Synthesis and structural investigation of *N*-acyl selenophosphoramides†

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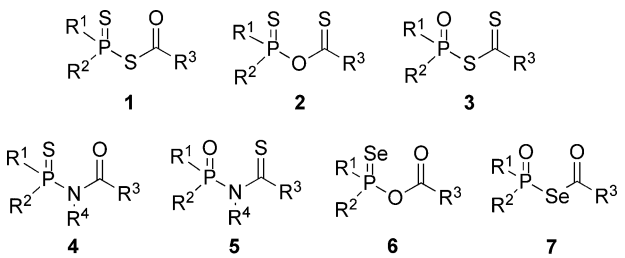
2-Amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane reacts with acyl chlorides (4-chlorobenzoyl chloride or pivaloyl chloride) yielding the respective *N*-acyl selenophosphoramides. These derivatives do not isomerise to the related selenocarbonyl imides. X-ray study of *N*-(4-chlorobenzoyl)-2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane indicates that the selenium atom is placed in the equatorial position. The next compound studied, *N*-pivaloyl-2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane, crystallises with both axial/equatorial conformers present in the asymmetric unit. Finally, 2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane is present in the solid state in the form with the selenium atom in the axial position. The results are presented together with X-ray structures of previously synthesised and described cyclic *O*-acyl monoselenophosphates.

Introduction

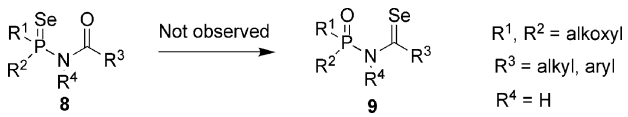
Selenium compounds play an important role in biological processes, and their synthesis has been intensively studied.[1] The sulfur analogues of acyl selenophosphates *S*-acyl dithiophosphates **1**[2,3] and *N*-acyl thiophosphoramides **4**[4–6] are not stable and isomerise to the respective thiocarbonyl derivatives **2**, **3** and **5** (Scheme 1). As a result, they can be used as an efficient and chemoselective thioacylating agents. The influence of substituents R^1 and R^2 at the phosphorus atom, R^3 at the acyl carbon and R^4 at the nitrogen atom on isomerisation was investigated, but the mechanism of this process has not been elucidated so far. It was established, however, that the presence of alkoxyl groups R^1, R^2 and an alkyl or aryl group R^4 is necessary for isomerisation.[2,6]



Scheme 1

Recently, we synthesized *O*-acyl monoselephosphates **6** in the reaction of the respective monoselenophosphoric acid salts >P(Se)O⁻ with acyl chlorides. Some of these compounds isomerise to *Se*-acyl derivatives **7** (Scheme 1). All the collected experimental data indicate that this process has a radical mechanism.[7]

In this paper we present a synthesis of *N*-acyl selenophosphoramides **8** together with their X-ray structures, and we discuss their tendency to isomerise. The isomerisation of imides **8** to **9** (Scheme 2) could give selenoacylating agents, analogous to sulfur derivatives **1** and **4**. The X-ray structures of **8** were compared with those obtained for *O*-acyl monoselenophosphates **6**.



Scheme 2

Results and discussion

For our investigations we chose derivatives of 2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane. These turned out to be stable and crystalline,[2] as is crucial for X-ray studies. The related *S*-acyl dithiophosphates **1** and *O*-acyl monoselenophosphates **6** with the same R^1 and R^2 groups are known to have a high tendency to isomerise.[2,7]

N-acyl selenophosphoramides **8a** and **8b** were prepared *via* reaction of selenophosphoric acid amide **11a** with acyl chlorides **12a,b** (Scheme 3).

The starting material for selenophosphoric acid amides was 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane **10**.[8] 2-Amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **11a** was obtained by addition of **10** to liquid ammonia followed by selenization. In the case of 2-phenylamino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **11b**, **10** was treated with aniline according to the procedure described by Stec and Zielinska *et al.*[9] 2-Methylamino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **11c** was synthesized by the reaction of 2-chloro-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane (obtained by heating **10** with selenium in toluene)[10] with a methanolic solution of methylamine.

