# SYNTHESIS AND STRUCTURE OF BIS(2-PHENYL-

### **ETHYL)PHOSPHINE SELENIDE**

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Bis(2-phenylethyl)phosphine selenide was obtained with 86% yield from bis(2-phenylethyl)phosphine and selenium. XRD, IR, UV, and multinuclear NMR spectroscopic studies revealed that the phosphorus atom in the bis(2-phenylethyl)phosphine selenide molecule is four-coordinated irrespective of the phase state (crystals or solution).

**Keywords:** bis(2-phenylethyl)phosphine selenide, four-coordinated phosphorus, selenone tautomeric form, XRD, spectral techniques.

#### **INTRODUCTION**

Secondary organylphosphine chalcogenides are convenient building blocks for the synthesis of tertiary phosphine chalcogenides [1-7] — unique ligands for the design of metallocomplex catalysts [8-10], synthons [11, 12], fire retardants [13], extractants, and flotation reagents [14]. However, this information was mostly obtained for phosphine oxides because of the low accessibility of organophosphorus compounds containing heavier chalcogen atoms. The lack of synthetic procedures for the preparation of secondary phosphines, used as precursors of phosphine chalcogenides, was another factor that hampered the investigation of secondary phosphine chalcogenides. The development of convenient methods for the synthesis of secondary phosphines employing elementary phosphorus [15, 16] opened up new opportunities for expanding the synthetic potential of these compounds and their derivatives. It became possible to further elaborate the highly topical aspect of the chemistry of secondary phosphine chalcogenides, namely, the existence of two tautomers (chalcogenone, chalcogenol) of these potentially ambident compounds [17].



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The present study is devoted to structural investigation of the novel compound bis(2-phenylethyl)phosphine selenide (prepared from accessible bis(2-phenylethyl)phosphine [18] and elementary selenium with 86% yield according to [19]) by X-ray diffraction and multinuclear NMR, IR, and UV spectroscopy.

#### **EXPERIMENTAL**

IR spectra were recorded with a Bruker IFS 25 specrophotometer; UV spectra were obtained with a UV/VIS Perkin Elmer Lamda 35 device. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>77</sup>Se NMR spectra were recorded with a Bruker DPX-400 spectrometer (400.13 MHz, 101.61 MHz, 161.98 MHz, and 76.27 MHz, respectively) in CDCl<sub>3</sub> (HMDS and dimethylselenide (for <sup>77</sup>Se) as internal standards, 85% H<sub>3</sub>PO<sub>4</sub> as external standard (for <sup>31</sup>P). Diffraction data were collected with an Enraf-Nonius CAD-4 diffractometer ( $\omega/2\theta$  scan mode, MoK<sub> $\alpha$ </sub> radiation, graphite monochromator) at room temperature.

**Bis(2-phenylethyl)phosphine selenide** was obtained by the reaction of bis(2-phenylethyl)phosphine with elementary selenium.



(Scheme 2)

A 100 ml three-neck flask equipped with a reflux condenser, a calcium chloride tube, a dropping funnel, a thermometer, and a bubbler was charged with toluene (25 ml) and selenium metal (2.07 g). A solution of bis(2-phenylethyl)phosphine (6.35 g) in toluene (20 ml) was added. The resulting suspension was boiled with stirring for 2 h. The solvent was removed in vacuum, and the gum thus obtained was allowed to stay for 72-80 h for crystallization. The product was rinsed with ethanol (three 1.5-2 ml portions) to give bis(2-phenylethyl)phosphine selenide (7.2 g, yield 86%). Recrystallization from hexane gave the target product as colorless platelets with mp 61-62°C. All synthetic procedures were performed in an inert atmosphere (argon). Calculated for  $C_{16}H_{19}PSe$  (M=321.26), %: C 59.82; H 5.96; Se 24.58; P 9.64; found: C 59.86; H 6.01; Se 24.46; P 9.34.

NMR spectra,  $\delta$ , ppm (*J*, Hz): <sup>1</sup>H: 2.31 m (4H, CH<sub>2</sub>P), 2.95 m (4H, CH<sub>2</sub>Ph), 6.00 d (1H, PH, <sup>1</sup>J<sub>P-H</sub> 433.5), 7.21 m (10H, Ph). <sup>13</sup>C: 29.49 d (PhCH<sub>2</sub>, <sup>2</sup>J<sub>P-C</sub> 2.3), 30.50 d (PCH<sub>2</sub>, <sup>1</sup>J<sub>P-C</sub> 43.7), 126.62 (C<sub>p</sub>), 128.22 (C<sub>o</sub>), 128.64 (C<sub>m</sub>), 139,.2 d (C<sub>i</sub>, <sup>3</sup>J<sub>P-C</sub> 12.4). <sup>31</sup>P: 2.17 d (<sup>1</sup>J<sub>P-H</sub> 433.5).<sup>77</sup>Se: -413.9 d (<sup>1</sup>J<sub>P-Se</sub> 711.3).

