X-ray and Solid State NMR Studies of Bis(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl) Disulfide and Diselenide

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Received November 24, 1993[®]

Crystals of bis(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl) disulfide (**1a**) grown from benzene are monoclinic, *Cc*, with $a = 6.762(2)$ Å, $b = 21.856(4)$ Å, $c = 12.061(3)$ Å, $\alpha = 90°$, $\beta = 93.49(2)°$, $\gamma = 90°$, $V = 1779.2(5)$ Å^3, $Z = 4$, and $D_c = 1.47$ g cm^{-3}. Refinement using 1789 reflections for 201 variables gives $R = 0.036$. Crystals of bis(5,5-dimethyl-2-thioxo-1.3,2-dioxaphosphorinan-2-yl) diselenide (**2b**) grown from a mixture of benzene/hexane contain benzene which upon exposure to the atmosphere diffuses out over several weeks giving the diselenide **2a**. Crystals of **2a** are rhombohedral, $R\bar{3}$, in a hexagonal setting with $a = b = 31.660(3)$ Å, $c = 9.702(1)$ Å, $V = 8422(38)$ Å^3, $Z = 18$, and $D_c = 1.732$ g cm^{-3}. Refinement using 3369 reflections for 181 variables gives $R = 0.054$. ^{13}C, ^{31}P, and ^{77}Se high-resolution solid state NMR data are consistent with results obtained from single crystal diffraction studies and confirm that in both compounds one molecule per unique volume is an independent unit. Principal elements of the ^{31}P and ^{77}Se chemical shift tensors calculated from spinning sideband intensities are discussed in terms of the local geometry of phosphorus and selenium.

Introduction

Because of the significance of six-membered organophosphorus rings in biological processes such compounds have received much attention. Cyclic organophosphorus compounds are postulated as intermediates or activated states in enzymatic reaction mechanisms.[1] c-AMP, fully discussed by Miller,[2] is one of the most often cited cases. 5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphorinanes, introduced by Edmundson,[3,4] have been found to be useful models for stereochemical and structural studies.[5] Several analogs were investigated by NMR and X-ray diffraction (XRD) techniques in order to see the conformation of the six-membered ring and geometry of the adjacent groups.[6−15]

We report X-ray studies of bis(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl) disulfide (**1a**) and diselenide (**2a**). We have used the disulfide and diselenide as model compounds for several reasons. First, despite the variety of studies the question of the conformation of six-membered rings and the placement of adjacent ligands remains open. Second, we have previously demonstrated unique features of the disulfide bond in the S=P−S−S−P=S skeleton.[16] Because of the unexpectedly low barrier of trans rotation around the S−S bond, bis(organothiophosphoryl) disulfides easily form the conformation with a P−S−S−P torsional angle of 180°[17,18] not observed in C−S−S−C analogs. The relationship between the S−S disulfide distance and the P−S−S−P unit in the region of 80−180° has been unambiguously demonstrated.[16,18] This class of compounds provides excellent models for studies of physical properties of the disulfide bond in a region which was not investigated before. Furthermore, we were attracted by the prospect of comparing disulfide **1** and diselenide **2** in terms of geometries of the P−S−S−P and P−Se−Se−P units.

High-resolution solid state NMR spectroscopy allows liquid-like spectra of powdered samples to be obtained.[19−21] We report the ^{13}C, ^{31}P, and ^{77}Se CP/MAS NMR spectra of two modifica-

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[®] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

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Table 1. Crystal Data and Experimental Details

	disulfide **1a**	diselenide **2a**
molecular formula	$C_{10}H_{20}O_4P_2S_4$	$C_{10}H_{20}O_4P_2S_2Se_2$
space group	*Cc* (No. 9)	$R\bar{3}$ (hexagonal, No. 148)
a (Å)	6.762(2)	31.660(3)
b (Å)	21.856(4)	31.660(3)
c (Å)	12.061(3)	9.702(1)
β (°)	93.49(2)	(90)
V (Å^3)	1779.2(5)	8422(38)
Z	4	18
D_c (g/cm^3)	1.47	1.732
μ (cm^{-1})	50.4	103.9
max 2*θ* (°)	58	150
radiation, *λ* (Å)	Mo Kα, 0.690 71	Cu Kα, 1.541 78
scan mode	*ω*/2*θ*	*ω*/2*θ*
scan width (°)	0.90 + 0.15 tan *θ*	0.70 + 0.14 tan *θ*
hkl ranges	*h* = −9 to 9	*h* = −39 to 39
	k = 0 to 29	*k* = −39 to 0
	l = 0 to 16	*l* = 0 to 12
no. of reflcns		
unique	2223	3857
with $F \geq 3\sigma(F)$	1789	3369
no. of params refined	201	181
largest diff peak (e/Å^3)	0.28	0.674
R	0.036	0.054

tions of disulfide **1** (labeled as **1a,b**) and also of diselenide **2** (labeled as **2a,b**). The results are discussed in terms of crystal and molecular structures established from XRD studies, and the relationship between ^{31}P and ^{77}Se spectral parameters and the phosphorus and selenium local geometry is described.

Experimental Section

Bis(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl) disulfide (**1**) and diselenide (**2**) were synthesized according to established procedures.[11,22-24] Disulfide **1** crystallizes from benzene solution by slow isothermal evaporation as modification **1a**. Crystals of **1b** are formed upon dropwise addition of hexane to a saturated benzene solution. Using the latter method for crystallization of diselenide **2**, crystals (**2b**) with included benzene are formed. The solvent molecule further diffused from the host lattice during several weeks exposure to the atmosphere giving the diselenide **2a**. Only disulfide **1a** and solvent-free diselenide **2a** gave good quality monocrystals which were refined by XRD. All modifications for both compounds were investigated by solid state NMR as powdered samples.

XRD Measurements. The crystals were attached in random orientation to glass fibers using epoxy resin. Disulfide **1a** crystallizes in the monoclinic system, space group *Cc* (No. 9 in the *International Tables*),[25] and diselenide **2a** crystallizes in the rhombohedral system, space group $R\bar{3}$, with a hexagonal setting (No. 148).[25] Crystal structure data and the experimental details are listed in Table 1.

