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Ground State Conformation of Diphenylvinylphosphine Sulfide and Selenide

K. Michał Pietrusiewicz* and Maciej Kuźnikowski

The Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Sienkiewicza 112, 90-363 Łódź, Poland

Wanda Wieczorek

Institute of General Chemistry, Technical University of Łódź, Żwirki 36, 90-924 Łódź, Poland

Alberto Brandi

Dipartimento di Chimica Organica "Ugo Schiff," Universita di Firenze, via G. Capponi 9, 50-121 Firenze, Italy

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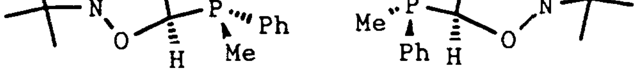
ABSTRACT

Single-crystal X-ray diffraction experiments have been performed on diphenylvinylphosphine sulfide (**1**)*:* $C_{14}H_{13}PS$, *space group* $P2_1/c$, a = *10.186(1)* Å, b = *11.918(1)* Å, c = *11.426* Å, β = *112.22(2)*°, V = *1284.1(2)* Å^3, Z = *4, and diphenylvinylphosphine selenide* (**2**)*:* $C_{14}H_{13}PSe$, *space group* Pbca, a = *9.141(3)* Å, b = *16.458(1)* Å, *c* = 17.451*(1)* Å, *V* = *2625.4(9)* Å^3, Z = *8. The structures were solved by direct methods and were refined by full matrix least-squares calculations to* R = *0.046 and* R_w = *0.058 using 2554 unique reflections with* $I > 3\sigma(I)$ *in the case of* **1**, and to R = *0.052 and* R_w = *0.065 using 1953 unique reflections with* $I > 3\sigma(I)$ *in the case of* **2**. *In close analogy to the previously studied vinyl phosphine oxides both* **1** *and* **2** *were found to exist in the s-cis conformation with the pertinent C═C–P═X dihedral angles equal to 12.5° and 2.9° for* **1** *and* **2**, *respectively.*

INTRODUCTION

It is now well accepted that simple conjugated olefins bearing strongly activating groups prefer the *s*-cis conformation in the ground state, and that they choose the same array for the reactive conformation under thermal conditions [1]. Similar conformational behavior of vinyl phosphine oxides was recently implied by the stereochemistry of their cycloadditions to nitrones and nitrile oxides [2,3], and was also corroborated by the crystal structures of three model compounds of this class [4,5]. As revealed in the same 1,3-dipolar cycloaddition studies [2,6,7], vinyl phosphine sulfides and vinyl phosphine selenides follow closely the reactivity pattern



X = O 2.5 : 1
X = S 4.0 : 1
X = Se 4.1 : 1

SCHEME 1

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†Dedicated to Professor Ernest L. Eliel on the occasion of his seventieth birthday.

*To whom correspondence should be addressed.

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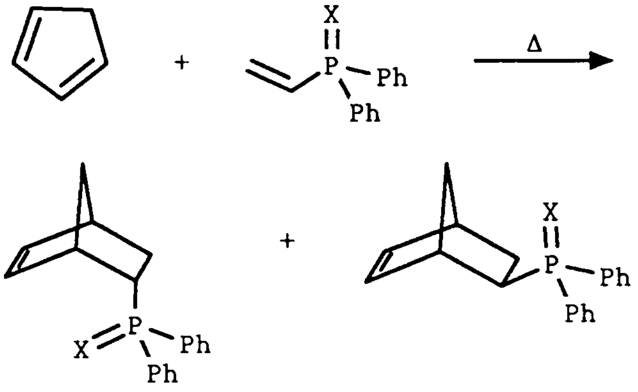
of the oxides offering, however, a considerably enhanced regio [6,7] and stereocontrol (Scheme 1) [2].



