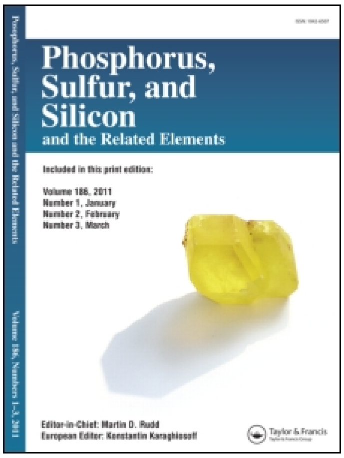

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Lönnecke, P. and Blachnik, R.(1997) '^{31}P NMR SPECTROSCOPIC EVIDENCE FOR THE MOLECULAR STRUCTURE OF $P_2Se_3Hal_2$ (Hal = Br, I)', Phosphorus, Sulfur, and Silicon and the Related Elements, 131: 1, 191 — 196
To link to this Article: DOI: 10.1080/10426509708031607
URL: http://dx.doi.org/10.1080/10426509708031607

Phosphorus, Sulfur, and Silicon, 1997, Vol. 131, pp. 191–196
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Printed in Malaysia.

Communication

^{31}P NMR SPECTROSCOPIC EVIDENCE FOR THE MOLECULAR STRUCTURE OF $P_2Se_3Hal_2$ (Hal = Br, I)

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(Received 16 July 1997)

The compounds $P_2Se_3Br_2$ **1** and $P_2Se_3I_2$ **2** were observed in CS_2 solution as by-products of the thermal synthesis of P_3Se_4Hal (Hal = Br, I). The analysis of their ^{31}P and ^{77}Se NMR spectra allowed to determine the structure of these molecules and revealed the relation between **1**, **2** and the bicycles P_3Se_4Hal and P_2Se_5.

Keywords: ^{31}P NMR spectra; 3,5-dibromo(iodo)-1,2,4,3,5-triselenadiphospholan

INTRODUCTION

Homonuclear S-S bonds have been observed frequently in monocyclic $(RP)_nS_m$ heterocycles.[1,2] Analogous compounds with Se-Se bonds are rare and only a few examples are described in the literature.[3,4] The molecular structures of P_2Se_5[5] and P_3Se_4I[6] reveal that excess selenium prefers homonuclear bonds instead of oxidizing P(III) to P(V). In the thermal synthesis of P_3Se_4Hal (Hal = Br, I) the five membered heterocycles **1** and **2** were observed as a by-product. They may be regarded as the parent compound of the bicycles P_3Se_4I and P_2Se_5.

RESULTS AND DISCUSSION

The products of the thermal reaction of red phosphorus, selenium and halogen in the atomic ratio 3:4:1 had been analyzed by NMR spectroscopy in CS_2 solution. Besides the well known compounds $PHal_3$, α-$P_4Se_3Hal_2$ and P_3Se_4Hal

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(Hal = Br, I) unknown signals were observed. Composition and molecular structure of these new compounds were gained from ^{31}P and ^{77}Se NMR spectroscopy. The ^{31}P- and ^{77}Se-NMR spectra of P_2Se_3I are given in Figure 1 and 2. The relation of the spin system of its ^{77}Se isotopomers with those of P_2Se_5[5] is evident. Three kinds of isotopomers were observed: the ^{31}P resonance signal of the ^{77}Se free isotopomer is flanked by two ^{77}Se satellite spectra. One isotopomer, $P_2{}^{77}Se_aSe_2I_2$ with ^{77}Se in the monoselenide bridge, gives rise to an A_2X spin system, the other one, $P_2{}^{77}Se_bSe_2I_2$ which contains ^{77}Se in the diselenide bridge, has an ABX spin system. Due to the low solubility the outer and less intense signals of the two AB subspectra can be observed only after a long accumulation time of the spectrum, similar to our observations for P_2Se_5. By combining these results with those of the ^{77}Se NMR measurement it was possible to determine all parameters (Table I).

For **1** the triplet of the $P_2{}^{77}Se_aSe_2Br_2$ isotopomer could not be observed in the ^{77}Se spectra. It is possible that these signals are superimposed by the multiplets of P_3Se_4Br or α-$P_4Se_3Br_2$ which are contained in higher concentrations in the CS_2 solution of the reaction products.

The chemical shifts of the phosphorus atoms in $P_2Se_3Hal_2$ moved to higher frequencies with the electronegativity of the halogen. This effect indicates, that the phosphorus atoms are directly bonded to the halogen. The magnitude of the changes were quite similar to those observed for corresponding monohalides P_3Se_4Hal.[6] This observation, the large negative $^1J_{PSe}$ coupling constants, the equivalent P atoms in the ^{77}Se free isotopomer and the characteristic spin systems of the ^{77}Se isotopomer allowed to determine the molecular structure of **1** and **2**, shown in Figure 3. In the five membered ring two P-Hal groups are connected by a mono- and a diselenide bridge. The measured intensities of the satellite spectra ($P_2{}^{77}Se_aSe_2Br_2 : P_2{}^{77}Se_bSe_2Br_2 = 0.94:2.06$ and $P_2{}^{77}Se_aSe_2I_2 : P_2{}^{77}Se_bSe_2I_2 = 0.91:2.08$) correlate well with the expected ratio of 1:2. These compounds are the first examples of phosphorus selenium heterocycles substituted only by halogen. The reaction of phosphorus, selenium and halogen in the ratio 2:3:2 yields a product in which **1** and **2** had been detected in higher concentrations. The preparation of pure **1** and **2** still failed because **1** decomposes during the evaporation of CS_2, and **2** could not be separated by fractional crystallization from the other products.