Totals of 1789 reflections for **1a** and 3369 reflections for **2a** with $F \geq 3\sigma(F)$ were used to solve the structures by direct methods and to refine them by full matrix least-squares methods using *F*'s. H atoms were placed at idealized positions 0.95 Å from the parent atoms and with fixed isotropic thermal parameters and were set as riding. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The final refinement converged to *R* = 0.036 for **1a** with unit weight for 201 refined parameters and 0.054 for **2a** for 181 refined parameters. All calculations were carried out with the Enraf-Nonius SDP crystallographic computing package[26] except that the structure solution was performed on the SHELXS86[27] or SHELXTL[28] package. Scattering factors were taken from ref 25.

Table 2. Atomic Coordinates and Isotropic Displacement Coefficients (Å^2) for $C_{10}H_{20}O_4P_2S_4$ (**1a**)

atom	*x*	*y*	*z*	*B*(eq)
P1	0.0132(2)	0.0723(1)	−0.0032(2)	3.05(4)
P2	0.2526(1)	0.1926(1)	0.2403(2)	3.64(4)
S1	0.1156(1)	0.1630(1)	−0.0190(2)	3.67(3)
S2	0.0189(1)	0.2059(1)	0.1174(1)	3.51(3)
S3	0.1701(1)	0.0208(1)	0.0930(2)	3.42(3)
S4	0.5108(1)	0.2095(2)	0.1957(1)	3.57(3)
O1	0.0125(2)	0.0526(2)	−0.1299(1)	3.86(6)
O2	−0.2067(2)	0.0766(2)	0.0269(1)	3.72(7)
O3	0.2315(2)	0.1279(2)	0.2898(1)	3.76(6)
O4	0.1762(1)	0.2395(2)	0.3297(2)	3.78(6)
C1	−0.1437(2)	0.0768(3)	−0.2081(2)	4.04(8)
C2	−0.3485(2)	0.0692(3)	−0.1660(2)	4.12(9)
C3	−0.3539(2)	0.1016(3)	−0.0526(2)	3.96(8)
C4	−0.4975(1)	0.1015(4)	−0.2466(3)	4.12(8)
C5	−0.4048(1)	0.0015(3)	−0.1565(2)	4.03(9)
C6	0.0507(3)	0.1131(3)	0.3447(2)	3.59(9)
C7	0.0242(2)	0.1580(3)	0.4402(2)	3.68(7)
C8	0.0044(3)	0.2225(3)	0.3912(2)	4.02(8)
C9	−0.1726(2)	0.1435(4)	0.4911(2)	4.10(8)
C10	0.1967(2)	0.1544(4)	0.5257(2)	4.11(8)

Table 3. Atomic Coordinates and Isotropic Displacement Coefficients (Å^2) for $C_{10}H_{20}O_4P_2S_2Se_2$ (**2a**)

atom	*x*	*y*	*z*	*B*(eq)
P1	0.08207(6)	0.32499(6)	0.8247(2)	2.66(4)
P2	0.00575(6)	0.15646(7)	0.7221(2)	2.86(4)
Se1	0.00756(3)	0.26270(3)	0.7670(1)	3.50(2)
Se2	0.03576(3)	0.22765(3)	0.60720(9)	3.54(2)
S1	0.11768(7)	0.36762(8)	0.6773(3)	4.57(5)
S2	−0.06306(8)	0.12294(9)	0.7513(3)	4.68(6)
O1	0.1097(1)	0.3014(2)	0.8989(5)	2.6(1)
O2	0.0683(2)	0.3511(2)	0.9412(1)	3.2(1)
O3	0.0357(2)	0.1673(2)	0.8606(5)	3.1(1)
O4	0.0236(2)	0.1279(2)	0.6250(6)	3.9(1)
C1	0.0928(2)	0.2794(2)	1.0362(8)	2.7(1)
C2	0.0916(2)	0.3163(2)	1.1349(8)	2.6(1)
C3	0.0543(2)	0.3297(2)	1.0807(8)	3.1(2)
C4	0.0722(3)	0.2904(3)	1.2706(9)	4.1(2)
C5	0.1418(3)	0.3607(3)	1.152(1)	4.2(2)
C6	0.0880(3)	0.1823(3)	0.8542(9)	3.7(2)
C7	0.0955(3)	0.1454(3)	0.7698(9)	3.8(2)
C8	0.0760(3)	0.1433(3)	0.6229(9)	4.2(2)
C9	0.1509(3)	0.1662(4)	0.759(1)	5.6(3)
C10	0.0713(4)	0.0957(3)	0.836(1)	5.4(2)

NMR Measurements. Powder samples of disulfide **1** and diselenide **2** were placed in a cylindrical rotor and spun at 2.0−4.5 kHz. ^{13}C, ^{31}P, and ^{77}Se NMR spectra with cross-polarization (CP) and high-power proton decoupling were recorded on a Bruker 300 MSL instrument at 75.5, 121.5, and 57.2 MHz, respectively. The free induction decay used 8K data points. The field strength for ^{1}H decoupling was 1.05 mT. A contact time of 5 ms, a repetition time of 6 s, and a spectral width of 20 kHz were used in the ^{13}C experiments. A total of 100−200 scans were accumulated to achieve a good signal-to-noise ratio. ^{13}C chemical shifts were measured indirectly through the glycine carbonyl peak at 176.3 ppm relative to tetramethylsilane.

A contact time of 5 ms, a repetition of 6 s, and a spectral width of 50−100 kHz were used in the ^{31}P experiments. A total of 100 scans were accumulated, and the ^{31}P chemical shifts were calibrated indirectly through bis(dineopentoxythiophosphoryl) disulfide set at 84.0 ppm.

The Hartmann−Hahn condition for ^{77}Se CP/MAS experiments was established using a powdered sample of ammonium selenate. A contact time of 5 ms, a repetition of 10 s, and a spectral width of 50 kHz were used. Several thousand scans were accumulated for diselenide **2**.