X = O 37 : 63
X = S 52 : 48
X = Se 59 : 41

SCHEME 2

In a similar way, in the related thermal Diels–Alder reactions of vinyl phosphine derivatives with cyclopentadiene, the endo/exo selectivity increased noticeably on going from the oxide [8] to the sulfide and to the selenide derivative (Scheme 2) [9]. To reveal whether the observed shifts in selectivity can be related to the possible differences in conformational bias in the vinyl phosphorus compounds that have been studied we have carried out single-crystal X-ray diffraction experiments on the two pertinent models, that is, diphenylvinylphosphine sulfide (**1**) and diphenylvinylphosphine selenide (**2**). Presented in this article are the details of the crystallographic analyses of **1** and **2** and comparison with the available data on vinyl phosphine oxides.

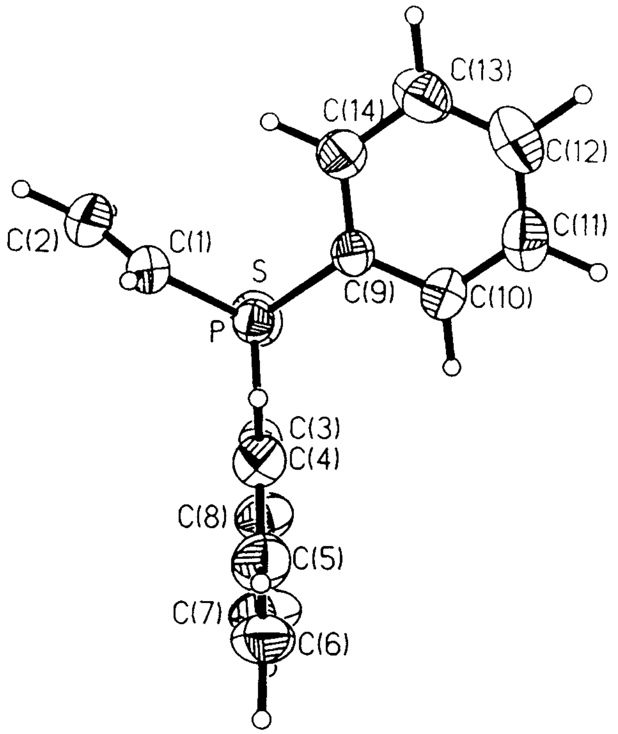


FIGURE 1 ORTEP view of **1** showing 50% probability elipsoids with atom numbering.

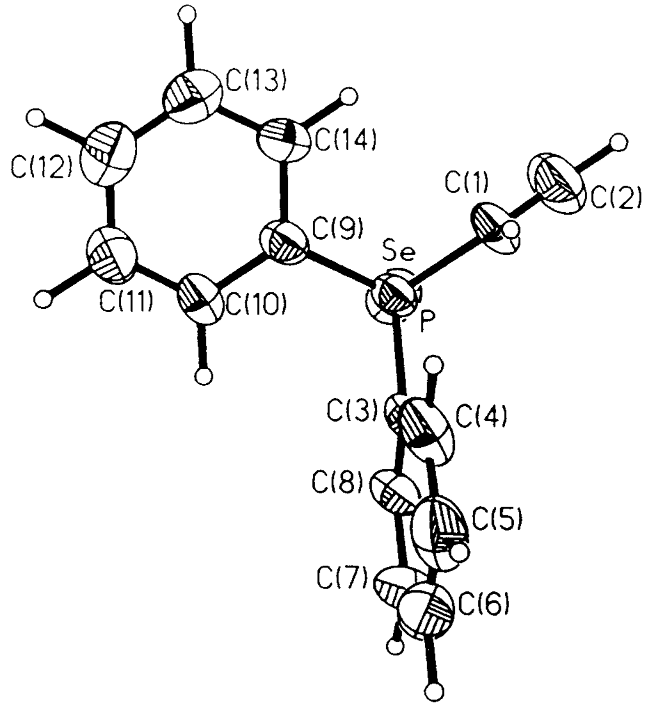


FIGURE 2 ORTEP view of **2** showing 50% probability elipsoids with atom numbering.

RESULTS AND DISCUSSION

The ORTEP drawings of the individual molecules of **1** and **2** are displayed in Figures 1 and 2, and the positional parameters for the two structures are listed in Tables 1 and 2, respectively. Table 3 lists selected bond lengths, bond angles, and torsion angles for the two compounds.

