Phenylamino (diphenyl)phosphine selenide: supramolecular aggregation via weak N-H⋯Se, C-H⋯π and π⋯π interactions

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Dedicated to Professor Heinz Heimgartner on the occasion of his 70th birthday

Abstract
Phenylamino (diphenyl)phosphine selenide 1 was synthesized and analyzed by X-ray. The analysis revealed a deformation of the phosphorus tetrahedron, the planar geometry around the nitrogen atom, and the torsion angle Se1-P1-N1-C11, corresponding to a synclinal conformation (-46.7(4)). It has been postulated that the conformation of 1 is stabilized by short intramolecular C-H⋯N, C-H⋯Se interactions, which generate rings of motifs S(5) and aromatic hydrogen bonds C-H⋯π. The crystal structure is stabilized by the weak N-H⋯Se intermolecular interactions, generating infinite chains, parallel to the c axis, of graph-set motif C(4). Additionally, there have been observed the C-H⋯π interactions, connecting chains N-H⋯Se into the sheet, parallel to (100), producing binary graph set \( N_2 = C_2^2(10) \) (with \( ab \) sequence) and \( N_2 = R_4^4(24) \) motifs (with \( abab \) sequence). The weak \( π⋯π \) interactions stack the layers in the crystal lattice.

Keywords: X-ray, phosphine selenide, supramolecular aggregation, weak hydrogen bonds

Introduction

For more than 50 years the Wadsworth–Emmons reaction of dialkyl(aryl)phosphoramidate anions with carbonyl electrophiles and their analogues has been as a convenient synthetic route to a plethora of unsaturated nitrogen derivatives, usually of cumulene-type.\(^1\) Additionally, from the mid seventies, this reaction has been commonly applied for the synthesis of \( P \)-chiral...
phosphoramidates. The exploration of synthetic applications of the $P$-chiral phosphoramidates led Stec and coworkers to be aware of the potential offered by the Wadsworth–Emmons reaction in the synthesis of disubstituted phosphates, phosphorothioates and phosphoroselenoates, with special focus upon the stereochemical consequences of the $PN \rightarrow PX$ conversions.

It turned out that the development of a synthetic approach involving the preparation of the $P$-chiral phosphoramidates (mostly anilidates) followed by replacement of an amidate function by oxygen or sulfur opened the way to the stereospecific preparation of a variety of $P$-chiral derivatives of phosphorus acids, including numerous biophosphates and their analogues.

This approach resulted in successful solution of the problem of a waste free, stereocconvergent synthesis of a single isomer of either $R_P$ or $S_P$ dinucleoside (3',5')-methanephosphonates from both isomers of diastereomically pure $R_P$ and $S_P$ 5'-O-DMT nucleoside -3'-O-methylphosphonoanilidates.

In the course of our studies we also synthesized and characterized several model phosphoro- and phosphono selenoamidates, which have been used to investigate the mechanism of the Stec reaction by NMR and DFT molecular modeling. Numerous studies carried out with different enantiomeric and diastereomeric amidates confirmed stereoretentive pathway for this reaction, however, still an involvement of postulated PV intermediates or transition states has not been verified experimentally.

Here we present the X-ray analysis of phenylamino (diphenyl)phosphine selenide 1. This selenoanilidate, in contrast to the catechol analogue, 2-aniline-2-seleno-1,3,2-benzodioxaphospholane reported previously, could be easily obtained in almost quantitative yields, and almost spontaneously crystallizes from non-polar solvents.

We postulate that high tendency to crystallization and high stability of 1 is a result of supramolecular aggregation through weak N-H···Se and C-H···π and π···π interactions. The parameters received from the X-ray analysis will be of importance for theoretical modeling of the Stec reaction.

**Scheme 1.** Synthesis of phenylamino (diphenyl)phosphine selenide 1.

The title compound 1 was prepared by reaction of chlorodiphenylphosphine 2 with 2.2 molar excess of aniline in toluene at room temperature under argon, and without isolation of phosphinoamidite 3, followed by an addition of excess of elemental selenium (overnight reaction at ambient temp.).
Selenoanilidate 1 was obtained in very high yield (<90%), and after aqueous workup crystallized from toluene. This compound has already been reported in the literature but without experimental part and with incomplete spectral data.7

**X-Ray analysis**

In the crystal structure of molecule 1 there was observed a deformation of the phosphorus tetrahedron. The smallest angle N1-P1-C31 101.88(15)° is probably result of intermolecular interaction N1-H1...Se1. Similar deformation has been previously reported for \( P,P' \)-iminobis (diphenylselenophosphine) tetrahydrofuran solvate.8 The valence angles N1-P1=Se in this tetrahedron range from 113.77(11)° to 114.39(12)° and are comparable with those found there. The observed significant difference between Se=P-C angles and others in the environment of central phosphorus observed in 1 (Table 1) stays in agreement with literature data.9 The value of the Se1-P1-N1-C11 torsion angle is -46.7(4)°, and suggests a –synclinal conformation.