EXPERIMENTAL

All operations were carried out under dry argon using standard Schlenk techniques. 0.62 g (20 mmol) red phosphorus, 2.37 g (30 mmol) grey selenium and 2.54 g (20 mmol) iodine, resp. 1.60 g (20 mmol) bromine were sealed under

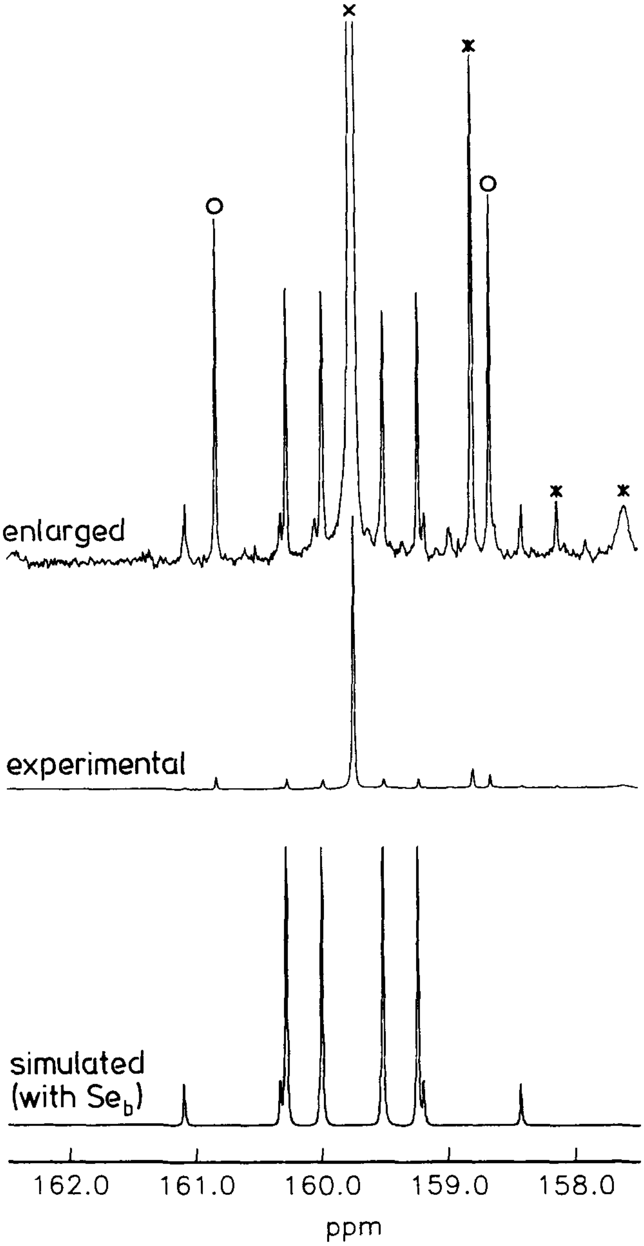

FIGURE 1 Experimental ^{31}P-NMR-spectrum of $P_2Se_3I_2$ with satellite signals: x: $P_2Se_3I_2$ main signal, o: doublet of the $P_2{}^{77}Se_aSe_2I_2$ isotopomer, *: impurities, simulated spectrum of the isotopomer with Se in position b