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Table 4. Bond Lengths (Å) and Bond Angles (°) for $C_{10}H_{20}O_4P_2S_4$ (**1a**) and $C_{10}H_{20}O_4P_2S_2Se_2$ (**2a**)

	1a	**2a**		**1a**	**2a**
		Bond Lengths			
S(Se)1—S(Se)2	2.036(2)	2.329(1)			
P1—S(Se)1	2.112(2)	2.262(2)	P2—S(Se)2	2.118(2)	2.255(2)
P1—S3(S1)	1.894(2)	1.902(3)	P2—S4(S2)	1.891(2)	1.908(3)
P1—O1	1.588(4)	1.579(6)	P2—O3	1.565(4)	1.581(5)
P1—O2	1.555(4)	1.584(6)	P2—O4	1.583(4)	1.594(8)
O1—C1	1.471(7)	1.475(8)	O3—C6	1.462(7)	1.48(1)
O2—C3	1.447(7)	1.479(9)	O4—C8	1.464(7)	1.47(2)
C1—C2	1.514(9)	1.53(1)	C6—C7	1.532(8)	1.54(1)
C2—C3	1.542(9)	1.53(1)	C7—C8	1.530(8)	1.54(1)
C2—C4	1.530(9)	1.51(2)	C7—C9	1.530(8)	1.54(1)
C2—C5	1.532(9)	1.516(8)	C7—C10	1.511(8)	1.51(1)
		Bond Angles			
P1—S(Se)1—S(Se)2	103.7(1)	95.68(6)	P2—S(Se)2—S(Se)1	104.2(1)	94.41(7)
S(Se)1—P1—S3(S1)	116.0(1)	115.0(1)	S(Se)2—P2—S4(S2)	116.1(1)	115.0(1)
S(Se)1—P1—O1	98.6(2)	106.5(1)	S(Se)2—P2—O3	107.6(2)	107.2(2)
S(Se)1—P1—O2	106.7(2)	101.1(2)	S(Se)2—P2—O4	97.8(2)	100.6(3)
S3(S1)—P1—O1	113.4(2)	113.9(2)	S4(S2)—P2—O3	112.6(2)	113.0(2)
S3(S1)—P1—O2	113.6(2)	112.7(3)	S4(S2)—P2—O4	115.0(2)	113.8(2)
O1—P1—O2	107.1(2)	106.5(4)	O3—P2—O4	106.3(2)	106.2(3)
P1—O1—C1	118.6(4)	118.6(5)	P2—O3—C6	118.3(4)	119.3(5)
P1—O2—C3	119.8(4)	120.8(5)	P2—O4—C8	119.1(4)	118.7(5)
O1—C1—C2	112.4(5)	110.4(6)	O3—C6—C7	109.8(5)	110.6(5)
O2—C3—C2	111.2(5)	110.2(7)	O4—C8—C7	112.1(5)	111.2(7)
C1—C2—C3	108.6(5)	108.3(6)	C6—C7—C8	108.2(5)	108.3(8)
C1—C2—C4	108.4(6)	106.9(6)	C6—C7—C9	108.2(5)	106.8(6)
C1—C2—C5	111.6(6)	111.3(7)	C6—C7—C10	111.0(5)	112.2(8)
C3—C2—C4	107.5(6)	106.8(7)	C8—C7—C9	106.7(6)	107.5(8)
C3—C2—C5	111.0(6)	112.2(7)	C8—C7—C10	110.9(5)	111.3(7)
C4—C2—C5	109.6(1)	111.2(6)	C9—C7—C10	111.7(5)	110.6(9)

Table 5. Torsional Angles (°) for $C_{10}H_{20}O_4P_2S_4$ (**1a**) and for $C_{10}H_{20}O_4P_2S_2Se_2$ (**2a**)

torsional angle	**1a**	**2a**	torsional angle	**1a**	**2a**
P1—S(Se)1—S(Se)2—P2	89.7	118.7			
S(Se)2—S(Se)1—P1—S3(S1)	−81.5	61.0	S(Se)1—S(Se)2—P2—Se(S2)	46.4	58.7
S(Se)2—S(Se)1—P1—O1	157.1	−66.2	S(Se)1—S(Se)2—P2—O3	−80.9	−67.8
S(Se)2—S(Se)1—P1—O2	46.3	−177.3	S(Se)1—S(Se)2—P2—O4	169.2	−178.7
S(Se)1—P1—O1—C1	−73.9	−69.3	S(Se)2—P2—O3—C6	−61.0	−66.5
S(Se)1—P1—O2—C3	65.8	75.4	S(Se)2—P2—O4—C8	72.5	71.9
S3(S1)—P1—O1—C1	162.8	162.9	S4(S2)—P2—O3—C6	169.8	165.8
S3(S1)—P1—O2—C3	−165.1	−161.3	S4(S2)—P2—O4—C8	−163.8	−164.6
O1—P1—O2—C3	−39.1	−35.7	O3—P2—O4—C8	−38.5	−39.7
P1—O2—C3—C2	52.8	49.1	P2—O4—C8—C7	49.3	52.7
O2—C3—C2—C1	−58.7	−59.7	O4—C8—C7—C6	−57.9	−59.9
C3—C2—C1—O1	57.5	63.1	C8—C7—C6—O3	61.4	59.9
C2—C1—O1—P1	−49.5	−54.8	C7—C6—O3—P2	−57.6	−53.6
C1—O1—P1—O2	36.6	38.0	C6—O3—P2—O4	43.0	40.4
O1—C1—C2—C4	174.1	177.9	O3—C6—C7—C9	176.6	175.4
O1—C1—C2—C5	−65.0	−60.6	O3—C6—C7—C10	−60.5	−63.3
O2—C3—C2—C4	−175.9	−174.5	O4—C8—C7—C4	−174.1	−174.9
O2—C3—C2—C5	64.2	63.6	O4—C8—C7—C5	64.1	63.9

^{77}Se chemical shifts were measured indirectly through ammonium selenate used as a secondary chemical shift reference standard, set at $\delta = 1040.2$ ppm.

The principal elements of the ^{31}P and ^{77}Se chemical shift tensors allowed for chemical shift, dipolar, and indirect coupling to ^{31}P and were calculated with the MASNMR program from Dresden[29] using the method of Herzfeld and Berger.[30] The convention $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ was used. The following notation was choosen for description of the isotropic chemical shift δ_{iso}, shielding anisotropy $\Delta\delta_{\text{max}}$, and axiality ϱ:

$$\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3 \qquad \Delta\delta_{\text{max}} = \delta_{11} - \delta_{33}$$

$$\varrho = (2\delta_{22} - \delta_{11} - \delta_{33})/\Delta\delta_{\text{max}}$$

Results and Discussion

X-ray Diffraction Studies. Atomic coordinates for disulfide **1a** and diselenide **2a** are reported in Tables 2 and 3, bond lengths and angles in Table 4, and torsional angles in Table 5. The thermal ellipsoidal plots and numbering schemes of disulfide **1a** and diselenide **2a** are shown in Figures 1 and 2.