The length of the P=Se 2.1092(10) Å bond is a typical length for selenides containing \( P^V=\text{Se} \), bonds being reported within 2.08 – 2.12 Å.8-10

The values of P=Se bonds in phosphate selenides range from 2.109(5) Å in tri-\( m \)-tolylphosphine selenide,11 2.106(1) and 2.11 Å in triphenylphosphine selenides12,13, and 2.1055(5) Å in 1,4-butenylenbis(diphenylphosphine selenide),14 respectively, this could indicate that a neighbourhood of nitrogen atom does not elongate this distance.

The P-N bond length of 1.662(3) Å is considerably shorter than a single-bond length of 1.78(6) Å [see Table 4.1.4 of International Tables for X-ray Crystallography (1968, Vol. III)]. The comparison similar data for numerous related compounds shows range of its values from 1.645(6) Å in \( \text{Ph}_2\text{P(Se)NH-c-NC}_3\text{H}_10 \) to 1.687(4) Å and 1.698(4) in \( (\text{Ph}_2\text{P(Se)NHCO})_2\text{NC}_3\text{H}_3 \).10b,15 As Balakrishna concludes, the P-N bonding distance has a multiple character because the \( P^V \) center has accepted much of the lone-pair electron density from the backbone N atom.16

The geometry around the nitrogen atom is distinctly planar, with sum of the valency angles being 358.7°. Displacements of atoms from the C11/P1/N1/H1 mean planes are: C11 0.0174(0.0038) Å, P1 0.0155(0.0034) Å, N1 0.0630(0.0125) Å and H1 0.0302(0.0060) Å, respectively. Planar configuration substituents around N atom are also found in 4-dimethylaminopyridinium.17 The valence angle P1-N1-H1 (118(2)°) is close to the one observed in bis(2,6-diphenylphosphino)picolinamide diselenide (120(5)°), but not the symmetrical \( p\)-\( \text{Ph}_3\text{P(Se)NHCH}_2(\text{C}_6\text{H}_4) \) \( \text{CH}_2\text{NHP-(Se)Ph}_2 \) where the valence angle is significantly lower (110(3)°).9a

The P1-C31 and P1-C21 bond lengths are 1.804(3) Å and 1.808(4) Å, respectively, and are lower than the reported for both \( P,P' \)-imino bis(diphenylselenophosphine) tetrahydrofuran solvate7 and 1,4-butenylenbis(diphenylphosphine selenide).14

The dihedral angle between the mean planes of the: C11-C16 and C21-C26 rings is 75.09(14)°; whereas for C21-C26 and C31-C36 rings is 89.55(13)°, and C11-C16 and C31-C36 rings is 86.88 (0.15)°, respectively. For comparison, the corresponding dihedral angle...
between phenyl ring substituents of phosphorus in [2-(chlorodimethylstanny)ethyl]diphenylphosphine selenide is 76.0(2)°. The molecular structure of 1 is presented in Fig.1a, and the selected geometric parameters are given in Table 1.

The conformation of the molecule is stabilized by the short intramolecular interactions C26-H26⋯N1, C32-H32⋯Se1 (Table 2), which, according to Desiraju and Steiner, can be considered as weak hydrogen bonds. These interactions generate planar rings, with graph-set notation S(5) (Fig. 1). In the network created by the C26-H26⋯N1 hydrogen bond, maximum deviations from mean plane are +0.0628(0.0017) Å and -0.0548(0.0019) Å, for P1 and C21 atoms respectively. In the motif formed by the interactions C32-H32⋯Se1 maximum deviations are +0.1195(0.0017) Å for atom P1, and -0.1036 (0.0021) Å for C31. It should be noted that intramolecular interactions C-H⋯Se with similar geometric parameters (H⋯Se 2.92Å, C-H⋯Se 101.7°) have also been observed in crystal structure of 6H, 12H-dibenzo[b,f][1,5]diselenocin, and confirmed by IR and NMR Spectra analysis. In molecular structure was also found aromatic hydrogen bond C36-H36⋯Cg2 (Cg2 is a centroid of the ring formed by C21-C26). Intramolecular aromatic hydrogen bond type C-H⋯Cg with parameters (H⋯Cg 3.14 Å, C⋯Cg 3.84 Å, C-H⋯Cg 121°) was reported.