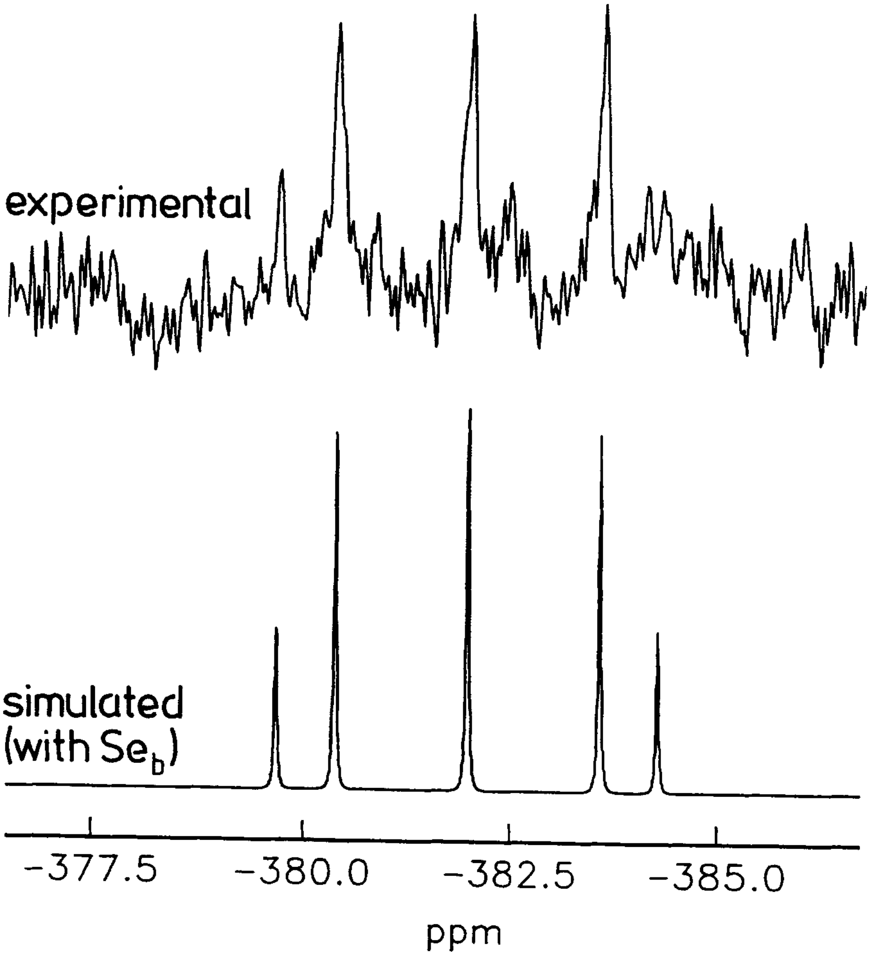

FIGURE 2 Experimental ^{77}Se NMR spectrum of $P_2Se_3I_2$, simulated spectrum of the isotopomer with Se in position b

vacuum in a Duran glass ampoule. The mixture was heated slowly to 200°C, then held at this temperature for one week. The homogeneous viscous melt was slowly cooled to room temperature. The resulting solid was stirred in 200 ml CS_2 for 1 d until the solid was finely ground. The solution was filtered through a filter tunnel for hot filtration to remove insoluble products.

The NMR spectra of the solutions were measured in a 10 mm diameter tube using a Bruker AC250 resp. AM 300 spectrometer with array processor operating at 101.256 MHz resp. 121.436 MHz for ^{31}P and 57.315 MHz for ^{77}Se.

TABLE I 31P-and 77Se-NMR-spectroscopic data of $P_2Se_3Hal_2$ (Hal = Br, I). solvens: CS_2; T = 298 K.

	δ_P	δ_{Se} [ppm]	$^1\Delta_{P^B}(Se)$ [ppb]	$^2J_{P^AP^B}$	$^1J_{P^ASe^a}$	$^2J_{P^ASe^b}$ [Hz]	$^1J_{P^BSe^b}$
$P_2Se_3Br_2$	180.96	—	—	—	—	—	—
$P_2{}^{77}Se_aSe_2Br_2$	—	...†	+4.7	—	−285.3	—	—
$P_2{}^{77}Se_bSe_2Br_2$	—	−410.76	+3.1	100.2(4)	—	−0.1(4)	−196.9(9)
$P_2Se_3I_2$	159.71	—	—	—	—	—	—
$P_2{}^{77}Se_aSe_2I_2$	—	...	...	—	−264.5	—	—
$P_2{}^{77}Se_bSe_2I_2$	—	−381.86	+4.0	98.3(1)	—	−3.9(5)	−181.0(2)

† triplett was possibly superimposed in the ^{77}Se-NMR-spectrum by the signals of P_3Se_4Br and/or α-$P_4Se_3Br_2$

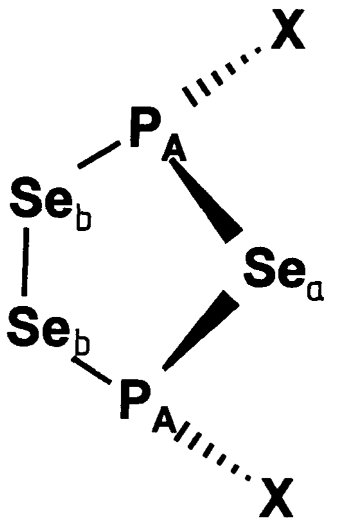

FIGURE 3 Structure of Triselenadiphospha-dihalide $P_2Se_3Hal_2$ (Hal = Br, I), Se_x = ^{77}Se

Measuring time was 15 h, measuring temperature 298 K. Precession capillaries containing C_6D_6 were used for locking und chemical shifts are reported relative to 85% H_3PO_4/H_2O (^{31}P) or saturated H_2SeO_3/H_2O solutions (^{77}Se). Spectra were analyzed using the programs NUMARIT[7] and WINDAISY.[8]

Acknowledgement

The authors wish to express their gratitude to the Deutsche Forschungsgemeinschaft and Fonds der Chemie for financial support.

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