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New Acyclic Neutral Phosphorus Sulfides and Sulfide Oxides

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Abstract. A great number of binary neutral phosphorus sulfides was discovered and investigated. However all stable representatives of this family of compounds adopt a polycyclic structure in contrast to their lighter homologues, the nitrogen oxides. Acyclic representatives can be stabilized by adduct formation with a nitrogen base. The bis(pyridine) adduct $py_2P_2S_5$ of the unstable acyclic phosphorus sulfide P_2S_5 is readily obtained stirring P_4S_{10} in pyridine at ambient temperature. X-ray diffraction studies on single crystals of $py_2P_2S_5$·0.5 py (**1b**) show a N_2O_5 like structure for the P_2S_5 framework. The long P–N distances of 1.86 Å indicate only weak coordination of the pyridine molecules to phosphorus. Single crystal X-ray diffraction studies on $py_2P_2S_{4.34}O_{0.66}$ (**2**) reveal the presence of $py_2P_2S_4O$ (**3**) together with $py_2P_2S_5$ in the crystal. Compound **3** contains the mixed phosphorus oxide sulfide molecule P_2S_4O stabilized as bis(pyridine) adduct. It is readily obtained from pyP_2S_5 by oxidation with $KMnO_4$ in pyridine. The oxygen atom occupies the bridging position between the two phosphorus atoms. Quantum chemical calculations at the MPW1PW91 level of theory as well as DTA/TG thermal analyses confirm the weak coordination of the pyridine molecules in $py_2P_2S_5$, $py_2P_2S_4O$, and $py_2P_2S_7$ to phosphorus.

Introduction

Binary neutral phosphorus sulfides have been known for a long time. It was *Berzelius*, who in 1843 was the first to investigate the behavior of sulfur towards phosphorus and synthesized the first representative of this class of compounds, the "P_2S_5".[1] This molecule was later discovered to be the dimer P_4S_{10}. Since then many more phosphorus sulfides P_4S_x (x = 3–10) have been discovered.[2] It is striking that all these neutral compounds adopt a polycyclic structure. This occurs due to the problem of an unfavorable $\sigma^3\lambda^5$ bonding situation at the phosphorus atom in acyclic representatives. In order to stabilize the $\sigma^3\lambda^5$-phosphorus in such a molecule the missing forth coordination partner might be provided by adduct formation, for example by coordination of a base like pyridine.

In fact 1967 *Fluck* and *Binder* were able to describe such a compound.[3] In the course of their investigations on perthiophosphonic acid anhydrides they discovered, that on heating P_4S_{10} in pyridine the bis(pyridine) adduct of the monomeric unit P_2S_5 is formed. This system has been used as sulfur removing agent in organic chemistry before. *Fluck* et al. described the synthesis of the bis(pyridine) adduct of P_2S_5 and reported its ^{31}P NMR chemical shift.

Meisel and co-workers used this compound as starting material to synthesize new betaines, containing pyridine and one phosphorus atom.[4] In 1982 *Wolf* and *Meisel* attempted to synthesize the structurally analogue adduct $py_2P_2O_5$.[5] They proposed this molecule to be generated by refluxing P_4O_{10} in pyridine but could not identify the product of this reaction by any means. In our group this experiment was repeated several times, however we were also not able to verify the existence of this molecule.

Shortly after this publication *Wolf* patented the compounds $py_2P_2S_5$ and $py_2P_2S_4$, which he claimed to have synthesized by refluxing P_4S_7 in pyridine.[6] Also in this case, however, no proper characterization of the products was given.

In 2009 our group presented the crystal structures of $py_2P_2S_5$ and $py_2P_2S_7$ together with a full characterization of these compounds.[7] The $py_2P_2S_7$ was synthesized by refluxing stoichiometric amounts of P_4S_{10} and elemental sulfur in pyridine. Two years later the swedish group of *Prof. Bergman* also published the crystal structure of $py_2P_2S_5$ and discussed its use as thionating agent.[8]

In the following an improved synthesis and the new structure of $py_2P_2S_5$·0.5 py are presented. Quantum chemical calculations at the MPW1PW91 level of theory using a polarized double-zeta basis set (aug-cc-pVDZ) were accomplished to verify the ^{31}P NMR spectroscopic properties and to enlighten the possible existence of a pyridine free acyclic phosphorus sulfide P_2S_5. Also the question whether analogous mixed phosphorus sulfide oxide molecules can be stabilized by pyridine coordination will be discussed.