There are also two short contacts H1⋯H16 (2.30 Å) and H12⋯P1 (2.88 Å) in the molecular structure.

The crystal structure is stabilized by weak N-H⋯Se intermolecular interactions (Table 2). The geometric parameters of this hydrogen bond stay in good agreement with those established for...
this type of weak interactions (H···Se 2.63(7) Å, N···Se 3.58(6) Å, N-H···Se 158(4)°).\textsuperscript{19} The
network of N1-H1···Se1 (x, 1/2-y, 1/2+z) bonds generates a infinite chain parallel to the c axis, of
graph-set motif C(4), (Fig.1b).\textsuperscript{20} Similar hydrogen bonded chains were earlier identified in
structure of Ph\textsubscript{2}P(Se)NHNHpy and in \textsuperscript{3}Pr\textsubscript{2}P(Se)NHP(Se)P\textsuperscript{3}Pr\textsubscript{2}.\textsuperscript{9,22}

The supramolecular aggregation is completed by the presence of C-H···π interactions (Table 2), which were obtained from
PLATON.\textsuperscript{23} The C33-H33···Cg1 (1-x, ½+y, 3/2-z) (Cg1 is
centroid of the ring formed by C11-C16) interaction generates chains parallel to the b axis of
graph-set motif C(8).\textsuperscript{20} The geometric parameters agree very well with those found in benzene
1,3,5-tris(p-toluenesulfonate) (H···Cg 2.98 , C···Cg 3.728 , C-H···π 142º).\textsuperscript{17}

The supramolecular aggregation is completed by the presence the π···π weak interactions,
with a Cg3-Cg2 distance of 5.506Å, stacking the layers in the crystal lattice.

From the above X-ray data the importance of weak N-H···Se intermolecular interactions and
C-H···π interactions in formation of the aggregates is clear. Further studies are continued to
support the inter- and intramolecular hydrogen bonding supramolecular network by means of
DFT/Gaussian calculations.

**Experimental Section**

**Synthesis of phenylamino (diphenyl)phosphine selenide (I)**

Chlorodiphenylphosphine \textsuperscript{3} (0.005 mmol) was dissolved in dry, deoxygenated toluene with 2.2
molar excess of freshly distilled aniline in toluene (15 mL) containing elemental selenium at rt
under positive pressure of argon, and left sealed overnight. After filtration of the precipitate, the
reaction mixture was diluted with CH\textsubscript{2}Cl\textsubscript{2}, washed with cold brine, dried with anhyd. MgSO\textsubscript{4}
and concentrated to get solidifying colorless oil (Yield 95%). The product was dissolved in
toluene, and slowly concentrated until crystallization started. The crude crystals were collected
and recrystallized slowly from toluene in dark. Single crystals suitable for X-ray diffraction were
dried and kept in dark under nitrogen.

\textsuperscript{31}P NMR: 44.18 ppm, \textsuperscript{1}J_{P-Se}=794 Hz (CDCl\textsubscript{3}). FTIR (KBr, ν/cm\textsuperscript{-1}): 3731,6; 3194,6; 2924,6;
2854,2; 2360,5; 2337,4; 1645,0; 1596,8; 1496,5; 1479,2; 1432,9; 1393,3; 1282,4; 1228,4;
1179,3; 1098,3; 920,9; 786,8; 748,3; 689,4; 542,9; 503,3; 478,3. FT-IR spectrum of I was
recorded with a Nexus (Nicolet, USA) at 293K and with a spectral resolution of 0,1 cm\textsuperscript{-1}. For
measurement 32 scans in the 500-4000 cm\textsuperscript{-1} frequency range were carried out.

**X ray analysis**

Crystal and molecular structure of I was determined on a Xcalibur 3 CCD area-detector
diffractometer with graphite monochromatized MoK\textsubscript{α} radiation up to a resolution of
(sinθ/λ)\textsubscript{max}=0.6268 Å\textsuperscript{-1}. The crystal structure was solved by a conventional direct method using
the SHELXL-97 program package, followed by the least squares structural refinement and
calculated difference density. Compound I crystallized in monoclinic system in space group
P21/c with the unit cell consisting of four molecules, without molecules of solvent(s) used for crystallization. An empirical absorption correction was applied by the use of the ψ-scan method. The structure was solved by the direct methods with total of 1888 reflections with I>2σ(I) used and refined by the full matrix least squares using F². The final refinement converged to R[F²>2σ(F²)] =0.040 for 3560 reflections. Non-H atoms were refined anisotropically, while H atoms (with the exception of N-H proton, whose positions were determined from a difference map) were positioned geometrically at C-H distances of 0.93 (Csp²-H), and were refined using a riding model, with Uiso(H) = 1.2Ueq(C).