IR spectrum, KBr pellets and vaseline oil, cm<sup>-1</sup>: 3103, 3081, 3061, 3019, 3000 ( $\nu$  = CH); 2943, 2921, 2891, 2859 ( $\nu$  C–H); 2365 ( $\nu$  P–H); 1601, 1580, 1494 ( $\nu$  C=C ring); 1453, 1442 ( $\delta$  CH<sub>2</sub>); 1394, 1137, 1030, 997, 956, 939, 914, 881, 817 ( $\delta$  CH ring); 761, 749 ( $\nu$  P–C); 729, 697 ( $\delta$  CH ring); 443 ( $\nu$  P=Se).

UV spectrum, acetonitrile, C 0.0009 mole/l, d = 0.1; 1 cm,  $\lambda$ , nm/log $\epsilon$ : 206 sh/4.39; 210 sh/4.36; 218 sh/4.20; 248/2.88; 252/2.82; 258/2.73; 264/2.60; 268/2.50.

**X-ray diffraction study.** The crystal structure was solved by direct methods and subsequent Fourier syntheses using the SHELXS-97 program [20]. The structure was refined in a full-matrix anisotropic approximation for all non-hydrogen atoms with SHELXL-97 [20]. An absorption correction was applied. Hydrogen atom positions were found experimentally and refined isotropically. Atomic labeling, bond lengths and angles, atomic thermal parameters, molecular geometry, and a fragment of the phosphine selenide crystal structure are shown in Figs. 1-3 and listed in Tables 1 and 2. Torsion angles:  $P(1)C(1)C(2)C(3) = 68.9^{\circ}$ ;  $P(1)C(9)C(10)C(11) = 179.8^{\circ}$ ;  $C(2)C(1)P(1)C(9) = 176.4^{\circ}$ ;  $C(1)P(1)C(9)C(10) = 79.7^{\circ}$ . The dihedral angle between the six-membered rings is 74.8°. The largest deviation from the planes of the six-membered cycles is 0.006 Å for the C(3) atom of the C(3)C(4)...C(8) cycle and 0.002 Å for the C(13) atom of the C(11)C(12)...C(16) cycle (Fig. 2). No  $\pi$ -stacking between the parallel phenyl rings has been observed (Fig. 3).



Fig. 1. Atomic numbering for the  $C_{16}H_{19}PSe$  molecule.



Fig. 2. Geometry of the phosphine selenide molecule.



Fig. 3. Fragment of the crystal structure of phosphine selenide.

## DISCUSSION

To elucidate the influence of the phase state on the tautomeric equilibrium of the synthesized bis(2-phenylethyl)phosphine selenide (Scheme 1) we investigated its structure in solution and in single crystal using IR, UV, and multinuclear NMR spectroscopy and XRD.

Formula	$C_{16}H_{19}PSe$
Crystal system	Triclinic
Space group	$P\overline{1}$
<i>a</i> , Å	6.466(1)
<i>b</i> , Å	9.309(2)
<i>c</i> , Å	13.182(3)
$\alpha$ , deg	88.76(3)
β, deg	89.35(3)
γ, deg	76.86(3)
$V, Å^3$	772.5(3)
Ζ	2
λ, Å	0.7107
$d_{\rm cale},{ m g}{ m \cdot}{ m cm}^{-3}$	1.38
$\mu$ , mm <sup>-1</sup>	2.516
Total No. of reflections	3975
Independent reflections	3975
Reflections with $[F_0 > 4\sigma(F_0)]$	1778
No. of parameters	239
$(2\theta)_{max}$ , deg	59.92
h range	$0 \le h \le 8$
k range	$-12 \le k \le 13$
<i>l</i> range	$-18 \le l \le 18$
$R(F_0 > 4\sigma(F_0)), wR_2$	0.048, 0.111