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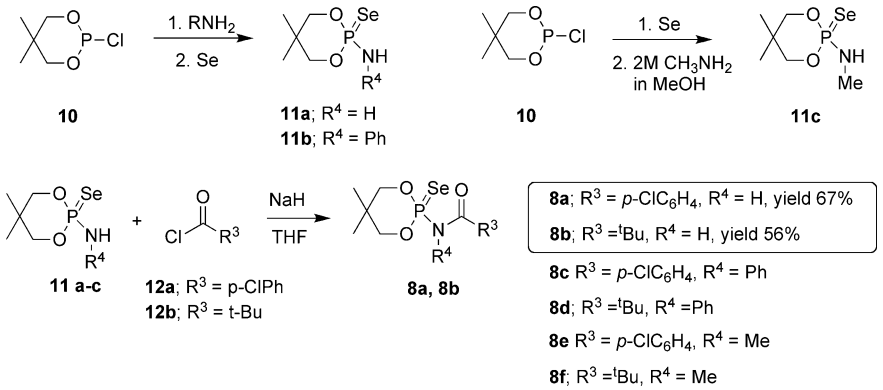
† Electronic supplementary information (ESI) available: X-ray data, Figs. S1–S3, and NMR spectra. CCDC reference numbers CCDC 717028 (**6c**), 717029 (**6d**), 717030 (**6e**), 717031 (**8a**), 717032 (**8b**) and 717033 (**11a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b907641g



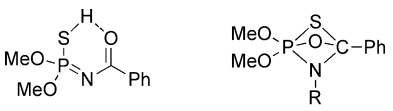
Scheme 3

Subsequently, selenophosphoric acid amides **11a–c** were metallated with sodium hydride in THF and then treated with acyl chlorides **12a,b**. These synthetic routes are presented in Scheme 3.

N-Acyl selenophosphoramides **8a** and **8b** were isolated and fully characterized. Attempts to synthesize **8c–f** *via* reactions of selenophosphoric acid amides **11b** and **11c** with acyl chlorides **12a,b** were not successful. Moreover, no isomerisation products **9** (according to Scheme 2) were observed. These results clearly indicate that the presence of a hydrogen atom at nitrogen is crucial for the stability and successful synthesis of *N*-acyl monoselenophosphates.

In the next stage of our studies, the stability of *N*-acyl selenophosphoramides **8a,b** was examined. The samples of **8a** and **8b** were heated in three different solvents (chloroform, benzene, toluene) and the progress of the reactions monitored by ^{31}P NMR spectroscopy. No isomerisation to **9** (according to Scheme 2) was observed; however, partial decomposition of the compounds in boiling toluene occurred.

The only similarity of *N*-acyl selenophosphoramides **8** to their sulfur analogues **4**, investigated by DeBruin,[4–6] was the stability of compounds with R^4 = H. To explain this, DeBruin suggested the formation of a tautomer **13**, which should be fairly stable due to an intramolecular hydrogen bond (Scheme 4) and which hinders **8** from forming a bicyclic intermediate **14** (postulated during isomerisation of **4** to **5**, and observed for R^4 = alkyl or aryl).[4] The selenium analogue of **14** could be less stable because of weaker bonds and stronger angle distortions[11] and thus decomposition instead of isomerisation was observed.



Scheme 4

However, our X-ray investigations of *N*-acyl selenophosphoramides **8a** and **8b** excluded formation of tautomers like **13** in the solid state. Thus, the explanation of the stability of **8** and related compounds in terms of the intramolecular stabilization of tautomer **13**[4] seems not to be acceptable. The basic crystal data, description of the diffraction experiment, and details of the structure refinement for the stable acyl monoselenophosphates **6c**, **6d** and **6e**, the *N*-acyl selenophosphoramides **8a** and **8b** and selenophosphoramide **11a** are given in Table S1†. The ORTEP[12] views of **6c**, **8b** and **11a** are shown in Figs. 1–3, and views of **6d**, **6e** and **8a**, Figs. S1–3, respectively.

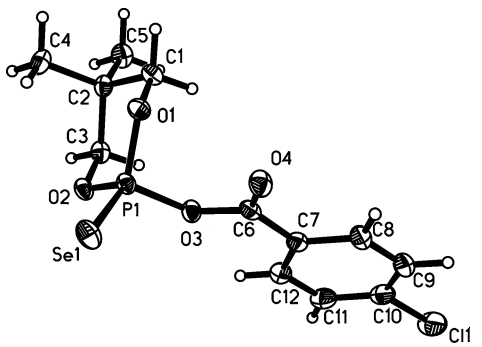


Fig. 1 The molecular structure of *O*-(*p*-chlorobenzoyl)-2-oxo-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **6c**. Displacement ellipsoids 50%. Selected bond lengths (Å) and angles (°): O1–P1 1.5693(13), O2–P1 1.5747(13), C6–C7 1.478(3), O1–P1–O3 104.93(7), O2–P1–O3 99.12(7), P1–O3–C6 122.19(11), Se1–P1–O3–C6 –65.46(13).