Results and Discussion

The Pyridine Adduct $py_2P_2S_5$ (1a)

In course of our investigations of $py_2P_2S_5$ (**1a**), we found that for its synthesis refluxing P_4S_{10} in pyridine is not neces-

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sary. The yield of **1a** can be improved by just stirring the starting material in pyridine at ambient temperature for a short period of time. Refluxing only causes the formation of larger amounts of $py_2P_2S_4O$ (**3**) as byproduct. This is shown in Figure 1, where the ^{31}P NMR spectra of the respective reaction solutions are compared. We observed the ^{31}P NMR shift of $py_2P_2S_5$ at δ = 104.4 ppm and the one for $py_2P_2S_4O$ at δ = 98.5 ppm.

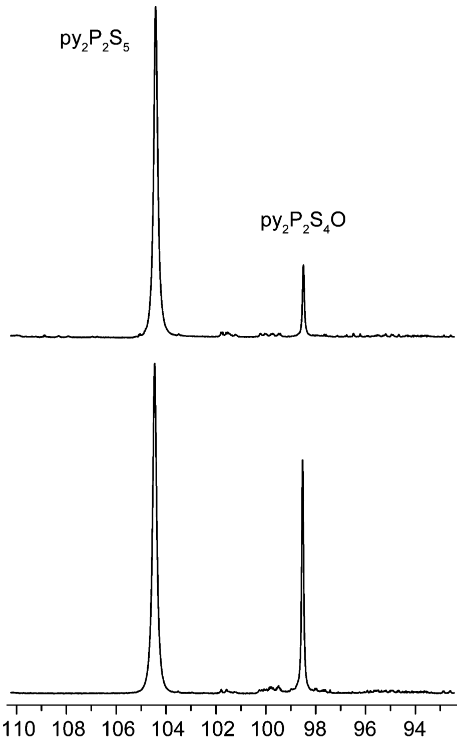

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of a solution of P_4S_{10} in pyridine before (top) and after (bottom) refluxing for 1 h at 120 °C.

Molecular Structure of $py_2P_2S_5 \cdot 0.5$ py (1b)

Colorless block-shaped single crystals of $py_2P_2S_5 \cdot 0.5$ py (**1b**) were isolated after refluxing a pyridine solution of $py_2P_2S_5$ and investigated by X-ray diffraction. Compound **1b** crystallizes in the triclinic space group $P\bar{1}$ with one molecule of $py_2P_2S_5$ and half a molecule of pyridine in the asymmetric unit (Table 1). Figure 2 shows the molecular structure of **1b** together with selected atom distances and bond angles.

Table 1. Details for X-ray data collection and structure refinement for compounds **1b** and **2**.

	$py_2P_2S_5 \cdot 0.5$ py (**1b**)	$py_2P_2S_{4,34}O_{0,66}$ (**2**)
Formula	$C_{12.5}H_{12.5}N_{2.5}P_2S_5$	$C_{10}H_{10}N_2P_2\ S_{4.25}O_{0.75}$
M /g·mol^{-1}	419.99	368.40
Color, habit	colorless block	colorless block
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$ (No. 53)
a /Å	8.976(2)	14.564(1)
b /Å	9.203(2)	11.061(1)
c /Å	12.672(2)	9.884(1)
α /°	102.547(5)	90
β /°	90.241(4)	92.890(7)
γ /°	118.501(6)	90
V /Å^3	890.870(10)	1590.2(2)
Z	2	4
ρ_{calc} /g·cm^{-3}	1.566	1.539
μ /mm^{-1}	0.826	0.346
θ range /°	4.44–28.28	4.20–25.00
Data collected	10688	17822
Data	4381	2893
Parameters	203	177
R_{int}	0.0329	0.0759
R_1 [$I > 2\sigma$]	0.0370	0.0574
wR_2 [$I > 2\sigma$]	0.0830	0.1401
R_1 [all data]	0.0537	0.1036
wR_2 [all data]	0.0933	0.1514
GOF on F^2	1.001	1.017