Both compounds are built from 5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinane rings bridged by disulfide or diselenide units. The conformation of the bridge involves torsional angles P—S(Se)—S(Se)—P (89.7° for **1a** and 118.7° for **2a**) and two S(Se)—S(Se)—P=S angles. For disulfide **1a** the torsional angles are different, −81.5 and 46°, while for the diselenide **2a** the angles are similar, 61.0 and 58.7°. The disulfide bond length was found to be 2.036 Å, in excellent agreement with the relationship between disulfide bond length and P—S—S—P torsional angle.[16] As shown elsewhere,[16,31,32] due to overlap of the p electron of the lone pair of sulfur and empty d_{xz} and d_{yz} orbitals of phosphorus the P—S bond lengths depend on the

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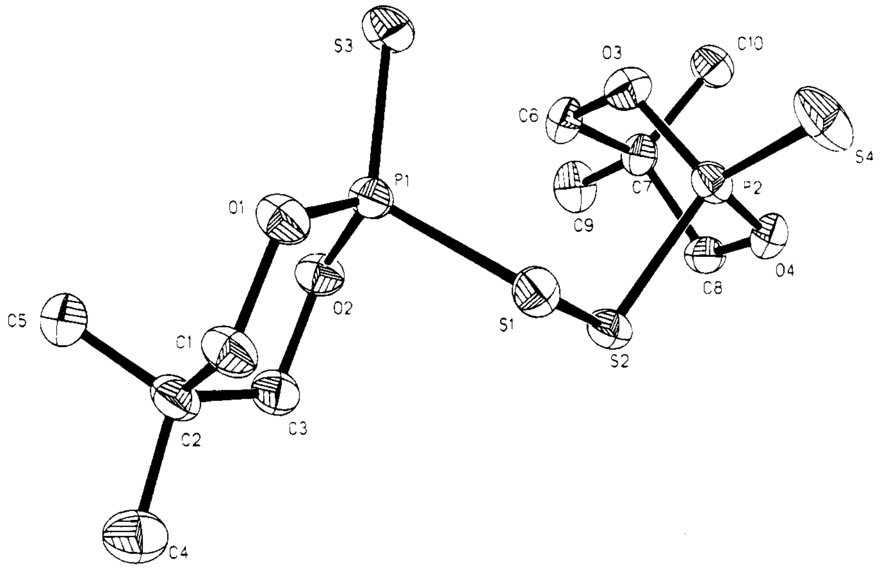

Figure 1. ORTEP plot of bis(5,5-dimethyl-2-thioxo-dioxaphosphorinan-2-yl) disulfide (**1a**).

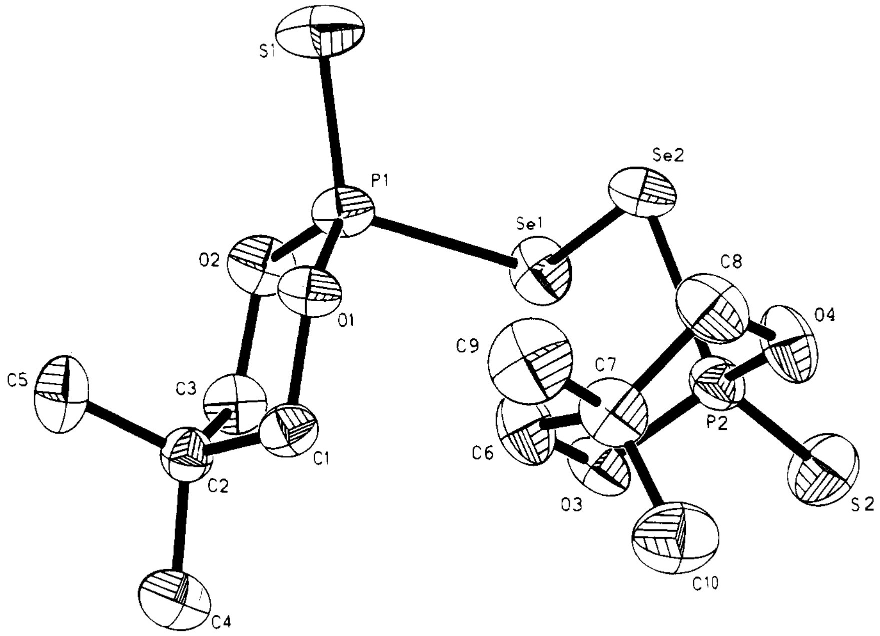

Figure 2. ORTEP plot of bis(5,5-dimethyl-2-thioxo-dioxaphosphorinan-2-yl) diselenide (**2a**).

conformation of the S—S—P=S unit. The P—S distances in disulfide **1a** (2.112 and 2.118 Å) further confirm this hypothesis. The P=S bond distances for disulfide **1a** and diselenide **2a** were found to be 1.89 and 1.90 Å, respectively.

Little is known about the nature of the Se—Se diselenide bond in the S=P—Se—Se—P=S backbone. Husebye[33] published XRD data for bis(diethylthiophosphoryl) diselenide. The diselenide bond distances for both structures were found to be 2.33 Å. Twice the covalent radius of selenium according to Pauling is 2.34 Å.[34] The P—Se—Se—P torsional angle for bis(diethylthiophosphoryl) diselenide is 104.5°, approaching the value found for diselenide **2a**. Both structures form a skew conformation, and the question regarding the possibility of a trans conformation for other bis(organothiophosphoryl) diselenides remains open. On the other hand, Hargittai and Rozsondai[35] demonstrated several structural analogies between disulfide and diselenide linkages in C—S—S—C and C—Se—Se—C units. It can be assumed that similar geometrical relationships can be expected for P—S—S—P and P—Se—Se—P analogs to those shown by Knopik et al.[16] and reported by Gallacher and Pinkerton[32] for bis(organothiophosphoryl) disulfides. Bis(alkoxythiophosphoryl) diselenides with isopropyl and neopentyl groups may therefore be expected to have a *trans* P—Se—Se—P conformation similar to that in their disulfide analogs.[17,18]

The 1,3,2-dioxaphosphorinane rings are in a chair conformation with bond distances and angles in **1a** and **2a** not significantly different from those found in other 1,3,2-dioxaphosphorinanes.[6-15] For both compounds the P=S thioxo sulfurs are in equatorial positions while the sulfurs of the disulfide or the seleniums of the diselenide bridge are axial. Ring deformation decreases the steric repulsion between the axial substituent at the phosphorus atom and the two hydrogen