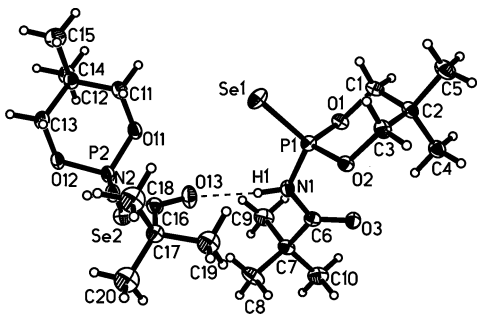
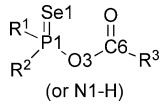


Fig. 2 The molecular structure of *N*-pivaloyl-2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **8b**. Displacement ellipsoids 50%. Selected bond lengths (Å) and angles (°): **8b-Se-*a*** O1–P1 1.5889(18), O2–P1 1.5898(17), C6–C7 1.528(3), O1–P1–N1 103.40(11), O2–P1–N1 105.13(10), P1–N1–C6 125.50(19), P1–N1–H1 114(2), C6–P1–H1 120(2), Se1–P1–N1–C6 173.37(18). **8b-Se-*e*** O11–P2 1.5745(18), O12–P2 1.5760(18), C16–C17 1.520(6), O11–P2–N2 106.76(11), O12–P2–N2 100.32(10), P2–N2–C16 122.95(13), P2–N2–H2 113(2), C16–N2–H2 120(2), Se2–P2–N2–C16 64.3(2).

The most diagnostic spectral parameters of these compounds are chemical shifts δ (ppm) and coupling constants $^1J_{P\text{-}Se}$

Table 1 ^{31}P NMR and X-ray structural analysis for the stable and crystalline anhydrides **6a–e** and imides **8** and **11a**



	R^1	R^2	R^3	^{31}P NMR: δ (ppm)/$^1J_{P\text{-}Se}$ (Hz)	P1=Se1 (Å)	P1–O3 or P1–N1 (Å)	O3–C6 or N1–C6 (Å)	C=O (Å)
6a	Ph	Ph	*p*-ClPh	81.2/859	2.0774(11)	1.653(3)	1.380(5)	1.197(5)
6b	Ph	Ph	*t*-Bu	78.6/852	2.0769(11)	1.650(3)	1.386(4)	1.200(4)
6c			*p*-ClPh	51.9/1056	2.0469(5)	1.6352(13)	1.382(2)	1.200(2)
6d			*p*-MeOPh	52.4/1057	2.0517(7)	1.628(2)	1.388(3)	1.194(3)
6e			*p*-NO$_2$Ph	51.4/1064	2.0433(11)	1.650(3)	1.369(5)	1.190(5)
8a			*p*-ClPh	56.4/941	2.0492(10)	1.674(3)	1.373(4)	1.207(4)
8b-Se-*e*			*t*-Bu	58.4/932	2.0647(8)	1.688(2)	1.382(3)	1.218(3)
8b-Se-*a*			*t*-Bu	58.4/932	2.0655(7)	1.651(2)	1.396(3)	1.214(3)
11a			—	71.0/894	2.0948(6)	1.604(2)	—	—

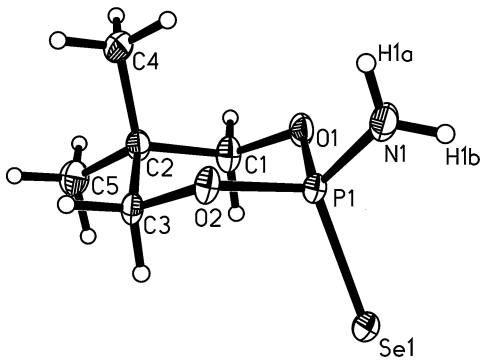


Fig. 3 The molecular structure of 2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **11a**. Displacement ellipsoids 50%. Selected bond lengths (Å) and angles (°): O1–P1 1.5855(16), O2–P1 1.5909(15), N1–H1a 0.81(3), N2–H1b 0.81(3), O1–P1–N1 107.27(11), O2–P1–N1 102.97(11), P1–N1–H1a 118(2), P1–N1–H1b 117(2), H1a–N1–H1b 118(2), Se1–P1–N1–H1a –180(2), Se1–P1–N1–H1b 31(2).