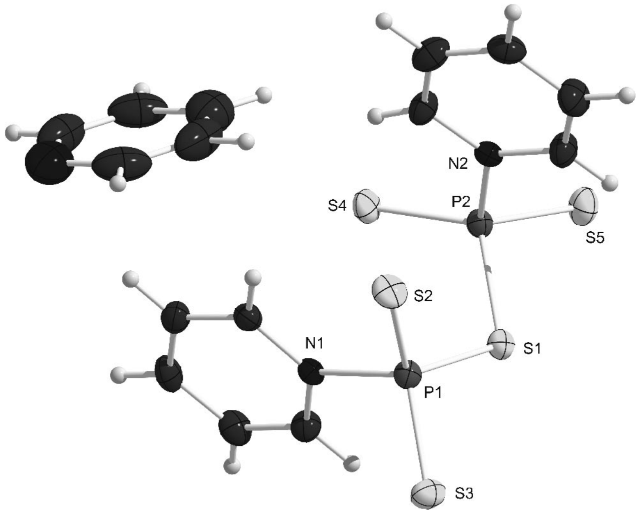

Figure 2. Molecular structure of **1b** in the crystal. Thermal ellipsoids are set at 50 % probability level. Selected atom distances /Å and angles /°: P1–S1/P2–S1 2.107(2)/2.121(2), P1–S2/P1–S3 1.931(2)/1.947(2), P2–S4/P2–S5 1.933(2)/1.945(2), P1–N1/P2–N2 1.863(2)/1.855(2); S1–P1–S2/S1–P2–S4 116.2(1)/114.7(1), S1–P1–S3/S1–P2–S5 103.6(1)/102.0(1), S2–P1–S3/S4–P2–S5 122.63(4)/124.5(1), P1–S1–P2 111.8(1).

The distance of the phosphorus atoms to the single coordinated sulfur atoms is with an average value of 1.939(1) Å within the range expected for a P–S double bond [1.922(14) Å].[9] The distance between the phosphorus atoms and the bridging sulfur atom is averagely 2.114(1) Å, which is in good accordance with the one expected for a single bond (2.11 Å[2a]). The P–N distances are with an average value of 1.859 Å around 0.2 Å longer than expected for a P–N single bond [1.652(24) Å],[9] which indicates only weak coordination of the pyridine molecule to phosphorus. Similar strongly elongated P–N distances have been reported for the solvent free $py_2P_2S_5$ [1.862(6) Å and 1.865(3) Å],[7] $py_2P_2S_7$ [1.869(3) Å and 1.865(3) Å],[7] and also for the pyridine adduct of the PS_3^- anion [1.906(2) Å],[10] in which a similar bonding situation is found.

The phosphorus atoms are surrounded distorted tetrahedrally by three sulfur atoms and one pyridine molecule. The largest values for S–P–S angles are found between the phosphorus and the two single coordinated sulfur atoms with 123.6°. The angles involving the bridging sulfur atom are smaller with val-

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ues around 102.8°. The P1–S1–P2 angle has a value of 111.9°. Although only a slight distortion of the tetrahedral environment around the phosphorus atom might be expected, the sum of the S–P–S angles indicates with a value of 341.8° a strong deviation towards a planar PS_3 arrangement. A similar situation is found for solvent free $py_2P_2S_5$[7], $py_2P_2S_7$[7] and for the pyridine adduct of the PS_3^- anion[10] with values of 341°, 344°, and 347°, respectively. This provides further evidence for an only weak coordination of the pyridine to the phosphorus.

Crystal Structure of $py_2P_2S_{4.34}O_{0.66}$ (2)

Crystals of $py_2P_2S_{4.34}O_{0.66}$ suitable for X-ray diffraction were obtained from the reaction of P_4S_3 with elemental sulfur in pyridine. The structure was solved in the monoclinic space group $P2_1/c$ (Table 1).

The crystal contains both, the compound $py_2P_2S_5$ and the related oxygen derivative $py_2P_2S_4O$, with the oxygen atom in the bridging position. The two molecules occupy the same positions in the crystal except for the bridging O1 and S5 between the two phosphorus atoms, which results in a disorder in this position. Figure 3 shows the molecular structure and contains selected atom distances and bond angles.

