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THE MOLECULAR STRUCTURE OF *CIS*-2-t-BUTYLAMINO-2-SELENO-4,4,6-TRIMETHYL-1,3,2-DIOXAPHOSPHORINANE C₁₀H₂₂NO₂PSe, AN EXAMPLE OF THE TWIST-BOAT CONFORMATION

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THE MOLECULAR STRUCTURE OF *CIS*-2-t-BUTYLAMINO-2-SELENO-4,4,6-TRIMETHYL-1,3,2-DIOXAPHOSPHORINANE $C_{10}H_{22}NO_2PSe$, AN EXAMPLE OF THE TWIST-BOAT CONFORMATION

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Diastereoisomeric 2-t-butylamino-2-seleno-4,4,6-trimethyl-1,3,2-dioxaphosphorinans have been prepared and separated into pure *cis*- and *trans*-isomers. The minor isomer (*cis*) was investigated by means of x-ray crystallography and its has been demonstrated, that in solid state it possesses twist-boat conformation.

INTRODUCTION

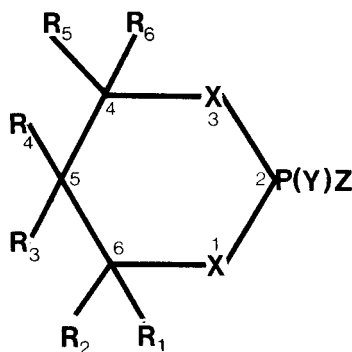
In a number of studies concerning the stereochemistry of cyclic six-membered ring phosphorus esters and amides of general formula (1), it has been established that these systems exist in solution, as well as in the solid state, in a flattened chair conformation,¹ and that their conformational stability and the spatial orientation of *Y* and *Z* substituents depends on their electronic and steric requirements.² The distortion of the ring from the “ideal” chair conformation also depends on the nature of the *X*, *Y*, *Z* and *R* substituents. Until now, the most pronounced distortions have been reported

for *trans*-2-triphenylmethyl-2-oxo-4,6-dimethyl-1,3,2-dioxaphosphorinane which in solid state possess the “chaise longue” conformation,³ and for *cis*-2,5-di-t-butyl-2-oxo-1,3,2-dioxaphosphorinane for which the boat conformation⁴ was claimed in solution on the basis of ¹H nmr studies.

RESULTS AND DISCUSSION

In this communication we wish to report the first example, as shown by means of x-ray crystallography of a “boat” conformation 1,3,2-dioxaphosphorinane. Reaction of 2-methylpentan-2,4-diol with phosphorus trichloride gave 2-chloro-4,4,6-trimethyl-1,3,2-dioxaphosphorinane (2) as a mixture of two isomers in the ratio 95:5. Its treatment with t-butylamine led to 2-t-butylamino-4,4,6-trimethyl-1,3,2-dioxaphosphorinane (3), as a mixture of the two isomers in the ratio 73:27 (*A*:*B*).

Reaction of this isomeric mixture (3) with an excess of elemental selenium produced the 2-t-butylamino-2-seleno-4,4,6-trimethyl-1,3,2-dioxaphosphorinane (4) with the isomeric ratio 62:38 (*A*:*B*). The diastereoisomeric (4*A*) and (4*B*) were separated by means of column chromatography and recrystallized from *n*-hexane giving (4*A*) |major, mp 114–115°C $\delta^{31}P$ A = –56.6 (to low field),



FORMULA 1

$^1J(\text{P—Se}) = 896 \text{ Hz}$ and **(4B)** |minor, mp 97–98°C, $\delta^{31}\text{PB} = -52.6$ (to low field), $^1J(\text{P—Se}) = 896 \text{ Hz}$. Because the crystals of **(4A)** were heavily twinned, only those of title compound, **(4B)** were investigated by means of x-ray crystallography. **(4B)** crystallizes in the triclinic space group $P1$ $a = 9.311$ (1), $b = 11.355$ (1), $c = 15.244$ (2) Å, $\alpha = 89.74$ (1), $\beta = 77.22$ (1), $\gamma = 71.11$ (1)°, with two independent molecules in the asymmetric unit, $Z = 4$. A total of 6418 reflections were collected, of which 2824 were considered unobserved ($2\sigma I \leq I$). The structure was solved by the heavy atom method and refined by least-squares techniques (2 blocks, one for each molecule) to a final R -value of 0.064 ($R_w = 0.071$). Further refinement proved unsuccessful because of high anisotropic motion of the methyl groups attached to the carbon atoms of the heterocycle, indicating a slight disorder problem. Consequently, standard deviations associated with these atomic