**Crystal data**

C₁₈H₁₆NPSeZ₂

Z = 4

Mr = 356.25

Dₐ = 1.435 g cm⁻³

Monoclinic, P2₁/c

Mo Kα radiation

a = 9.589 (3) Å

b = 15.569 (4) Å

c = 12.032 (3) Å

β = 113.38 (2)°

V = 1648.8 (8) Å³

Plate, colourless

0.32 x 0.22 x 0.06

**Data collection**

Xcalibur 3 CCD area-detector

1888 reflections with I > 2σ(I)

ω scan

Rint = 0.048

Absorption correction: empirical (using θmax = 27.0° intensity measurements)

h = -12 → 12

k = -19 → 19

l = -15 → 15

**Refinement**

Refinement on F²

Mixture of independent and constrained H-atom refinement

R[F²>2σ(F²)] = 0.040

Calculated weights w = 1/[σ²(Fo²) + (0.0568P)²] where P = (Fo² + 2Fc²)/3

wR(F²) = 0.111

(δ/σ)max <0.0001

S = 0.98

δρmax = 0.69 e Å⁻¹

3560 reflections

δρmin = -0.43 e Å⁻¹

194 parameters

Extinction correction: none
Table 1. Selected geometric parameters (Å, °)

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
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<tbody>
<tr>
<td>Se1—P1</td>
<td>2.1092 (10)</td>
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<tr>
<td>N1—C11</td>
<td>1.411 (4)</td>
</tr>
<tr>
<td>N1—H1</td>
<td>0.73 (3)</td>
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<tr>
<td>N1—P1—Se1</td>
<td>114.39 (12)</td>
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<tr>
<td>N1—P1—C21</td>
<td>105.88 (17)</td>
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<tr>
<td>C21—P1—Se1</td>
<td>113.77 (11)</td>
</tr>
<tr>
<td>C31—P1—Se1</td>
<td>114.38 (12)</td>
</tr>
<tr>
<td>P1—N1—H1</td>
<td>118 (2)</td>
</tr>
<tr>
<td>C11—N1—P1</td>
<td>127.7 (2)</td>
</tr>
<tr>
<td>Se1—P1—N1—C11</td>
<td>-46.7 (4)</td>
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<tr>
<td>C21—P1—N1—C11</td>
<td>79.4 (3)</td>
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<tr>
<td>C31—P1—N1—C11</td>
<td>-170.7 (3)</td>
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<td>P1—N1—C11—C12</td>
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<tr>
<td>P1—N1—C11—C16</td>
<td>161.5 (3)</td>
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<tr>
<td>N1—C11—C12—C13</td>
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<td>N1—C11—C16—C15</td>
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<td>Se1—P1—C21—C22</td>
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<td>N1—P1—C21—C22</td>
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<tr>
<td>C31—P1—C21—C22</td>
<td>77.1 (4)</td>
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<tr>
<td>Se1—P1—C21—C26</td>
<td>136.5 (3)</td>
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<tr>
<td>N1—P1—C21—C26</td>
<td>10.1 (3)</td>
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Table 2. Hydrogen-bonding geometry (Å, °)

<table>
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<tr>
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<th>D—H</th>
<th>D—A</th>
<th>D—H...A</th>
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<tbody>
<tr>
<td>C26—H26...N1</td>
<td>0.93</td>
<td>2.59</td>
<td>3.031 (6)</td>
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<tr>
<td>C32—H32...Se1</td>
<td>0.93</td>
<td>2.99</td>
<td>3.500 (4)</td>
</tr>
<tr>
<td>C36—H36...Cg2</td>
<td>0.93</td>
<td>3.41</td>
<td>3.988</td>
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<tr>
<td>N1—H1...Se1(^i)</td>
<td>0.73 (3)</td>
<td>2.85 (3)</td>
<td>3.583 (3)</td>
</tr>
<tr>
<td>C33—H33...Cg1(^ii)</td>
<td>0.93</td>
<td>2.98</td>
<td>3.729</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x, 1/2-y, 1/2+z; (ii) 1-x, 0.5+y, 1.5-z; (iii) -x,1-y,1-z

Note: Cg1 is the centroid of the of the C11-C16 aromatic ring, Cg2 is the centroid of the of the C21-C26 aromatic ring.

Crystallographic data for 1 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 792807. Copies of these data can be
References