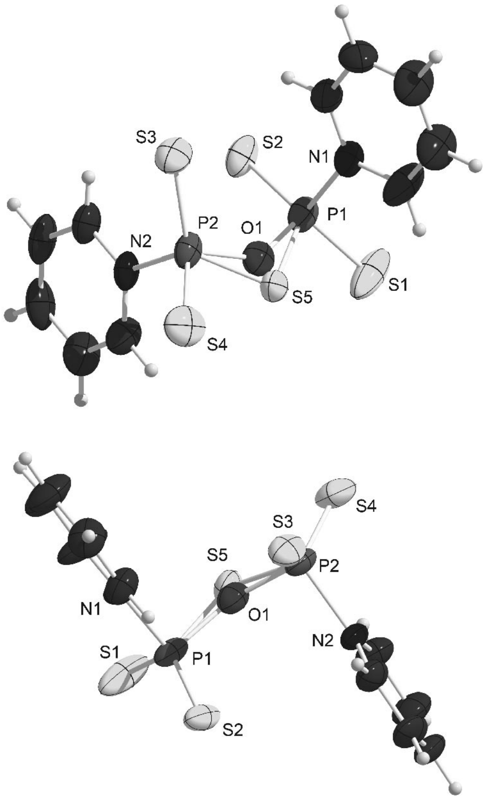

Figure 3. Molecular structure of **2** in the crystal (two different viewing directions). Thermal ellipsoids are set at 50 % probability level. Selected atom distances /Å and angles /°: P1–S1/P1–S2 1.928(2) / 1.925(2), P1–S5/P2–S5 1.968(9)/2.013(9), P1–O1/P2–O1 1.687(11)/ 1.695(11), P1–N1/P2–N2 1.852(4)/1.854(4); S1–P1–S2/S3–P2–S4 123.0(1)/123.7(1), S1–P1–S5/S4–P2–S5 92.5(3)/93.2(3), S2–P1–S5/ S3–P2–S5 125.2(3)/124.1(3), S1–P1–O1/S4–P2–O1 109.7(5)/ 109.9(5), S2–P1–O1/S3–P2–O1 110.0(5)/110.7(4).

The phosphorus atoms are again surrounded distorted tetrahedrally by two single coordinated sulfur atoms, one molecule of pyridine, and the bridging sulfur or oxygen atom, completing the tetrahedron. The oxygen atom can be found with 66 %, while the sulfur is occupying the bridging position with 34 %. Because of the different P–O and P–S distances and the deviation in the angles at the bridging chalcogen atoms, the positions of the two atoms could be identified and the atoms refined anisotropically. The distances between the phosphorus and the single coordinated sulfur atoms differ with a value of 1.930(2) Å only slightly from the distance expected for a P–S double bond [1.922(14) Å[9]). Due to the disorder in the crystal all values are afflicted with higher standard uncertainties.

The nitrogen atom of the pyridine molecule has a distance of 1.853(4) Å to the phosphorus atom, which is elongated compared to the expected 1.652(24) Å[9] for a P–N single bond. So this indicates again only a weak coordination of the pyridine molecules to the phosphorus. This is further supported by the sum of the S–P–S(O) angles of 341.0(5)° and 344.3(4)° respectively, which again show a deviation towards a planar surrounding of phosphorus by the chalcogen atoms.

The Pyridine Adduct $py_2P_2S_4O$ (3)

The bis(pyridine) adduct $py_2P_2S_4O$ (**3**) (n = 1) is the first member of a series of pyridine stabilized mixed phosphorus sulfide oxides $P_2S_{5-n}O_n$ (n = 1–4), which fill the gap between $py_2P_2S_5$ and the still unknown adduct $py_2P_2O_5$. Compound **3** can be obtained by stirring **1a** and $KMnO_4$ in pyridine for 2 d at ambient temperature. It is identified by the ^{31}P NMR signal at δ = 98.5 ppm (Figure 4), which fits the one predicted by quantum chemical calculations (see below).

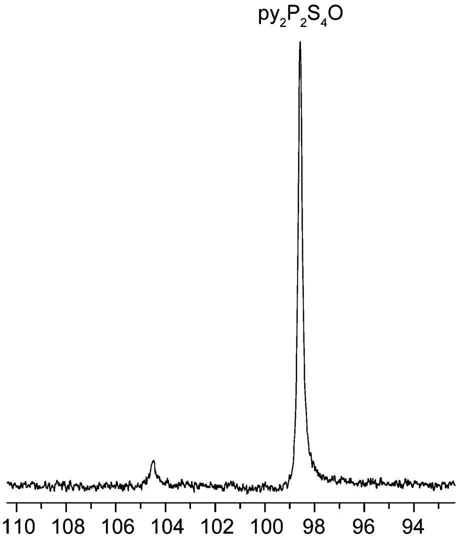

Figure 4. $^{31}P\{^1H\}$ NMR spectrum of **3** in pyridine.