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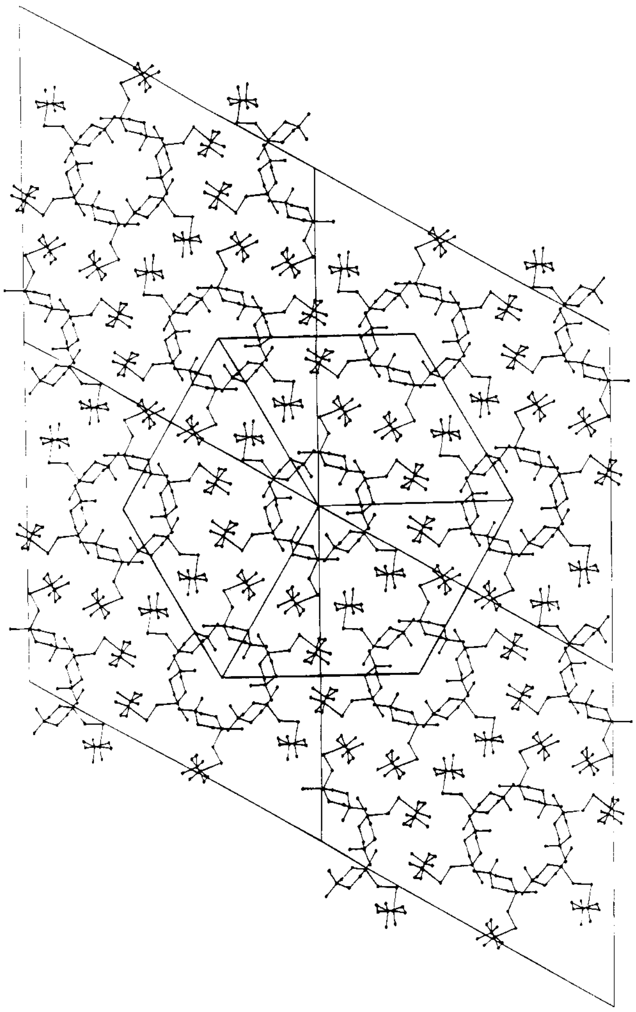

Figure 3. Molecular packing in the unit cell of the diselenide **2a**. The projection is through four rhombohedral unit cells to show the hexagonal setting.

atoms at the 4,6-diaxial positions.[6,13] This deformation was characterized by the dihedral angles between the least-squares planes [O1(3),O2(4),C1(6),C3(8)] and the planes [O1(3), P1(2),O2(4)]: 32.7° (34.8°) for **1a** and 31.4° (34.3°) for **2a**, respectively. These values indicate a typical ring flattening at the phosphorus end for 1,3,2-dioxaphosphorinanes with an axial position for the P—S or P—Se bond. The dihedral angles between the least-squares planes [O1(3),O2(4),C1(6),C3(8)] and the planes [C1(6),C2(7),C3(8)] are in the range 52–56°, characteristic for cyclohexane rings.

The disulfide **1a** crystallized in the space group Cc with $Z = 4$ and the diselenide **2a** in the space group $R\bar{3}$ with $Z = 18$ for hexagonal cell, both with one molecule as an independent unit per unique volume. In unique cells of both compounds two corresponding molecules are related to another by a center of symmetry; they are conformational enantiomers. In solution these two types of molecules which are different in the crystal lattice are related by conformational motions around the P1—S1-(Se1), S1(Se1)—S2(Se2), and S2(Se2)—P2 bonds.

Figure 3 shows the molecular packing in diselenide **2a**. The "holes" formed by the phosphorinane ring may be occupied by benzene molecules forming the diselenide **2b** as shown in Figure 4.

The calculated diameter of the "tunnel" was found to be 5.7 Å, smaller than the diameter of the benzene molecule (6.8 Å). The lattice arrangement of benzene in diselenide **2b** may be different with larger "holes" and a presumably distorted P—Se—Se—P unit compared with **2a**. With gradual loss of solvent, when the benzene is displaced from the lattice, the "tunnels" are fully locked. Such changes would require only minimal motion of the P—Se—Se—P fragment and very small modification of the molecular structure.

Table 6. ^{31}P and ^{77}Se NMR Data for Solid Samples of $C_{10}H_{20}O_4P_2S_4$ (**1a,b**), $C_{10}H_{20}O_4P_2S_2Se_2$ (**2a**), and $C_{10}H_{20}O_4P_2S_2Se_2{\cdot}C_6H_6$ (**2b**)

nucleus	compd	spin	δ_{iso}	$\delta_{11}(T_{11})$	$\delta_{22}(T_{22})$	$\delta_{33}(T_{33})$	$\Delta\delta_{max}$ (ΔT_{max})	ϱ
^{31}P	**1a**	A	85.2	184	152	−81	265	0.76
		B	73.6	184	142	−106	290	0.71
	1b	A	80.7	185	147	−90	275	0.72
		B	76.4	183	142	−96	279	0.71
	2a	A	68.4	187	114	−97	284	0.49
		B	63.7	182	103	−95	277	0.43
	2b	A	70.5	187	118	−93	280	0.51
		B	69.3	177	105	−74	251	0.42
^{77}Se	**2a**[a]	A^+	424.5	742	422	108	634	−0.01
		A^-	417.2	751	423	76	675	0.03
		B^+	381.2	703	425	−13	716	0.30
		B^-	373.7	686	464	−30	716	0.38
	2b[b]	A^-	404.3	692	340	181	511	−0.38
		A^+	396.3	685	339	165	520	−0.33
		B^-	351.8	618	411	27	591	0.30
		B^+	344.7	625	414	−6	631	0.33

[a] The signals are split by the scalar coupling, $^1J_{P-Se} = 424$ Hz (A and B), $m_x = \pm^1/_2$. [b] The signals are split by the scalar coupling, $^1J_{P-Se} = 434$ Hz (A) or 458 Hz (B) Hz, $m_x = \pm^1/_2$.

Table 7. ^{13}C Chemical Shifts (ppm) of Solid Samples of $C_{10}H_{20}O_4P_2S_4$ (**1a,b**), $C_{10}H_{20}O_4P_2S_2Se_2$ (**2a**), and $C_{10}H_{20}O_4P_2S_2Se_2{\cdot}C_6H_6$ (**2b**)

compd	OCH_2	C_{quat}	$CH_{3\,ax}$	$CH_{3\,eq}$
1a	81.3, 80.9, 79.7, 78.5	34.0, 33.8	22.2, 22.2	21.7, 21.1
1b	82.6, 81.0, 79.3, 77.7	33.2, 33.1	22.4, 21.7	21.2, 20.5
2a	82.5, 80.5, 79.3, 77.7	33.4, 33.1	22.6, 22.3	21.7, 20.7
2b[a]	80.5, 79.4,[b] 78.7	33.3, 32.3	22.7, 20.7	20.7, 19.7

[a] The included benzene has a chemical shift of 129.2 ppm. [b] Double intensity.