(^{31}P NMR). The NMR measurements for mixed anhydrides **6** were reported previously.[7] In this paper we compare them with those received for mixed imides **8**. The selected parameters of X-ray results for **6c–6e**, **8a**, **8b** and **11a** are presented in Table 1 together with data of acyclic compounds **6a**[13] and **6b**[14] and compared with NMR-data.

Table 1 shows data for anhydrides **6c–6e** known to crystallise as anomers with the large selenium atom in the equatorial position. This is in accordance with an increasing tendency to adopt an axial position with the electron-withdrawing character of an anomeric substituent,[15] here the P1–O3 bond. The R^1, R^2 substituents at phosphorous have significant impact on δ, $^1J_{P\text{-}Se}$, and also the P=Se bond length in the case of mixed anhydrides **6a–6e**. The acyclic compounds **6a** and **6b** with R^1 = R^2 = Ph indicate longer P1–Se1 distances and smaller $^1J_{P1\text{-}Se1}$ coupling constants than the cyclic ones **6c**, **6d** and **6e**.

These differences are not due to the cyclic arrangement of R^1 and R^2 in **6c–6e** but due to the alkoxyl character of these groups. Triphenoxyphosphine selenide has a P=Se bond length of 2.052 Å,[16] very near to the P=Se distances in **6c**, **6d** and **6e**. The substituents in the phenyl ring of the acyl part in **6c**, **6d** and **6e** exert small, but distinct influences on the bond lengths. The electron-withdrawing substituents shorten the P1–Se1 and C6–O3 bonds and lengthen the P1–O3 bond.

In the next series of X-ray measurements we attempted to characterise the structures of imides **8a** and **8b**. Similarly to anhydrides **6c–6e**, the selenium in **8a** was found to be in the equatorial position. Imide **8b** crystallized with two molecules in the asymmetric unit, one with the selenium atom in the equatorial position (**8b-*Se-e***) and one with Se in the axial (**8b-*Se-a***) position.

The preference for the axial position in the chair conformations of six-membered rings is higher for more electronegative groups,[17] and increases if the anomeric substituent X (N, O or Se) has electron-withdrawing character, due to lowering the energy of the exocyclic σ*(P–X) orbital.[18] Hence, we have competition between Se and the other group to occupy the axial position.

Acyloxy groups -O–CO–R show a high tendency to prefer axial positions, so in **6c–6e** selenium atoms adopt the equatorial position exclusively. The amido groups –NH–CO–R have a lower preference for the axial positions.

The imide **8b** bears a bulky, electron-donating group in its acyl part. Thus the tendency to occupy the axial position is lower for **8b** than for **8a**, which results in an equilibrium between **8b-*Se-e*** and **8b-*Se-a***. It is noteworthy that imide **8b** had a sufficiently weakened axial preference of amido group to have an axial P=Se bond, despite the presence of the electron-withdrawing carbonyl group connected to the bridging NH unit.

The geometry around the N1 atom in **8a** is not strictly planar, the sum of angles being 357(3)°. The torsion angle C6–N1–P1–Se1 is 63.4(3)°. The conformation around P–N bond puts the lone pair of the almost planar N1 atom[19] antiperiplanar to P1=Se1 and antiperiplanar to the P1–O1 bonds, and thus the reverse anomeric interactions $n_N \rightarrow \sigma^*$(P1=Se1) and $n_N \rightarrow \sigma^*$(P1–O1) are possible.

In the literature are reported structural evaluations concerning 5,5-dimethyl-2-(phenylamino)-1,3,2-dioxaphosphorinane-2-selenide,[20] 5,5-dimethyl-2-(*o*-nitrophenyl)amino-1,3,2-dioxaphosphorinane-2-selenide[21] and 2-((3,5-dichlorophenyl)amino)-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-selenide,[22] in which the nitrogen atom bears an electron-withdrawing group. All these compounds display in the solid state axial P–N bonds and Se in the equatorial position.