Quantum Chemical Calculations

The compounds $py_2P_2S_5$ and $py_2P_2S_7$ can be viewed as loose pyridine adducts of the acyclic phosphorus sulfides P_2S_5

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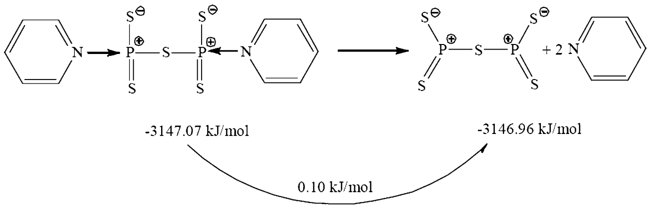
and P_2S_7. It is interesting to investigate how the coordination of pyridine influences the atom distances and the structures of the free P_2S_5 and P_2S_7 molecules. In order to give an answer to this question quantum chemical calculations at the MPW1PW91 level of theory using a polarized triple-zeta basis set (aug-cc-pVTZ) for $py_2P_2S_5$ and a polarized double-zeta basis set (aug-cc-pVDZ) for the free P_2S_5 were carried out. Furthermore energy values for both molecules were determined on the level of CBS-4M and the ^{31}P NMR spectroscopic data for $py_2P_2S_5$ and $py_2P_2S_4O$ were calculated.

The optimized structure of the P_2S_5 molecule is shown in Figure 5. The calculated atom distances and bond angles within the $py_2P_2S_5$ molecule correspond very well to those observed for **1b** in the crystal (Table 2). Remarkably the calculated atom distances and bond angles for the pyridine free sulfide P_2S_5 also do not differ much from the calculated and experimentally determined values for $py_2P_2S_5$. Obviously adduct formation has little influence on the bonding situation within the P_2S_5 framework. Coordination of pyridine affects mainly the arrangement around the phosphorus atom causing a slight deviation from planarity for the PS_3 moiety.

Table 2. Calculated and experimentally observed distances /Å and bond angles /° of **1** (average values).

	$py_2P_2S_5$ (obs.)	P_2S_5 (calcd.)	$py_2P_2S_5$ (calcd.)
Distances /Å			
P–N	1.86	–	1.86
P–S_{sc}	1.93	1.92	1.94
P–S_{tc}	2.12	2.13	2.12
S–S			
Angles /°			
S_{sc}–P–S_{sc}	123	134	128
S_{sc}–P–S_{tc}	104/115	107/118	103/115
S_{tc}–S_{tc}–S_{tc}			
P–S_{tc}–P	112	113	112

a) sc = single coordinated; tc = twofold coordinated.



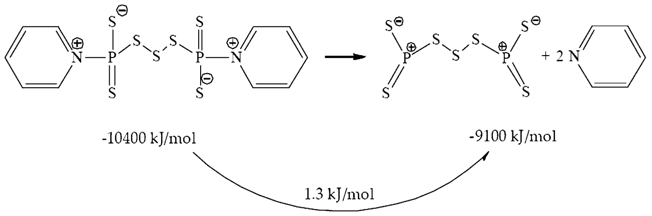
Scheme 1. Dissociation of $py_2P_2S_5$ in P_2S_5 and pyridine.

Furthermore quantum chemical calculations on the level of CBM-4M were carried out to compare the enthalpy values of **1** and the pyridine free compound P_2S_5 (Scheme 1).

The difference in the enthalpies resulting from the calculations is 0.10 kJ·mol^{-1}. Thus the composition according to the reaction in Scheme 1 is slightly endothermic. This small difference of enthalpy fits well to the experimentally determined strongly elongated P–N distance in the bis(pyridine) adduct **1b**. Both suggest that the P–N bonds in **1** should be cleaved easily at higher temperatures generating free P_2S_5, which should be stable in the gas phase.