parameters are unusually high, and bond distances are artificially shortened. Selected bond distance and angles averaged over both independent molecules are as follows: Se1—P1 2.096 (5) Å, P1—N1 1.619 (2) Å, P1—O1(2) 1.58 (1) Å, O1(2)—C1(3) 1.48 (2) Å, N1—C6 1.51 (2) Å, Se1—P1—O1(2) 114.5 (1.0)°, Se1—P1—N1 110.6 (6)°, O1(2)—P1—N1 106.6 (9)°, O1—P1—O2 103.3 (1)°, P1—N1—C6 129.6 (1.1)°, P1—O1(2)—C(3) 122 (3)°. Atomic coordinates and thermal parameters are shown in Table I. Both molecules are approximately mirror images of each other. The conformation of one single molecule is shown in Figure 1. Both independent molecules are similar in their bond distances. The conformation of the six-membered rings, however, is slightly different. The dihedral angles P1—O1—C1—C2 (16.8°) and P1—O2—C3—C2 (3.1°) show a marked difference in one molecule, but are similar in the second

TABLE I

Atomic coordinates ($\times 10^4$) with esd's in parentheses and anisotropic thermal parameters ($\times 10^3$). The temperature factor is expressed in the form $\exp[-2\pi^2(U_{11}h^2(a^*)^2 + \dots + 2U_{13}hla^*c^* + \dots)]$

Atom	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Se1	992 (1)	1025 (1)	969 (1)	45	115	75	-22	-5	-16
Se2	2212 (1)	4977 (1)	3869 (1)	64	80	79	11	-3	30
P1	-1407 (2)	1744 (1)	1561 (1)	45	74	51	-17	-8	-4
P2	531 (2)	6536 (1)	3542 (1)	64	54	52	-2	-8	10
N1	-2332 (5)	918 (4)	1218 (3)	43	69	65	-21	-12	1
N2	-1171 (6)	6688 (5)	4171 (3)	59	72	78	10	-1	19
O1	-2260 (5)	3143 (4)	1368 (3)	74	64	78	-20	-22	-5
O2	-1793 (5)	1776 (5)	2619 (2)	66	118	47	-29	-9	-10
O3	353 (5)	6486 (4)	2531 (2)	72	73	57	-16	-14	15
O4	850 (6)	7801 (4)	3644 (3)	118	70	65	-27	-17	4
C1	-2535 (16)	4254 (10)	1961 (7)	285	100	111	-124	-103	35
C2	-1458 (11)	3849 (10)	2598 (7)	105	134	107	-73	-0	-33
C3	-1766 (12)	2871 (11)	3134 (6)	92	163	48	-5	-13	-34
C4	-2343 (27)	5209 (16)	1449 (12)	608	197	268	-235	-265	42
C5	-2993 (22)	3228 (16)	3852 (10)	287	270	165	-156	-59	-20
C5A	-352 (18)	2304 (13)	3577 (9)	234	187	189	-32	-112	-29
C6	-4041 (7)	1169 (6)	1333 (4)	47	72	59	-18	-9	-4
C7	-4603 (8)	1950 (7)	580 (5)	59	107	93	-33	-19	24
C8	-4971 (8)	1859 (7)	2235 (4)	67	114	62	-26	-7	-1
C9	-4249 (9)	-94 (8)	1255 (5)	79	106	73	-54	-2	-0
C10	1510 (10)	6721 (8)	1762 (5)	93	91	51	-15	-4	11
C11	2456 (9)	7399 (8)	2131 (5)	75	106	80	-27	-16	34
C12	1565 (9)	8361 (7)	2883 (5)	86	87	88	-35	-39	24
C13	2405 (15)	9099 (11)	3265 (9)	173	165	209	-95	-111	87
C14	506 (11)	7507 (8)	1176 (5)	142	113	69	-53	-37	31
C15	2502 (12)	5495 (9)	1287 (6)	146	122	73	-13	2	-12
C16	-2676 (9)	7781 (8)	4286 (5)	70	88	69	28	6	15
C17	-2850 (11)	8459 (10)	3462 (6)	96	148	116	49	-2	34
C18	-2903 (14)	8491 (11)	5125 (8)	165	147	141	100	-69	-55
C19	-4019 (12)	7237 (12)	4456 (9)	78	186	229	4	-60	76