There are small but distinct differences in bond distances in **8b-*Se-a*** and **8b-*Se-e***. Isomer **8b-*Se-a*** with axial Se has slightly shorter P–N and C=O bonds and slightly longer P=Se and

Table 2 Results of theoretical calculations, and comparison of energies for equatorial and axial conformers of **8b**. All optimised structures were checked that they represented true minima by calculating the IR spectra, in which no imaginary frequencies were present[a]

Method	b3lyp/3-21G*	MP2/3-21G*	HF/3-21G*
8b-*Se-e* (a.u.)	−3400.16073652	−3395.21504485	−3393.6072951
8b-*Se-a* (a.u.)	−3400.16132766	−3395.21870627	−3393.6040368
ΔE(*e*–*a*) (a.u.)	0.00059114	0.00366142	−0.00325
ΔE(*e*–*a*) (kcal/mol)	0.37	2.30	−2.04

[a] Note that the two molecules of **8b** are additionally involved in intermolecular hydrogen bonding of the N–H···O type, which can also facilitate deformation of torsion angles.

C–N bonds than **8b-*Se-e***. There are, however, major differences in conformations around the P–N bonds and geometries around the N atoms.

The structural features of **8b-*Se-e*** are similar to those of **8a**. The P2 atom and the N2–H2 and C16–O13 bonds are almost in one plane, but the P2=Se2 bond is out of plane. The torsion angle Se2–P2–N2–C16 is 64.3(2)°, and the sum of angles around N2 is 356(2)°. The lone electron pair of N2 can be mixed with σ*(P2=O11) and with σ*(P2–Se2) in reverse anomeric interactions, although additional NBO calculations (see below) indicate that the energetic stabilization due to this interaction is of minor importance.

In **8b-*Se-a*** the geometry around N1 is planar, while the sum of angles around N2 is 360(2)°. The P1=Se1, N1–H1 and C6–O3 bonds are almost in one plane, and the torsion angle Se1–P1–N1–C6 is 173.37(18)°. The lone pair of the planar N1 atom[19] cannot be antiperiplanar to the P1=Se1 bond, and thus it cannot act as a donor in anomeric interaction $n_N \rightarrow \sigma^*$(P=Se). It is almost antiperiplanar to the P1–O1 and to P1–O2 bonds and can act in anomeric interactions $n_N \rightarrow \sigma^*$(P1–O1) and $n_N \rightarrow \sigma^*$(P1–O2). The lone pairs of endocyclic O1 and O2 atoms are antiperiplanar to the P1=Se1 bond and can act as donors in anomeric interactions $n_O \rightarrow \sigma^*$(P=Se).

The selenium atom can adopt the equatorial position in *trans*-2-*t*-butylamino-4-methyl-1,3,2-dioxaphosphorinane-2-selenide,[23] or the axial position in *cis*-2-*t*-butylamino-4-methyl-1,3,2-dioxaphosphorinane-2-selenide[24] and *cis*-2-*t*-butylamino-4,4,6-trimethyl-1,3,2-dioxaphosphorinane-2-selenide.[25] It is worth pointing out that the imido compound **8b** and amido compounds[23,24,25] with a *t*-butyl group show similar axial–equatorial preferences.

In order to get a deeper insight into relative stability of axial and equatorial conformers of **8b**, additional theoretical investigations were carried out. The results of the optimisations (see Table 2) indicate that the axial conformer is energetically more stable, although a method including electron correlation (more advanced than simple HF) should be used to reach this conclusion.

The difference in energy between the two forms is not crucial for excluding one specific conformer from crystalisation. One additional explanation for co-crystallisation can be hydrogen bond formation between the two molecules (see Fig. 2). In all investigated compounds (**6c**, **6d**, **6e**, **8a**, **8b** and **11a**) predictions based on the anomeric effect are in accordance with X-ray structure determinations.

Interestingly, the torsion angle Se–P–N–C in both theoretically optimised structures **8b** was very similar (*ca.* 180°). Calculation of vibrational spectrum for both **8b** conformers shows that the two least energetically demanding vibration modes can be described as rotations of the terminal *tert*-butyl group and deformation of the above-mentioned Se–P–N–C torsion. This helps us to rationalise the facts that one of the *tert*-butyl groups is disordered and that the torsion is altered in the solid state (compared to the isolated molecule).

