} bonds in **4c** (dihedral angles P–C7–C10–C17 178°, P–C8–C9–C11 –176°) and *gauche, trans* – in **4b** (dihedral angles P–C7–C10–C17 71°, P–C8–C9–C11 –179°). Among the energetically preferred conformers **4a–c** two are equally probable: **4a** corresponding to the energy minimum and **4c** (Table 2), their calculated using additive scheme dipole moments are almost equal to the experimental values for **4** both in benzene and in dioxane. Based on the correlation of the theoretical and experimental polarity data, there is a conformational equilibrium of **4a**, **4b**, and **4c** in solution.

For compound **5**, three preferred conformers were found according to quantum chemical calculations (Fig. 6, Table 2). The energy minimum corresponds to conformer **5a**, in which the C_{sp³}–C_{sp³} bonds of phenylethyl substituents at the P atom are arranged *gauche, gauche* relative to the P=Se bond (dihedral angles Se=P–C7–C10 45°, Se=P–C8–C9 55°), and the phenyl ring at the nitrogen atom is *trans* oriented relative to the P=Se bond (dihedral angle Se=P–N–C6 –162°).

Relative energies of **5a** and **5b** conformers are almost equal, the arrangement of phenylethyl fragments in **5a** and **5b** is similar (dihedral angles Se=P–C7–C10 40°, Se=P–C8–C9 48°), but in **5b** the N–C_{sp²} bond is *gauche* oriented relative to the P=Se bond (dihedral angle Se=P–N–C6 is 54°), and the same orientation of the C_{sp³}–C_{sp³} and N–C_{sp²} bonds is observed in **5c** (dihedral angles Se=P–C7–C10 42°, Se=P–C8–C9 53°, Se=P–N–C6 54°). The phenyl rings are *gauche, trans*-oriented relative to the P–C_{sp³} bond in **5a** (dihedral angles P–C7–C10–C17 72°, P–C8–C9–C11 –178°) and **5c** (dihedral angles P–C7–C10–C17 72°, P–C8–C9–C11 –176°), and *gauche, gauche* – in **5b** (dihedral angles P–C7–C10–C17 73°, P–C8–C9–C11 73°).

In solution of amide **5**, **5a**, **5b**, and **5c** forms are in conformational equilibrium (ratio 1.2 : 1.7 : 1 respectively), which is supported by the similarity between values of the calculated using vector additive scheme

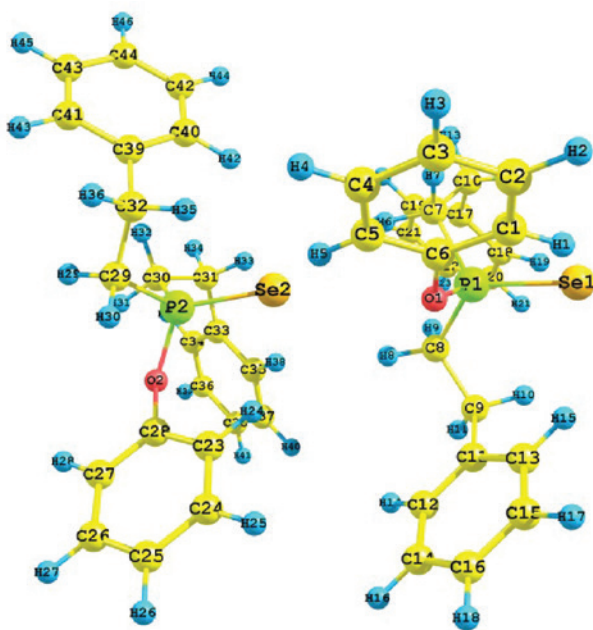


Fig. 7: Dimer structure of **1** according to DFT B3PW91/6-311++G(df,p) method.

and experimental dipole moments. The theoretical dipole moments are in a good agreement with calculated and experimental data.

In order to explain slightly lower theoretical values of dipole moments relative to the experimental values we carried out quantum chemical calculation of the dimer of **1** (Fig. 7). According to the quantum chemical calculation, the energy of the dimer is lower by $36.1 \text{ kJ}\cdot\text{mol}^{-1}$ (i.e. energy gain is twice the energy of the monomer). The dipole moment of dimer **1** increases and is equal to 8.5 D (see polarity value of **1** in Table 2).

Both molecules of dimer **1** have symmetrical propeller structure, and the substituents at the phosphorus atoms in these molecules maintain *gauche, gauche, gauche*-orientation (the $\text{C}_{\text{sp}^3}\text{-C}_{\text{sp}^3}$ and P–O bonds) relative to the P=Se bond (dihedral angles Se1=P1-C7-C10 36° , Se1=P1-C8-C9 33° , Se1=P1-O1-C6 63° ; Se2=P2-C29-C32 37° , Se2=P2-C30-C31 31° , Se2=P2-O2-C28 63°), all $\text{C}_{\text{sp}^2}\text{-C}_{\text{sp}^3}$ bonds of the phenylethyl fragments are also *gauche*-oriented relative to the $\text{C}_{\text{sp}^3}\text{-P}$ bond (dihedral angles P1-C7-C10-C17 74° , P1-C8-C9-C11 77° ; P2-C29-C32-C39 72° , P2-C30-C31-C33 80°).