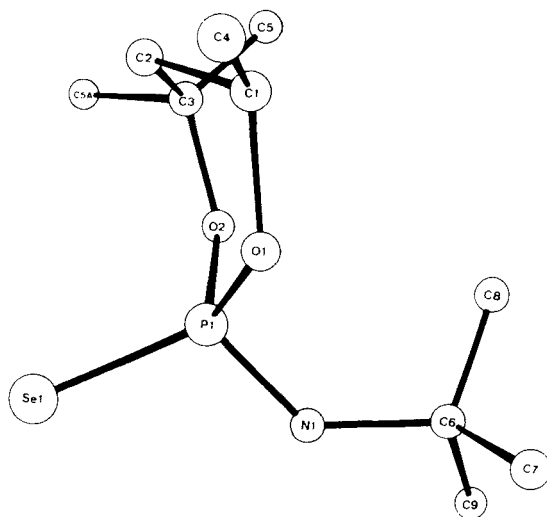


FIGURE 1

molecule (21.6°, resp. 18.4°). Inspection of the packing arrangement shows that the *t*-butylamino group of molecule **4B**₂ is within the neighbourhood of C1—C2—C3 of molecule **4B**₁, causing a relative flattening of this part of the six-membered ring by steric interaction. In our estimation the reason for the “twist-boat” conformation of (**4B**) lies in 2,4-steric interaction between axial 4-Me and 2-*t*-BuNH groups, because both isomers of 2-*t*-butylamino-2-seleno-4-methyl-1,3,2-dioxaphosphorinane exist in the chair conformation.⁶ The fact, that the *trans*-isomer of this last compound exists in solution in the fast (on an nmr time scale) equilibrium $4\text{Me}_{\text{eq}}-2\text{Se}_{\text{eq}} \rightleftharpoons 4\text{Me}_{\text{ax}}-2\text{Se}_{\text{ax}}$, strongly supports this explanation. Because the 2-*t*-BuNH group should possess unhindered rotation around the P—N bond,⁷ steric interactions of this bulky substituent with the 4Me_{ax} group in (**4B**) force the ring to flip into the boat form. Ring inversion to the other chair conformer cannot occur owing to strong 4–6 methyl-diaxial interaction.

Although the structure of (**4A**) was not assigned, we anticipate that this molecule would exist in the chair conformation with axially oriented selenophosphoryl group. This prediction is based on the measurements of direct spin-spin coupling between ³¹P and ⁷⁷Se atoms in both isomers (**4A**) and (**4B**).⁸ Spin-spin coupling ¹*J*(P—Se) in both (**4A**) and (**4B**) has the same absolute value what is consistent with the view that in solution the selenium atom occupies axial (pseudoaxial) position in both isomers. Analysis of the ¹³C nmr data for (**4A**) and (**4B**) (see Table II) strongly speaks for such a conformational assignment. Although the Karplus-type relationship for the CCOP system has not yet been established, the vicinal spin-spin coupling ³*J*(PC₅) for (**4B**) has a much higher value than in other investigated systems and supports the conclusion about periplanar arrangements of O—P and C₄₍₆₎—C₅ bonds.

EXPERIMENTAL

All mps and bps are uncorrected. Solvents and commercial reagents were purified and dried by conventional methods before use.

