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Dedicated to V. F. Mironov on His 60th Anniversary

## **Polarity of Selected Derivatives of Diselenophosphinic Acid**

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**Abstract**—Polarity of diselenophosphinates in benzene solution has been determined by second Debye method. We suggest that these compounds exist as a mixture of several conformers with *cis* and *gauche* arrangement of substituents at the phosphorus atom with respect to the P=Se bond.

Keywords: diselenophosphinate, dipole moments, additive scheme

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Derivatives of diselenophosphinic acids are interesting as highly efficient "single-source" precursors of nanomaterials with unique semiconductive, magnetooptical, and electrical properties, ligands for the design of coordination structures, extractants of heavy metals, additives to lubricating oils, precursors for pharmaceuticals, and building blocks in organoelemental synthesis [1].

We determined for the first time the polarity of Semethyldiphenyldiselenophosphinate **1**, Se-propyldiphenyldiselenophosphinate **2**, Se-benzyldiphenyldiselenophosphinate **3**, Se-methyldiphenethyldiselenophosphinate **4**, Se-ethyldiphenethyldiselenophosphinate **5**, and Sebenzyldiphenethyldiselenophosphinate **6** in benzene solution.



 $R^1 = Ph, R^2 = Me(1); R^1 = Ph, R^2 = Pr(2); R^1 = Ph, R^2 = Bn$ (3);  $R^1 = Ph(CH_2)_2, R^2 = Me(4); R^1 = Ph(CH_2)_2, R^2 = Et(5);$  $R^1 = Ph(CH_2)_2, R^2 = Bn(6).$ 

The coefficients of the derived equations, values of the orientation polarization, and dipole moments (experimental and calculated via vector additive scheme) of compounds 1-6 in benzene solution are given in the table.

Spatial structure of diselenophosphinates 1-6 was investigated by means of dipole moment and quantum chemistry methods. The results of experimental and theoretical conformational analysis of these compounds in solution will be reported separately. Preliminary theoretical calculations data indicated that each of diselenophosphinates 1-6 existed in solution as a mixture of several conformers due to the internal rotation about P–C<sub>sp</sub>3, P–Se, or Se–C<sub>sp</sub>3 bond. Dipole

Coefficients of the computational equations, orientation polarizations, and dipole moments (experimental and calculated via the vector additive scheme<sup>a</sup>) of compounds 1-6

Comp. no.	α	γ	P <sub>or</sub>	μ <sub>exp</sub> , D	$\mu_{calc}, D^{a}$
1	8.165	0.393	523.864	4.94	4.79
2	6.644	0.199	468.550	4.76	4.68
3	7.955	0.382	645.007	5.59	4.47
4	4.827	0.333	350.245	4.17	4.06
5	5.473	0.289	417.886	4.50	4.07
6	6.324	0.296	556.307	5.19	4.11

<sup>a</sup>  $\mu_{calc}$  values are given for conformers with zero relative energy.

moments of the favorable conformers were calculated using the vector additive scheme (see table).

From comparison of the experimental and calculated dipole moments of compounds 1-6, we suggested that the forms with zero relative energy took significant part in the equilibrium of *cis* and *gauche* (with respect to the P=Se bond) conformers.

For determination of experimental values of dipole moments, we applied the second Debye method based on the measurement of dielectric constants of dilute solutions of polar substances in a nonpolar solvent. The experimental dipole moments were calculated using Eq. (1) [2]. The orientation polarizations were calculated using the Guggenheim–Smith equation (2) [2].

$$\mu = 0.01283 \sqrt{P_{\rm or} T},$$
 (1)

$$P_{\rm OP} = M/d \left[ \frac{3\alpha}{(\epsilon_0 + 2)^2} - \frac{3\gamma}{(n_0^2 + 2)^2} \right],$$
 (2)

with *M*, molar mass of the compound; *d*, density of the solvent;  $\alpha$  and  $\gamma$ , slopes of the  $\varepsilon_i - w_i$  and  $n_i^2 - w_i$  linear plots;  $\varepsilon_i$ ,  $n_i$ , and  $w_i$ , dielectric constant, refractive index, and mass fraction of the dissolved substance for the *i*th solution.