In dimer of **1** in contrast to the isolated molecules the formation of contacts between the selenium atom of the P2=Se2 group of one of the molecules and different hydrogen atoms is possible, both intramolecular $\text{P2=Se2}\cdots\text{H24-C}_{\text{sp}^2}(\text{OPh})$ (2.710 Å), $\text{P=Se2}\cdots\text{H38-C}_{\text{sp}^2}(\text{Ph1})$ (2.886 Å), $\text{P=Se2}\cdots\text{H42-C}_{\text{sp}^2}(\text{Ph2})$ (2.896 Å), and intermolecular $\text{P=Se2}\cdots\text{H5-C}_{\text{sp}^2}(\text{Ph})$ (2.801 Å), and $\text{P=Se2}\cdots\text{H24-C}_{\text{sp}^3}$ (2.857 Å), which stabilize the dimer structure. It can be concluded that the lower value of the theoretical dipole moment of phosphinoselenoate **1** as compared to the experimental value can be attributed to the partial dimerization of the molecules in solution.

Experimental

O-Phenyl diphenethylphosphinoselenoate **1** and *O*-(naphthalen-1-yl) diphenethylphosphinoselenoate **2** were synthesized according to procedure [16], *S*-ethyl diphenethylphosphinoselenothioate **3** and *S*-phenyl diphenethylphosphinoselenothioate **4** were prepared according to procedure [15], and *P,P*-diphenethyl-*N*-phenylphosphinoselenoic amide **5** was synthesized using procedure [17]. The solvents were purified using standard procedures.

The experimental values of the dipole moments were determined according to the second Debye method. Physical parameters of **1** and **3–5** were measured from series consisting of 4–6 solutions in benzene or 1,4-dioxane at 25°C , while the measurements for **2** were only conducted in benzene because of its poor solubility in 1,4-dioxane. The dielectric permittivity of solutions of **1–5** was determined on a BI-870 instrument (Brookhaven Instruments Corporation), the accuracy is ± 0.01 . The refractive indices of solutions were determined on a RA-500 refractometer (Kyoto Electronics), the accuracy is ± 0.0001 .

The experimental dipole moments were calculated by the formula [28]:

$$\mu = 0.01283 \sqrt{P_{\text{or}} T}$$

The orientation polarizabilities P_{or} were calculated by the Guggenheim-Smith formula [31, 32]:

$$P_{\text{or}} = \frac{M}{d} \left[\frac{3\alpha}{(\varepsilon_0 + 2)^2} - \frac{3\gamma}{(n_0^2 + 2)^2} \right],$$

where M is the molecular weight of a substance, d is the density of the solvent, α and γ are the slope tangents of the straight lines in the coordinates $\varepsilon_i - w_i$ and $n_i^2 - w_i$; and ε_i , n_i , and w_i are the dielectric permittivity, refractive index, and weight fraction of the solute in i^{th} solution, respectively. The coefficients α and γ were calculated by the formulas: $\alpha = (\varepsilon_i - \varepsilon_0)/w_i$ and $\gamma = (n_i^2 - n_0^2)/w_i$, where ε_0 and n_0 are the dielectric permittivity and refractive index of the solvent, respectively.

Quantum chemical calculations were carried out using density functional theory (DFT) method B3PW91 with 6-311++G(df,p) basis set by the GAUSSIAN 09 program [33] with the total optimization of geometry. Correspondence of the obtained stationary points to the energy minima was proved by calculation of

the second derivatives in all cases. The calculations were performed in Kazan Federal University and Kazan Branch of Joint Supercomputer Center of the Russian Academy of Sciences.

Conclusion

We carried out experimental and theoretical conformational analysis of *O*-phenyl diphenethylphosphinoseleenoate, *O*-(naphthalen-1-yl) diphenethylphosphinoseleenoate, *S*-ethyl diphenethylphosphinoseleenothioate, *S*-phenyl diphenethylphosphinoseleenothioate, and *P,P*-diphenethyl-*N*-phenylphosphinoseleenoic amide by the method of dipole moments and DFT calculations. In all cases, the theoretical results are in a good agreement with the experimental data obtained. We concluded that the conformations of the examined compounds fit into the overall conformational picture for compounds of tetra-coordinated phosphorus with alkyl and aryl substituents [34], namely, these derivatives of bis(2-phenylethyl)selenophosphinic acid exist as a conformational equilibrium of non-eclipsed *gauche* and *trans* forms with propeller arrangement of the substituents relative to the P=Se bond, and eclipsed *cis* orientation of thioethyl substituent may be caused by the formation of intramolecular hydrogen interaction Se...H.

The studied polyfunctional compounds are prospective ligands for the preparation of metal complexes, precursors for the design of biologically active compounds, single-source precursors of nanomaterials, and building blocks for synthesis of novel organophosphorus compounds. Besides theoretical value, the results of the present study can be useful for prediction and rationalization of reactivity of phosphinoseleenoic esters, thioesters, and amides.

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