³¹P and ¹³C nmr proton decoupled spectra were recorded at 24.24 and 15.03 MHz, respectively, with JEOL-FX60 spectrometer. δ³¹P are listed in ppm relative to external H₃PO₄ in C₆D₆ and negative values are given for those compounds absorbing at lower field than H₃PO₄. The data for x-ray structure determination were collected on CAD-4 diffractometer, molybdenum source with graphite monochromator, λ = 0.71069 Å.

2-Chloro-4,4,6-trimethyl-1,3,2-dioxaphosphorinane (2)

To a solution of phosphorus trichloride (27.6 g, 0.2 m) and pyridine (37.6 g, 0.4 m) in benzene (400 ml) was added dropwise at 0–5°C, with vigorous stirring and external cooling, 2-methylpentan-2,4-diol (23.5 g, 0.2 m). Stirring at room temperature was continued for 2 h. Pyridine hydrochloride was filtered off and washed with benzene. The combined benzene solutions were evaporated, the precipitated pyridine hydrochloride was filtered off again, and the residue was distilled under reduced pressure to give (**2**) as a mixture of two isomers in a yield 11.5 g (30%), bp 53–55°/2 mm, *n*_D²⁵ = 1.473, δ³¹P = –145.9 (to low field), 95% *trans* (l.p. equatorial, ³*J*(P—C₅) = 4.9 Hz).⁹

TABLE II

¹³C nmr data of both isomers of (**4**). Chemical shifts (in C₆D₆) are relative to TMS (in ppm). Coupling constants (*J*(PC), Hz) are given in parentheses

	C ₄	C ₅	C ₆	4Me	6Me
4A	82.0 (5.8)	43.7 (5.1)	69.5 (4.4)	31.8 (7.3); 26.2 (—)	21.7 (11.0)
4B	81.5 (5.9)	41.5 (15.4)	72.4 (5.9)	29.6 (—); 28.2 (3.7)	22.7 (5.2)

2-t-Butylamino-4,4,6-trimethyl-1,3,2-dioxaphosphorinane (3)

A solution of *t*-butylamine (7.3 g, 0.1 m) in benzene (20 ml) was slowly added to a stirred solution of (2) (9.1 g, 0.05 m) in benzene (100 ml) at 0–5°C. The mixture was stirred at room temperature for 0.5 h. Amine hydrochloride was filtered off and washed with benzene. The combined benzene solutions were evaporated and the residue was distilled under reduced pressure to give (3) as a mixture of two isomers in the ratio 73:27 (A:B), bp 69–71°/0.8 mm, yield 6.9 g (60%), $n_D^{25} = 1.463$, $\delta^{31}\text{P}(3\text{A}) = -135.3$ (to low field), $^3J(\text{P}-\text{C}_3) = 9.5$ Hz, $\delta^{31}\text{P}(3\text{B}) = -128.2$ (to low field), $^3J(\text{P}-\text{C}_3) = 5.9$ Hz.

2-t-Butylamino-2-seleno-4,4,6-trimethyl-1,3,2-dioxaphosphorinane (4)

Elemental selenium (2.2 g) was added in small portions to the stirred solution of distilled (3) (5.5 g, 0.025 m) in benzene (50 ml). An exothermic reaction accompanied with disappearance of selenium was observed. Stirring was continued for 2 h and the unreacted selenium was filtered off. The resulting solution was evaporated to give (4) as a mixture of isomers in the ratio 62:38 (A:B). Column chromatography (silicagel, 100–200 mesh, 500 g, benzene-*n*-hexane-acetone 10:10:1 as eluent) of the raw material gave two fractions: the faster migrating (4A), 3.4 g (after crystallization from *n*-hexane) R_f 0.42 (TLC in solvent as above), mp 114–115°, $\delta^{31}\text{P} = -56.6$ (to low field), $^1J(\text{P}-\text{Se}) = 896$ Hz, and the slower migrating (4B), 2.1 g, R_f 0.36, mp 97–98° (from *n*-hexane), $\delta^{31}\text{P} = -52.6$ (to low field), $^1J(\text{P}-\text{Se}) = 896$ Hz.

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