Geometry parameters from theoretical calculations and the moments of bonds and groups: m(P=>Se) 4.00 D, calculated from  $\mu_{exp}$  Et<sub>3</sub>P=Se [3];  $m(C_{sp} \rightarrow P) 0.94 \text{ D}$ , calculated from  $\mu_{exp}$  Et<sub>2</sub>POEt [3];  $m(C_{ph} \rightarrow P) 1.09 \text{ D}$ , calculated from  $\mu_{exp}$  Ph<sub>3</sub>P [4];  $m(C_{sp} \rightarrow C_{sp^2}) 0.75 \text{ D}$ , calculated from  $\mu_{exp}$  C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> [2];  $m(Se \rightarrow P) 1.24 \text{ D}$ , calculated from  $\mu_{exp}$  4-methyl-2-(methylselanyl)-1,3,2dioxaphosphinan-2-oxide [3];  $m(C_{sp} \rightarrow Se) 0.95 \text{ D}$ , calculated from  $\mu_{exp}$  Et<sub>2</sub>Se [2];  $m(H \rightarrow C_{sp^3}) 0.28 \text{ D}$  [5] were used for the calculation of dipole moments via the vector additive scheme.

Synthesis of compounds 1 and 4–6 was reported elsewhere [6].

**Synthesis of organyl diphenyldiselenophosphinates 2 and 3.** A mixture of 0.76 g (0.2 mmol) of potassium diphenyldiselenophosphinate, 12 mL of ethanol, 0.36 g (0.21 mmol) of *n*-propyl iodide or 0.27 g (0.21 mmol) of benzyl chloride was stirred for 30 min at  $50-55^{\circ}$ C. The solution was filtered under reduced pressure, and the excess of the organic halide was removed. Yield 0.60 g (60%) of compound **2** or 0.62 g (72%) of compound **3**. The constants for compound **3** coincided with [7].

Se-Propyldiphenyldiselenophosphinate (2). IR (KBr), v, cm<sup>-1</sup>: 3052, 2961, 2928, 2869, 3000, 1584, 1478, 1454, 1435, 1377, 1332, 1308, 1279, 1211, 1181, 1159, 1091, 1069, 1027, 998, 744, 689, 618, 553, 506, 475, 420. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ, ppm (J, Hz): 0.92 t (3H, Me,  ${}^{3}J_{HH} = 7.2$ ), 1.65 sextet (2H, C<u>H</u><sub>2</sub>Me,  ${}^{3}J_{HH} =$ 7.2), 2.97 d.t (2H, CH<sub>2</sub>Se,  ${}^{3}J_{HH} = 7.2$ ,  ${}^{3}J_{HP} = 13.1$ ), 7.43 m (6H, *m,p*-Ph), 7.92 m (4H, *o*-Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta_{C}$ , ppm: 14.02 (Me), 23.28 (<u>C</u>H<sub>2</sub>Me), 33.47 (CH<sub>2</sub>Se), 128.15 (p-Ph), 131.28 and 131.37 (o,m-Ph), 132.35 d (ipso-Ph,  ${}^{3}J = 7.2$  Hz).  ${}^{31}P$  NMR (CDCl<sub>3</sub>),  $\delta_{P}$ , ppm: 40.85 + d.d of satellites ( ${}^{1}J_{PSe}$  = 369.0,  ${}^{1}J_{P=Se} = 764.0$  Hz).  ${}^{77}Se$  NMR (CDCl<sub>3</sub>),  $\delta_{Se}$ , ppm:  $-174 \text{ d} ({}^{1}J_{\text{P=Se}} = 764.0 \text{ Hz}), 290.4 \text{ d} ({}^{1}J_{\text{PSe}} = 369.0 \text{ Hz}).$ Found, %: C 46.39; H 4.61; P 8.12; Se 40.96. C<sub>15</sub>H<sub>17</sub>PSe<sub>2</sub>. Calculated, %: C 46.65; H 4.44; P 8.02; Se 40.89.

Dielectric constants of solutions of compounds 1–6 were measured in benzene at 25°C using a BI-870 (Brookhaven Instruments Corporation) instrument with the accuracy of  $\pm 0.01$ . Refractive indexes of the solutions were measured using an RA-500 (Kyoto Electronics) refractometer with the accuracy of  $\pm 0.0001$ .

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