A similar situation is found for the bis(pyridine) adduct of P_2S_7. The results of a quantum chemical study of the bonding situation in this compound compared to free P_2S_7 (Figure 6) have been discussed in detail.[7b]

For the dissociation of $py_2P_2S_7$ in free P_2S_7 and pyridine (Scheme 2) an enthalpy difference of 1.3 kJ·mol^{-1} was calculated. This result suggests that in this case it might also be



Scheme 2. Dissociation of $py_2P_2S_7$ in P_2S_7 and pyridine.

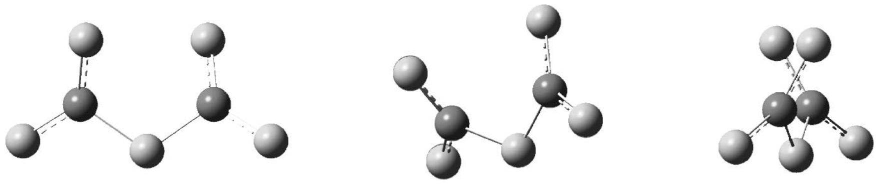


Figure 5. Optimized structure of P_2S_5 (three different orientations).

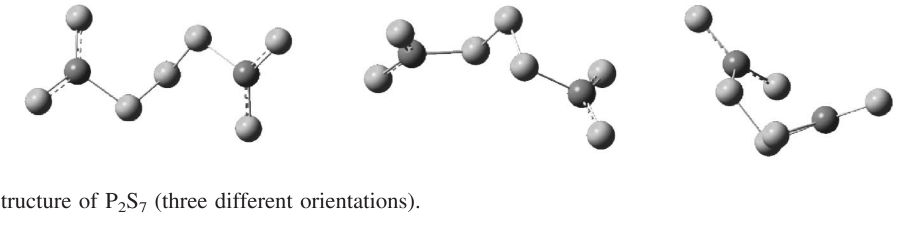


Figure 6. Optimized structure of P_2S_7 (three different orientations).

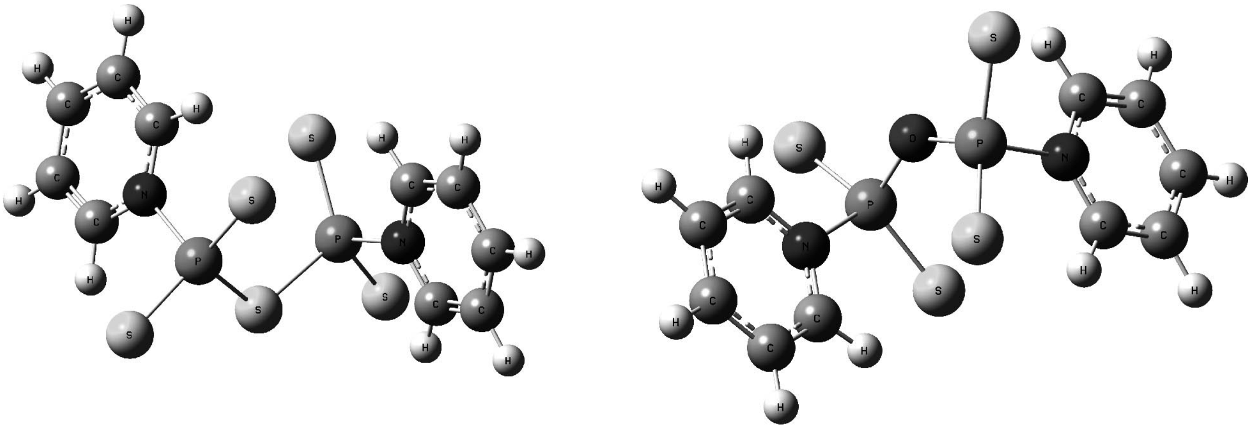


Figure 7. Computed C_2 structures of $[(py)PS_2]_2S$ (left) and $[(py)PS_2]_2O$ (right) at MPW1PW91/aug-cc-pVDZ level of theory.

possible to promote the dissociation thermally as depicted in the Scheme above and thus to generate free acyclic P_2S_7 in the gas phase.