Solid State NMR Studies. High-resolution solid-state ^{31}P NMR spectra for disulfide **1** and diselenide **2** are shown in Figures 5 and 6, respectively.

As a result of the crystallographic inequivalence of the two phosphorus sites for molecule **1a**, the spectrum contains two sideband systems. The very large difference of ca. 11 ppm between the corresponding values of δ_{iso} (see Table 6) corresponds to significant differences of the local environments of the P1 and P2 atoms, which can be seen by comparison of the torsional angles around the S1—P1 and S2—P2 bonds. The spectrum of crystals of **1b** shows two, albeit less different (ca. 4 ppm), isotropic chemical shifts, so that the two phosphorus atoms are again crystallographically inequivalent.

As with disulfide **1**, two sideband systems corresponding to crystallographically inequivalent phosphorus sites were predicted for diselenide **2**. However, the ^{31}P CP/MAS NMR spectrum of diselenide **2**, measured 2 and 4 weeks after preparation, is more complex (Figure 6b). In addition to the isotropic lines at 70.5 and 69.3 ppm (indicated as **2b**), it contains another sideband pattern with two isotropic lines at 68.4 and 63.7 ppm (indicated as **2a**). After 6 weeks, only the upfield system of diselenide **2a** was observed (Figure 6a). Spectra of freshly prepared crystals show only the **2b** pattern (Figure 6c). In conclusion, after the addition of hexane to a benzene solution, crystals of **2b** contain some amount of included benzene which alters their properties. The solvent gradually evaporates forming the crystals **2a**. Note that for both modifications of diselenide **2**

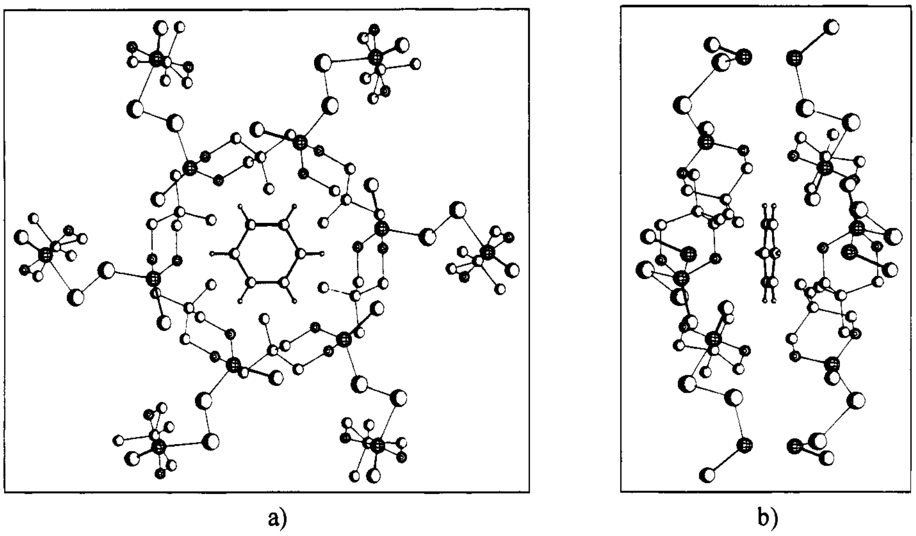

Figure 4. Hypothetical fragment of bis(5,5-dimethyl-2-thioxo-dioxaphosphorinan-2-yl) diselenide with a benzene molecule included in the lattice: (a) View along the axis *c*; (b) view with 80° rotation about the vertical axis of (a). The solvent molecule was included by computer modeling.

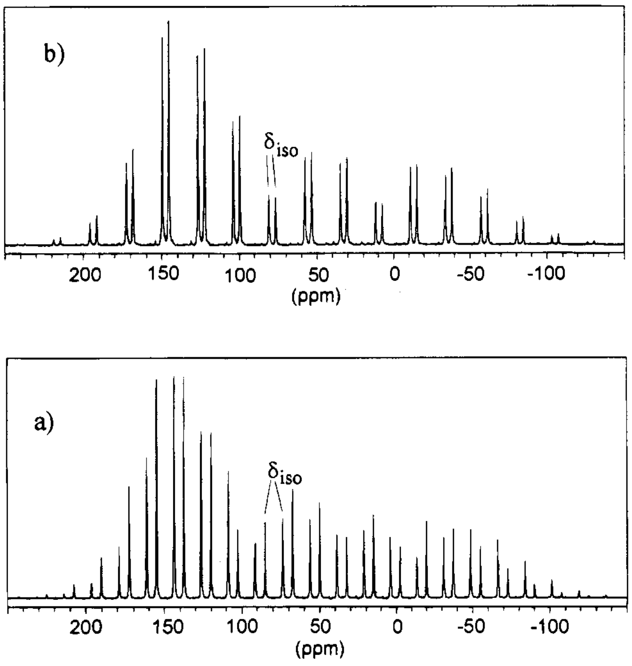

Figure 5. ^{31}P CP/MAS spectra of bis(5,5-dimethyl-2-thioxo-dioxaphosphorinan-2-yl) disulfides, crystallized from (a) benzene (**1a**), γ_{rot} = 2130 Hz, and (b) a mixture of benzene and hexane (**1b**), γ_{rot} = 2180 Hz.

the structure of **2a** free from solvent molecules in the lattice was assigned by XRD.