The natural bond orbitals (NBO) analysis[30] of the optimised structures suggests that the most (energetically) important donor–acceptor intramolecular interactions are $lp_N \rightarrow \pi^*$(C=O), then $lp_{Se} \rightarrow \sigma^*$(P–N), $lp_{Se} \rightarrow \sigma^*$(P–O), $lp_O \rightarrow \sigma^*$(P–N) and $lp_O \rightarrow \sigma^*$(Se–P). The program interprets the P–Se system as a single bond with separated charges and three lone pairs on the selenium atom. Two of the pairs have mainly *p*-character, while the last pair has a big *s*-function contribution, and is inactive in intramolecular donor–acceptor interactions.

In amide **11a** selenium atoms adopt the axial position, exclusively. This compound has the shortest P–N and the longest P=Se distances of all derivatives **6** and **8** under investigation (and the smallest $^1J_{P-Se}$ value as well). The geometry around N atom is not planar, and the sum of angles around N1 is 353(2)°; the lone pair at N1 cannot act as a donor to σ*(P1–Se1). The solid-state structure of the related 5,5-dimethyl-2-ethylamino-1,3,2-dioxaphosphorinane-2-selenide[27] has similar features.

Solid-state intermolecular interactions

The packing of molecules **6c–e** and **8a** is reinforced by π–π stacking interactions between phenyl rings. The centroid-to-centroid distances for the neighbouring rings are given in Table 3. This interaction is the strongest for nitrophenyl-substituted derivative **6e**.

A relatively strong N–H···O hydrogen bond is found in structure **8b** between the two axial/equatorial conformers. Interestingly, both hydrogen atoms in **11a** are directed towards the selenium atoms, which could be an indication of a weak hydrogen bond of the N–H···Se type. Due to the partial negative charge of the Se atom, its acceptor properties should be enhanced.

Conclusions

The presence of the hydrogen at the nitrogen bridge atom is crucial for stability of *N*-acyl selenophosphoramides **8**. The substituents in the acyl part and the type of the bridge atom determine the conformation of the six-membered cyclic derivatives of selenophosphoric acid **6c–e** and **8a,b**. The amido group -NH–CO–C_6H_5–4-Cl in imide **8a** occupies the axial position, as for the acyloxy groups -O–CO–R in anhydrides **6c–e**. In contrast, *N*-pivaloyl selenophosphoramide **8b** gave two chair conformations **8b-*Se-a*** and **8b-Se-e** due to a lower electron-withdrawing effect

Table 3 Data concerning π–π stacking interactions between phenyl rings in **6c–e** and **8a**

Compound	**6c**	**6d**	**6e**	**8a**
Centroid-to-centroid distance (Å)	4.626	4.026	3.717	4.223

of the acyl part and a higher energy of the antibonding P–N orbital. These results clearly indicate a correlation between anomeric interactions $n_O \rightarrow \sigma^*$(P–X) (where X = O or NH) and the conformer distribution for **6c–e** and **8a,b**. This relationship is extended to derivatives without an acyl group at the N atom, *viz.* selenophosphoramide **11a**, in which selenium is found only in the axial position despite its size.

Experimental

O-Acyl monoselenophosphates **6** were obtained by the reaction of the respective monoselenophosphoric acid salt with acyl chloride.[7] Preparation of mixed imides **8** was carried out under argon in THF dried over potassium with benzophenone as indicator. Chromatography was carried out on Silica Gel 60 (0.05–0.2mm) Macherey Nagel®. NMR was performed on a Varian Gemini 500 MHz, *J* values are given in Hz. IR spectra were acquired on a Bruker IFS66 instrument. Mass spectra were acquired on a MASPEC II system [II32/99D9] in the EI mode if not otherwise specified.

X-ray structural analysis

Experimental diffraction data were collected on KM4CCD kappa-geometry diffractometer, equipped with a Sapphire2 CCD detector. An enhanced X-ray Mo Kα radiation source with a graphite monochromator was used. The preliminary calculations were made using CrysAlis software package.[28] Structure solution and final refinement were carried out using the SHELX-97 program package.[29]

Structures were solved by direct methods and all of the non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least squares procedure based on F^2. All C–H hydrogen atoms were refined using isotropic model with U_{iso}(H) values fixed to be 1.5 times U_{eq} of C atoms for CH_3 or 1.2 times U_{eq} for CH_2 and CH groups. All N–H hydrogen atoms were refined freely without restraints. Analytical absorption corrections based on a multi-faceted model of crystal shape were applied using CrysAlis171 program.[28]

The structure of **8b** contains one *tert*-butyl group (C17–C20) in molecule **8b-*Se-e*** disordered over two positions occupied with probabilities 0.778(6)/0.222(6).