NMR Spectroscopy

In order to estimate the ^{31}P NMR chemical shift of $[(py)PS_2]_2S$ (**1**) and $[(py)PS_2]_2O$ (**3**), the isotropic magnetic shielding was computed using the GIAO (Gauge-Independent Atomic Orbital) method implemented in G03.[11,12] The structures were optimized in C_2 symmetry (Figure 7) and the frequencies calculated (*NIMAG* = 0) at MPW1PW91/aug-cc-pVDZ level of theory. Subsequently, the NMR shielding tensors were calculated at the same level of theory using the GIAO method.[11,12] Table 3 summarizes the computed isotropic magnetic shielding and relative ^{31}P NMR chemical shifts (ppm) referenced to H_3PO_4.

Table 3. Computed isotropic magnetic shieldings (GIAO method[11,12], MPW1PW91/aug-cc-pVDZ) and relative ^{31}P chemical shifts /ppm referenced to H_3PO_4.

	$py_2P_2S_5$	$py_2P_2S_4O$	H_3PO_4
$-E$/ a.u.	3170.462064	2847.464794	644.135802
NIMAG	0	0	0
p.g.	C_2	C_2	C_3
δ = ^{31}P , calcd. isotr. shielding	249.9	260.8	364.3
δ = ^{31}P , calcd. (ref. to H_3PO_4)	114.3	103.5	0.0
δ = ^{31}P , exptl., (ref. to H_3PO_4)	104.4	98.5	0.0

The calculated ^{31}P NMR chemical shifts for $py_2P_2S_5$ and the oxygen derivative $py_2P_2S_4O$ compare well to the experimentally observed values. Introduction of oxygen in the bridging position in place of sulfur causes only a small shift of $\delta^{31}P$ to higher field.

Thermal Analyses

In order to gain further insight into the thermal stability of the pyridine adducts **1a**, **1b**, **2**, and $py_2P_2S_7$ and investigate the possibility of generating the pyridine free phosphorus sulfides and sulfide oxides DTA/TG thermal analyses were performed. For this purpose the compounds were heated up to 400 °C in steps of 5 °C•min^{-1}. In the thermograms (Figure 8, Figure 9, Figure 10, and Figure 11) the dashed curve shows the weight signal, while the black one represents the heat flow signal, which indicates changes in the energy at a certain temperature.

The thermal analysis of the bis(pyridine) adduct of P_2S_5 **1a** is shown in Figure 8. The endothermic heat flow signal at 168 °C derives from the two pyridine molecules leaving the solid, while the sharp peak at 261 °C quotes the melting point of the resulting P,S material. The melting point of P_4S_{10} is reported to be 288 °C[13] and thus differs by 27 °C from that observed for the P,S material obtained. The resulting material almost immediately starts to decompose releasing volatile products.

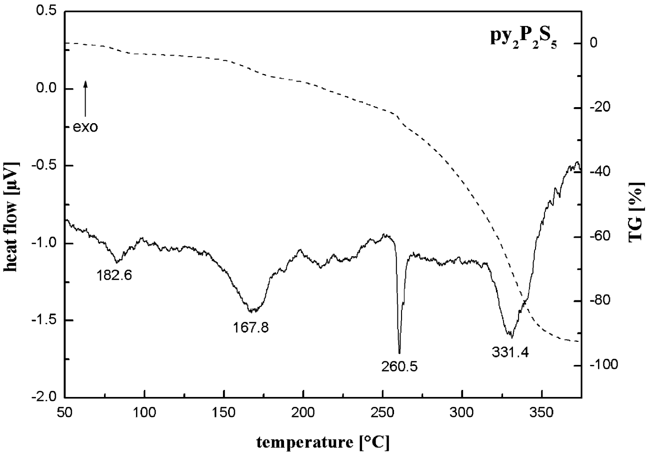


Figure 8. Thermogram of $py_2P_2S_5$ (**1a**).

The thermal behavior of the bis(pyridine) adduct of P_2S_5 **1b** is particularly interesting as it contains an additional free pyridine molecule in the crystal. Its thermogram is depicted in Figure 9. The first endothermic heat flow signal can be assigned to the free pyridine being released. This temperature is in accordance to the melting point of $py_2P_2S_5$•0.5 py **1b** (115 °C). The other three signals correspond very well to those observed for the adduct $py_2P_2S_5$ **1a**.