Each line in the ^{31}P spectrum is symmetrically flanked by scalar-coupled ^{31}P—^{77}Se satellites, labeled with asterisks on the expanded isotropic lines of Figure 6a (top trace). The low intensity of satellites is related to the low natural abundance (7.58%) of ^{77}Se. The ^{31}P—^{77}Se scalar coupling constant in the solid was found to be 424 Hz for both phosphorus atoms in **2a** and 434 Hz for the lowfield phosphorus and 458 Hz for the highfield one in **2b**. In CDCl$_3$ solution both phosphorus atoms are chemically equivalent and give a coupling constant of 475 Hz. The values of $^1J(^{31}P—^{77}Se)$ are similar to that for single

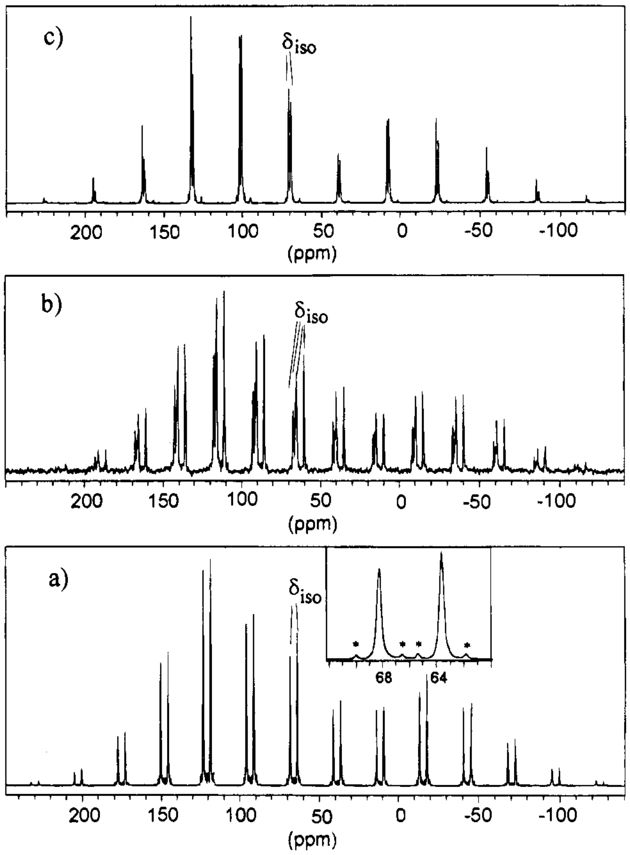

Figure 6. ^{31}P CP/MAS spectra of bis(5,5-dimethyl-2-thioxo-dioxaphosphorinan-2-yl) diselenides, crystallized from a mixture of benzene/hexane. (a) Spectrum recorded 6 weeks after crystallization, where sample contains only **2a**, γ_{rot} = 3315 Hz. The top trace displays the expanded central part of the spectrum. The ^{31}P—^{77}Se satellites are labeled with asterisks. (b) Spectrum of a mixture of two modifications **2a,b** recorded 4 weeks after crystallization, γ_{rot} = 3070 Hz. (c) Spectrum recorded immediately after crystallization (**2b**), γ_{rot} = 3780 Hz.

P—Se bond in related compounds shown elsewhere.[36] Different coupling constants indicate that the conformation of the S=P—Se—Se—P=S unit in **2a,b**, and also for the molecules in solution, is slightly different.

The calculated values of the principal elements of the ^{31}P chemical shift tensor and shielding parameters for disulfide **1** and diselenide **2** are given in Table 6.

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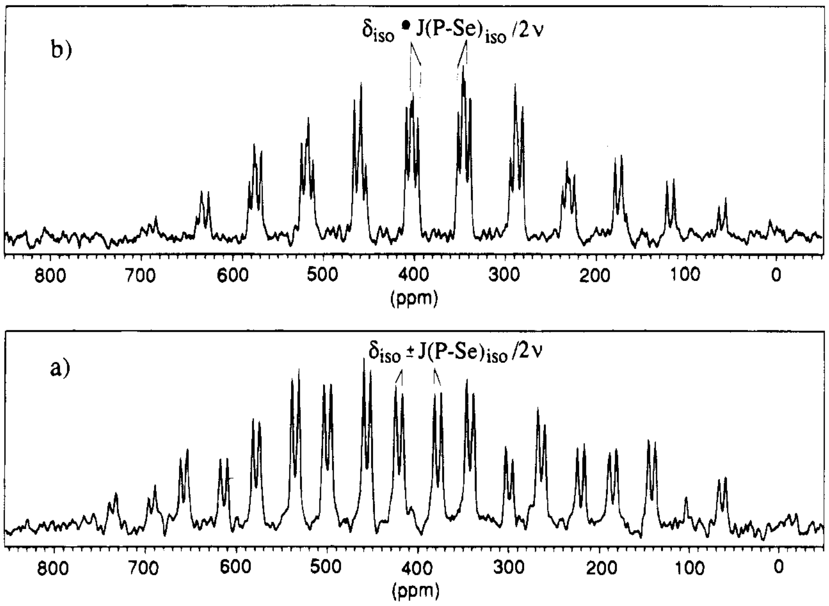
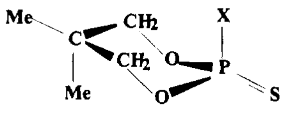
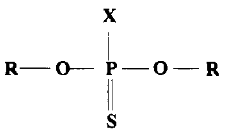


Figure 7. ^{77}Se CP/MAS spectra of bis(5,5-dimethyl-2-thioxo-dioxaphosphorinan-2-yl) diselenides: (a) Recorded immediately after crystallization, where sample contains only **2b**, ν_{rot} = 3290 Hz; (b) recorded 6 weeks after crystallization, where sample contains only **2a**, ν_{rot} = 4510 Hz.

The anisotropy parameter was shown to correlate very well with the local geometry of P in the S—P═S unit.[37,38] The values δ_{max} of 265 and 290 ppm for **1a** and 275 and 279 ppm for **1b** are ca. 50 ppm larger than for noncyclic bis(organothiophosphoryl) compounds. This can be explained by the changes of the conformation around the P—O bonds in the O—P—O—C moiety of the six-membered ring **I** compared to compounds with ester groups in the form of linear chains **II**.



I



II

X= S, Se

The dihedral angles O—P—O—C for disulfide **1a** and diselenide **2a** are in the range 36—43°, while for disulfides with R = *i*-Pr,[17] Me, and *neo*-Pe[18] and diselenide with R = Et[33] they are in the range 170—180°. The distortion caused by the six-membered ring affects also the S—P═S and Se—P═S bond angles found to be 116.0 and 115.0°, respectively. Both values are higher than those for noncyclic bis(organothiophosphoryl) compounds (105—107°). Dutasta et al.[39] found the anisotropy of δ_{max} = 252 ppm for a cyclic thiophosphonate of the type **I** with X = Me close to those for disulfides **1**.

The substitution of S by Se causes the shielding of the principal value δ_{22} of ca. 40 ppm, while the other principal values are unchanged. We conclude that the axis 2 is nearly perpendicular to the plane S—P═S in **1** and Se—P═S in **2**. From IGLO calculations of other thiophosphoryl compounds[40] it may be concluded that the axis 3 nearly coincides with the P═S bond.