Theoretical quantum-chemical calculations

Calculations were carried out at the Academic Computer Center in Gdańsk (TASK). The Gaussian 03 program package, including the NBO module,[30] was used for the entire investigation. Both conformers of **8b** were cut out of the X-ray structure and their geometry optimised using the Gaussian 03 package.[26] Density functional theory with B3LYP functional and Møller–Plesset second-order perturbation theory were selected as the minimisation methods.

Synthesis

2-Chloro-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane. This was prepared from 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane **10**[8] according to the procedure described by Michalska *et al.*[10]

2-Amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane 11a. 2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane **10**[8] (0.05 mol) was added portionwise to liquid ammonia (100–125 mL) at –33 °C with stirring. After vigorous reaction, selenium powder (0.05 mol) was added and stirring continued for 6 h. Then, cooling bath (acetone + CO_2) was taken away and ammonia evaporated with stirring. THF (50 mL) was poured onto the remaining material and the reaction mixture was stirred for 12 h. The solids were filtered off and washed with THF. The solvent was removed in vacuum, and the crude product purified by column chromatography (eluent: petroleum ether–dichloromethane) to give **11a** (6.87 g, 60%). The product was crystallized (petroleum ether–dichloromethane) for crystallography purposes.

Mp 69–71 °C; δ_P (acetone-d_6) 71.0 ($^1J_{PSe}$ 894); δ_H (acetone-d_6): 0.86 (3H_a, s, CH_3), 1.20 (3H_e, s, CH_3), 3.72 (2H_a, dd, $^2J_{Ha-He}$ 10.5, $^3J_{Ha-P}$ 26.4, CH_2O), 4.26 (2H_e, dd, $^2J_{He-Ha}$ 10.5, $^3J_{He-P}$ 5.1, CH_2O), 5.24 (2H, s, NH_2); δ_C (acetone-d_6) 20.08, 21.90, 32.33 (d, *J* 5.0), 78.60 (d, *J* 5.0); ν_{max}/cm^{-1} 518 (P=Se); *m/z* 228.9779 ($C_5H_{12}NO_2P^{80}Se$ requires 228.9771).

2-Phenylamino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane 11b. This was prepared from 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane **10**[8] according to the procedure described by Stec and Zielinska *et al.*[9]

Mp 174–175 °C (Lit.,[9] mp 175–176 °C); δ_P ($CDCl_3$) 65.9 ($^1J_{PSe}$ 909) (Lit.,[9] δ_P ($CDCl_3$) 62); δ_H($CDCl_3$) 0.92 (3H_a, s, CH_3), 1.11 (3H_e, s, CH_3), 3.83 (2H_a, dd, $^2J_{Ha-He}$ 11.0, $^3J_{Ha-P}$ 25.1, CH_2O), 4.44 (2H_e, dd, $^2J_{He-Ha}$ 10.7, $^3J_{He-P}$ 5.8, CH_2O), 5.6 (1H_{amide}, s), 7.15 (1H_{arom}, m), 7.23 (2H_{arom}, m), 7.32 (2H_{arom}, t, ^3J 7.8).

2-Methyloamino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane 11c. To a solution of 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane **10**[8] (17.8 mmol) was added triethylamine (17.8 mmol). Then, to the reaction mixture was added dropwise methylamine (9.0 mL, 2 M in methanol) at room temperature with stirring. After 2 h the solvent was evaporated and the crude product purified by column chromatography (eluent: CH_2Cl_2–petroleum ether 1:2) to give **11c** (15.17 g, 53%).

Mp 79–81 °C; δ_P ($CDCl_3$) 71.2 ($^1J_{P-Se}$ 893); δ_H($CDCl_3$) 0.89 (3H_a, s, CH_3), 1.28 (3H_e, s, CH_3), 2.78 (3H, d, $^3J_{H-P}$ 13.2, NCH_3), 3.75 (2H_a, dd, $^2J_{Ha-He}$ 11.2, $^3J_{Ha-P}$ 25.9, CH_2O), 4.41 (2H_e, dd, $^2J_{He-Ha}$ 10.7, $^3J_{He-P}$ 3.4, CH_2O); *m/z* 243.9998 ($C_6H_{14}NO_2P^{80}Se$ requires 244,0000) in ESI mode.