TABLE 1. Crystal Data and Details of Experiment

**TABLE 2.** Bond Lengths d (Å) and Angles  $\omega$  (deg)\*

Bond	d	Angle	ω	Bond	d	Angle	ω
P(1)–C(1)	1.819(5)	C(1)-P(1)-C(9) C(1)-P(1)-Se(1) C(9)-P(1)-Se(1) C(9)-P(1)-Se(1) C(1)-P(1)-Se(1) C(1)-P(1)-Se(1) C(1)-P(1)-Se(1) C(1)-P(1)-C(9) C(1)-P(1)-C(9) C(1)-P(1)-C(9) C(1)-P(1)-C(9) C(1)-P(1)-Se(1) C(1)-Se(1)-Se(1) C(1)-Se(1)-Se(1)-Se(1) C(1)-Se(1)-Se(1)-Se(1) C(1)-Se	107.3(2)	C(10)–C(11)	1.528(6)	C(3)–C(8)–C(7)	121.0(5)
P(1)–C(9)	1.825(4)		113.8(1)	C(11)–C(16)	1.360(7)	C(10)–C(9)–P(1)	112.3(3)
P(1)–Se(1)	2.108(1)		114.5(2)	C(11)–C(12)	1.372(7)	C(9)–C(10)–C(11)	112.3(4)
C(1)-C(2)	1.531(6)	C(2)=C(1)=P(1)	113.8(3)	C(12)-C(13)	1.396(8)	C(16)–C(11)–C(12)	118.1(4)
C(2)-C(3)	1.503(6)	C(3)=C(2)=C(1)	114.7(4)	C(13)-C(14)	1.338(8)	C(16)–C(11)–C(10)	120.6(4)
C(3)-C(4)	1.371(7)	C(4)=C(3)=C(8)	117.6(5)	C(14)-C(15)	1.356(8)	C(12)–C(11)–C(10)	121.3(5)
C(3)-C(8)	1.376(7)	C(4)=C(3)=C(2)	121.3(5)	C(15)-C(16)	1.370(7)	C(11)–C(12)–C(13)	119.8(5)
C(4)-C(5) C(5)-C(6) C(6)-C(7) C(7)-C(8) C(10)	1.394(9) 1.362(9) 1.322(9) 1.381(8) 1.504(6)	C(8)-C(3)-C(2) C(3)-C(4)-C(5) C(6)-C(5)-C(4) C(7)-C(6)-C(5) C(6) C(7) C(8)	121.1(4) 119.8(6) 121.2(6) 118.8(6) 121.6(6)			C(14)-C(13)-C(12) C(13)-C(14)-C(15) C(14)-C(15)-C(16) C(11)-C(16)-C(15)	120.6(5) 119.9(5) 120.0(5) 121.6(5)

\*The positional parameters of atoms are available from CCDC, CCDC No. 273553.

Analysis of multinuclear NMR data for a CDCl<sub>3</sub> solution of bis(2-phenylethyl)phosphine selenide reveals that the resonances corresponding to the magnetic interactions of the <sup>31</sup>P nucleus with its nearest neighbors (<sup>1</sup>H, <sup>13</sup>C, <sup>77</sup>Se) are most informative in respect of the tautomeric equilibrium in question. Thus the resonances of these nuclei, as well as the doublets

in the <sup>1</sup>H and <sup>31</sup>P spectra manifesting direct spin-spin coupling (<sup>1</sup>J 433.5 Hz), unambiguously prove (within the limits of NMR sensitivity) that bis(2-phenylethyl)phosphine selenide occurs in the selenone form in solution. The IR spectrum of this compound has P=Se and P–H stretching vibrations near 443 cm<sup>-1</sup> and 2365 cm<sup>-1</sup> in accordance with the literature data [21]. Near 250-280 nm, the UV spectrum of bis(2-phenylethyl)phosphine selenide displays a characteristic absorption band of the phenyl ring with poorly resolved vibrational structure and with maxima at 248 nm, 252 nm, 258 nm, 264 nm, and 268 nm. Moreover, there is an absorption shoulder around 200-230 nm with maxima at 206 nm, 210 nm, and 218 nm, which may be attributed to an overlap of the bands that are due to the  $\pi$ - $\pi$ \* transitions in the phenyl ring and the P=Se group.

The structure of bis(2-phenylethyl)phosphine selenide in the crystalline state was confirmed by XRD data. The P(1)=Se(1) distance of 2.108(1) Å agrees with the P=Se distances known from the literature [22, 23].

Single crystal data for bis(2-phenylethyl)phosphine selenide evidence that in the crystal phase the phosphorus atom in the molecule has tetrahedral coordination; i.e., as in solution, the tautomeric equilibrium is entirely shifted toward the selenone form.

#### CONCLUSIONS

Thus the four-coordinated environment of the phosphorous atom found in the bis(2-phenylethyl)phosphine selenide molecule makes it possible to predict the reactivity of this compound; in nucleophilic or radical addition reactions, phosphine selenides should behave like phosphorous-centered radicals of nucleophiles.

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