The ^{13}C CP/MAS data are listed in Table 7. Two signals for the quaternary carbons for each species in the samples of **1** and **2** and four signals for the methylene carbons clearly indicate that one molecule per unique volume is an independent unit. Two of the methyl group signals overlap, so that only three signals are different for one molecule.

The peak from occluded benzene at 129 ppm in the spectrum of diselenide **2b** is an unambiguous proof of the assumption made on the basis of the ^{31}P CP/MAS spectra. When the sample is stored for 6 weeks, this peak is absent. There are no solvent molecules in the lattice of **1b**.

The ^{77}Se CP/MAS spectrum of diselenides **2a,b** given in Figure 7 shows a complicated pattern of sideband systems for the two types of crystals. The XRD reveals that one molecule per unique volume is an independent unit; hence, two crystallographically and chemically inequivalent selenium sites Se1 and Se2 are predicted. Since each selenium nucleus is coupled to a phosphorus, four sideband systems for each type of crystal should be observed.

For isolated $I = {}^1/_2$ spin pairs ^{77}Se—^{31}P in the solids, scalar and dipolar interactions as well as *J*-coupling anisotropy must be taken into consideration in addition to chemical shielding.[41,42] Consequent analysis of sideband intensities gives the principal values of the tensors $\mathbf{T}_{ii}^{+}$ and $\mathbf{T}_{ii}^{-}$. The values of the chemical shift δ_{iso} and of the isotropic coupling constant $^1J(^{77}\mathrm{Se}—^{31}\mathrm{P})$ can be obtained directly. Unfortunately, it is not possible to obtain the details of the anisotropy of *J* or the orientation of the principal axes with respect to the axis of dipolar interaction. The principal values of the chemical shift tensor may be approximated by the mean values of $\mathbf{T}_{ii}^{+}$ and $\mathbf{T}_{ii}^{-}$.

Table 6 shows the principal values of the ^{77}Se tensors $\mathbf{T}_{ii}^{+}$ and $\mathbf{T}_{ii}^{-}$ for diselenides **2a,b**. The principal elements for Se in the two halves of one molecule are seen to be substantially different. For **2a** XRD shows very similar local environments for the Se1 and Se2 atoms. However, careful inspection of XRD results reveals small differences in P1—Se1 and P2—Se2 bond lengths [2.262(2) and 2.255(2) Å], in P1—Se1—Se2 and Se1—Se2—P2 angles [95.68(6) and 94.41(7)°], and in the torsional angles involving the Se atoms (see Table 5). As these differences are very small, the ^{77}Se chemical shifts are very sensitive to changes of local geometry.

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The ^{77}Se data for the second modification **2b** show lower values for δ_{11} and δ_{22} and higher values for δ_{33}. The conformation around the P—Se and Se—Se bonds in crystals of **2b** is probably slightly different than that in **2a**. Solid state ^{77}Se NMR indicates that the two modifications have different molecular structures. As a possible explanation for the differences of ^{31}P and ^{77}Se NMR shielding parameters for **2a,b**, we have assumed the presence of benzene molecules inside "tunnels" formed by molecules of diselenide **2**.

The question of polymorphism of the bulk materials and ambiguity of the space group versus solid state NMR parameters has attracted the attention of several research groups. Using ^{31}P CP/MAS of phosphine transition metal complexes and tertiary phosphines, Davies and co-workers[43–46] have shown that results obtained from XRD single crystal diffraction are not always consistent with NMR data of powdered samples. A similar conclusion was reported by Penner and Wasylishen,[47] who have found more signals than expected from XRD results in a commercial sample of trimesitylphosphine, due to presence of two polymorphs in the bulk material. Harris et al. have shown that two pseudopolymorphic forms in the solid androstanolone can be resolved by ^{13}C CP/MAS.[48] Our results provide another example of this phenomenon.

Conclusions

Our data reveal the power of a multitechnique approach for the study of solids. A comparison of molecular structures for disulfide **1a** and diselenide **2a** gained from single crystal XRD measurements reveals that both compounds are in synclinal range with 89.7 and 118.7° torsional angles for the P—S—S—P and P—Se—Se—P units. For both compounds one molecule in the unit cell is an independent unit although their crystal structures are very different. In both the disulfide **1a** and diselenide **2a** the thioxo sulfurs occupy the equatorial positions. The presence of thioxo sulfur or selenium in an axial position causes flattening of six-membered rings at the phosphorus end.

Multinuclear high-resolution solid state NMR clearly shows that disulfide **1** and diselenide **2** crystallize in two different forms. Due to the low quality and/or instability of monocrystals **1b** and **2b** their molecular structures cannot be resolved by XRD but can be successfully characterized by NMR. The principal elements of the ^{31}P and ^{77}Se chemical shift tensors and the shielding parameters were calculated from spinning sideband intensities. From analysis of these data it was concluded that disulfides **1a,b** have slightly different molecular structures. The same conclusion was drawn for diselenides **2a,b**. Moreover, for diselenide **2b** it was assumed that the presence of a benzene molecule in the "tunnel" causes an increase of the size and a small distortion of the geometry of the P—Se—Se—P unit. The principal elements of the ^{31}P shielding tensor for disulfide **1** and diselenide **2** are similar. In addition, the values of δ_{22} indicate that axis 2 is nearly perpendicular to the S—P=S or the Se—P=S plane.

To the best of our knowledge, our ^{77}Se CP/MAS NMR results are the first attempt to use the technique for structural elucidation of selenothiophosphates. The results are consistent with those from ^{31}P NMR. We note ^{77}Se CP/MAS NMR is very sensitive even to small changes of local geometry. Determination of crystal and molecular structures of samples with a tendency to form polymorphic structures depends on the casual choice of the sample. Solid state NMR can confirm or exclude the existence of other crystallographic forms.

Acknowledgment. The authors are grateful to Dr. J. Klinowski for reading this manuscript and providing helpful comments. This project was supported by Polish Committee for Scientific Research (KBN) Grant no. 2P30303705 and the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. M.J.P. is indebted to the European Community for a "Go West" fellowship (ERB3510PL922142/4423), and G.G., for a "Go East" fellowship (ERB3510PL925251).

Supplementary Material Available: Tables of anisotropic thermal parameters, atom coordinates and *B* values, H atom coordinates, bond distances and angles, torsion angles, least-squares planes, rms amplitudes, and asymmetry parameters (6 pages). Ordering information is given on any current masthead page. Structure factors are deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen, Germany.

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