Selenophosphoryl carbonyl imides 8a and 8b. To a suspension of sodium hydride (10–12 mmol) in 15 mL of THF was added 2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **11a** (5 mmol) at 0 °C. After all hydrogen had evolved, the respective acyl chloride **12a,b** (5 mmol) was added portionwise and stirring was continued at room temperature for 1 h. Then, the reaction mixture was filtered, evaporated under reduced pressure, dissolved in chloroform (100 mL) and washed with 1 M NH_4Cl. Subsequently, the organic layer was separated, dried over $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography (eluent: petroleum ether–dichloromethane). The product was crystallized (petroleum ether–dichloromethane) for crystallography purposes.

***N*-(*p*-Chlorobenzoyl)-2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane 8a** (2.46 g, 67%), mp 163–164 °C with decomposition, δ_P ($CDCl_3$) 56.4 ($^1J_{PSe}$ 941); δ_H($CDCl_3$) 1.19 (3H_a, s, CH_3),

1.26 (3H$_e$, s, CH$_3$), 4.28 (2H$_a$, dd, $^2J_{Ha–He}$ 10.7, $^3J_{Ha–P}$ 12.7, CH$_2$O), 4.38 (2H$_e$, dd, $^2J_{He–Ha}$ 10.7, $^3J_{He–P}$ 14.2, CH$_2$O), 7.46 (2H$_{arom}$, d, $^3J_{H–H}$ 8.3), 7.59 (1H$_{amide}$, d, $^2J_{H–P}$ 17.1); 7.78 (2H$_{arom}$, d, $^3J_{H–H}$ 8.8); δ_C(CDCl$_3$) 22.01; 22.53; 32.89 (d, *J* 7.6), 79.05 (d, *J* 8.0), 129.49, 129.58, 130.65 (d, *J* 7.6), 140.03, 165.25 (d, *J* 8.0); ν_{max}/cm^{-1} 566 (P=Se), 1653 (C=O); *m*/*z* 366.9648 ($C_{12}H_{15}NO_3P^{80}Se^{35}Cl$ requires 366.9643).

***N*-Pivaloyl-2-amino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane 8b** (1.75 g, 56%), mp 119–120.5 °C; δ_P (CDCl$_3$) 58.4 ($^1J_{PSe}$ 932); δ_H(CDCl$_3$) 1.10 (3H$_a$, s, CH$_3$), 1.22 (9H, s, CH$_3$), 1.24 (3H$_e$, s, CH$_3$), 4.20–4.27 (4H, m), 6.93 (1H$_{amide}$, d, $^2J_{H–P}$ 18.1); δ_C(CDCl$_3$) 22.16, 22.35, 27.34, 32.88 (d, *J* 7.6), 40.32 (d, *J* 6.1), 78.70 (d, *J* 7.6); 177.91 (d, *J* 11.4); ν_{max}/cm^{-1} 536 (P=Se), 562; 1688, 1716 (C=O); *m*/*z* 313.0358 ($C_{10}H_{20}NO_3P^{80}Se$ requires 313.0346).

Attempted synthesis of *N*-substituted mixed imides 8c–8f. To a suspension of sodium hydride (5–6 mmol) in 15 mL of THF was added 2-phenylamino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **11b** (5 mmol) or 2-methylamino-2-seleno-5,5-dimethyl-1,3,2-dioxaphosphorinane **11c** (5 mmol) at 0 °C. After all the hydrogen had evolved, the respective acyl chloride **12a,b** (5 mmol) was added portionwise and stirring was continued at room temperature for 1 h. ^{31}P NMR analysis of the crude reaction mixtures indicated numerous side-products. There was no resonance signal for expected product **8c–8f** or for the isomerisation products **9c–9f**.

Thermodynamic stability of 8a and 8b. A solution of corresponding imide **8a,b** (1 mmol) in chloroform (5 mL) was prepared and monitored by ^{31}P NMR spectroscopy at room temperature. Both imides were stable when the solutions were refluxed in chloroform (b.p. 61 °C) for 4 h, and no reaction was detected. Other solvents were also examined (benzene (b.p. 80 °C), toluene (b.p. 111 °C)) with a 4 h monitoring time. During heating in toluene, initial symptoms of decomposition were observed. No isomerisation was noted in these experiments.

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