The C–C and P–C bond lengths found and the valence angles represent rather typical values and are practically the same for **1** and **2**. Similarly, the observed P═S and P═Se bond distances of 1.953 and 2.099 Å, respectively, are close to the corresponding average values of 1.936 Å and 2.098 Å derived from the literature data recorded for 61 structures containing the P═S bond and for 7 structures containing the P═Se bond, respectively [10]. It should be noted that in the two compounds the phosphorus tetrahedron is deformed to a nearly identical extent showing increased X–P–C angles

TABLE 1 Positional Parameters (× 10^5) for P and S Atoms (× 10^4) for the C Atoms, and Equivalent Thermal Parameters (Å^2 × 10^4) for **1**

	x	y	z	U_{eq}
P	75935(4)	71383(3)	4294(4)	387(2)
S	72726(6)	58779(4)	−7385(5)	582(2)
C(1)	6409(2)	7185(2)	1263(2)	510(7)
C(2)	5263(2)	6562(2)	943(3)	690(10)
C(3)	9354(2)	7159(1)	1660(2)	412(6)
C(4)	9732(2)	8011(2)	2555(2)	489(7)
C(5)	11054(2)	8009(2)	3527(2)	595(8)
C(6)	12002(2)	7151(2)	3607(3)	680(9)
C(7)	11640(2)	6309(2)	2711(3)	767(11)
C(8)	10313(2)	6316(2)	1730(2)	571(7)
C(9)	7381(2)	8493(1)	−341(2)	388(5)
C(10)	8456(2)	8922(2)	−671(2)	488(7)
C(11)	8260(3)	9917(2)	−1338(2)	601(9)
C(12)	6998(3)	10493(2)	−1675(2)	636(9)
C(13)	5911(3)	10068(2)	−1355(2)	624(9)
C(14)	6101(2)	9077(2)	−685(2)	513(7)

of 113.3(1)–114.4(1)° and 113.1(1)–113.8(1)° and correspondingly decreased C–P–C angles of 104.4(1)–105.4(1)° and 104.3(2)–105.9(2)°, in **1** and **2**, respectively.

Although the packing of **1** and **2** in the crystal required different relative orientations of the molecules no intermolecular interactions were revealed and the individual conformations of the two compounds turned out to be very similar. As indicated by the torsion angles listed in Table 3, in both compounds one of the phenyl rings is coplanar with P=X and forms a characteristic "edge-to-face" array with the other. Likewise, for both compounds the same *s*-cis conformation of the vinyl-P=X unit is revealed. Because such a conformational preference has already been recorded for the related vinyl phosphine oxides [4,5], this particular finding reinforces the notion that the whole family of vinyl phosphine derivatives [11] probably favors uniformly a nearly coplanar *s*-cis conformation in the ground state.

TABLE 2 Positional Parameters (× 10^5) for the Se Atom (× 10^4) for the P and C Atoms, and Equivalent Thermal Parameters (Å^2 × 10^4) for **2**

	x	y	z	U_{eq}
Se	6844(5)	41238(3)	5622(4)	641(2)
P	2342(1)	3242(1)	567(1)	433(3)
C(1)	2712(5)	2821(3)	−365(2)	615(14)
C(2)	2051(7)	3068(5)	−999(3)	874(22)
C(3)	1931(4)	2363(2)	1160(2)	439(10)
C(4)	2791(6)	1664(3)	1101(3)	677(16)
C(5)	2420(11)	981(3)	1537(5)	848(22)
C(6)	1259(10)	1013(4)	2034(4)	928(26)
C(7)	403(8)	1689(5)	2086(3)	906(24)
C(8)	748(5)	2383(3)	1640(3)	585(14)
C(9)	4082(4)	3629(2)	908(2)	459(10)
C(10)	4385(5)	3661(3)	1689(2)	565(14)
C(11)	5649(6)	4032(3)	1943(3)	638(18)
C(12)	6640(5)	4339(3)	1421(3)	703(18)
C(13)	6345(6)	4316(4)	656(3)	709(20)
C(14)	5061(6)	3954(3)	370(3)	547(13)

TABLE 3 Selected Bond Lengths (Å), Bond Angles (°), and Torsional Angles (°) for **1** and **2**

1	**2**
S–P 1.953(1)	Se–P 2.099(1)
C(1)–P 1.799(2)	C(1)–P 1.800(4)
C(3)–P 1.813(2)	C(3)–P 1.818(4)
C(9)–P 1.812(1)	C(9)–P 1.814(4)
C(2)–C(1) 1.313(3)	C(2)–C(1) 1.325(7)
C(1)–P–S 114.4(1)	C(1)–P–Se 113.5(1)
C(3)–P–S 113.7(1)	C(3)–P–Se 113.8(1)
C(3)–P–C(1) 104.7(1)	C(3)–P–C(1) 104.3(2)
C(9)–P–S 113.3(1)	C(9)–P–Se 113.1(1)
C(9)–P–C(1) 104.4(1)	C(9)–P–C(1) 105.5(2)
C(9)–P–C(3) 105.4(1)	C(9)–P–C(3) 105.9(2)
C(2)–C(1)–P 122.6(2)	C(2)–C(1)–P 123.4(4)
S–P–C(3)–C(8) −1.7(2)	Se–P–C(3)–C(8) −10.2(4)
S–P–C(1)–C(2) −12.5(2)	Se–P–C(1)–C(2) 2.9(5)
S–P–C(9)–C(10) 84.4(3)	Se–P–C(9)–C(10) −78.8(8)

EXPERIMENTAL

Crystals of **1** and **2** [7] suitable for X-ray investigation were obtained by slow evaporation of benzene and benzene–heptane (1 : 1) solutions of **1** and **2**, respectively. Accurate unit-cell dimensions were obtained by the least-squares fit to the θ values of 25 reflections measured on an Enraf Nonius CAD4 diffractometer. Diffraction data were collected using graphite-monochromated CuKα radiation and the ω-2θ scan technique. The intensity data were corrected for Lorentz, polarization, absorption [12], and extinction effects. Crystal and experimental details for **1** and **2** are listed in Table 4.

The structures were solved by direct methods using SHELXS-86 programs [13] and were refined by full-matrix least-squares method using SHELX-76 [14]. During the refinement of the nonhydrogen atoms with anisotropic thermal parameters, the hydrogen atoms contributions were included in the structure factors, after calculating their positions on the basis of idealized geometry and refining them isotropically in the riding mode. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized; a weighting scheme of the form $w^{-1} = \sigma^2(F_o) + gF_o^2$ was employed with the final g value of 0.006 for **1** and 0.005 for **2**. Convergence was obtained at $R = 0.046$, $R_w = 0.058$ for **1** and $R = 0.052$, $R_w = 0.065$ for **2**. The final difference Fourier map did not show any peaks higher than 0.30 eÅ^3 for **1** and 0.41 eÅ^3 for **2**. Most of the computations were performed on an AMSTRAD 1512 minicomputer [15].

TABLE 4 Crystal Data and Experimental Parameters for **1** and **2**

	1	**2**
Molecular formula	$C_{14}H_{13}P$ S	$C_{14}H_{13}P$ Se
M_r	244.29	291.19
Space group	$P2_1/c$	*Pbca*
a (Å)	10.186(1)	9.141(3)
b (Å)	11.918(1)	16.458(1)
c (Å)	11.426(1)	17.451(1)
β (°)	112.22(2)	
V (Å^3)	1284.1(2)	2625.4(9)
Z	4	8
F(000)	512	1168
Crystal color	colorless	colorless
Crystal dimensions (mm)	0.25, 0.30, 0.28	0.35, 0.27, 0.25
D_x (Mg m^{-3})	1.26	1.47
D_m (Mg m^{-3}) (flotation method)	1.25	1.46
μ (CuKα) (mm^{-1})	3.14	4.88
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$
2θ range (°)	2 - 150	2 - 150
Reflections with $I \geq 3\sigma(I)$	2554	1953
Parameters refined	159	159
Reflections/parameters	16	12
R	0.046	0.052
R_w	0.058	0.065

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