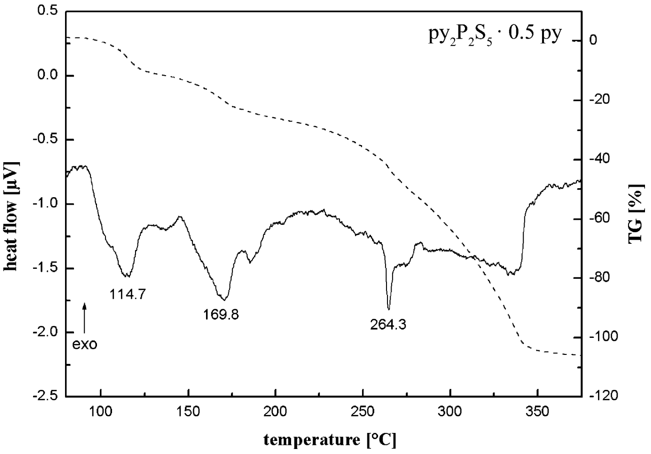


Figure 9. Thermogram of $py_2P_2S_5 \cdot 0.5$ py (**1b**).

The thermogram of $py_2P_2S_{4.34}O_{0.66}$ **2** (Figure 10), which in fact contains $py_2P_2S_5$ **1** and $py_2P_2S_4O$ **3**, shows a slightly different behavior. The two pyridine molecules leave the solid already at 148 °C. The resulting material, which in addition to phosphorus and sulfur now contains also oxygen, undergoes a further transformation at 226 °C and melts at 300 °C, followed by decomposition and release of volatile products.

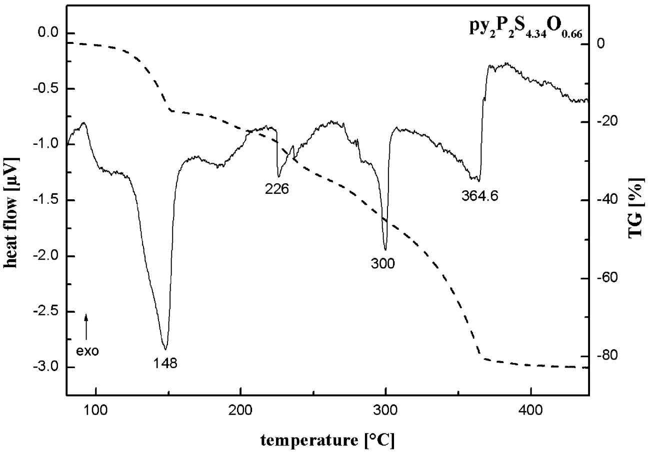


Figure 10. Thermogram of $py_2P_2S_{4.34}O_{0.66}$ (**2**).

In the case of the bis(pyridine) adduct of P_2S_7 (**4**), in the thermogram (Figure 11) only two endothermic transformations can be observed. The first one occurs at 161.6 °C and is assigned to the loss of pyridine. Thus a material of the composition P_2S_7 remains. At a temperature of 242.4 °C it melts and begins to decompose releasing volatile products. Decomposition is complete at 298 °C.

The results of the thermal analysis of the adducts **1**–**4** show, that all adducts release pyridine at temperatures between 140 °C and 170 °C before melting, thus confirming the relatively weak coordination of pyridine to phosphorus.

Conclusions

The bis(pyridine) adduct of the acyclic binary phosphorus sulfide P_2S_5 is readily obtained by stirring P_4S_{10} in pyridine at ambient temperature. Single crystal X-ray diffraction studies on $py_2P_2S_5 \cdot 0.5$ py (**1**) confirm stabilization of the P_2S_5 framework by weak coordination of the pyridine molecules to phosphorus. X-ray diffraction studies on $py_2P_2S_{4.34}O_{0.66}$ (**2**) provide first evidence for the existence of $py_2P_2S_4O$, a bis(pyridine)adduct of the mixed phosphorus sulfide oxide P_2S_4O with oxygen bridging the two phosphorus atoms. These results point to a general concept of stabilizing reactive phosphorus species containing $\sigma^2\lambda^5$ phosphorus atoms by weak coordination of a nitrogen base to phosphorus. It should be possible to extend this concept to other small molecules with three coordinated phosphorus(V) atoms. Thermogravimetric investigations on $py_2P_2S_5$, $py_2P_2S_{4.34}O_{0.66}$, and $py_2P_2S_7$ confirm the weak coordination of pyridine to phosphorus and indicate, that these adducts might be of interest as precursors for the generation of gaseous acyclic phosphorus sulfides and sulfide oxides.

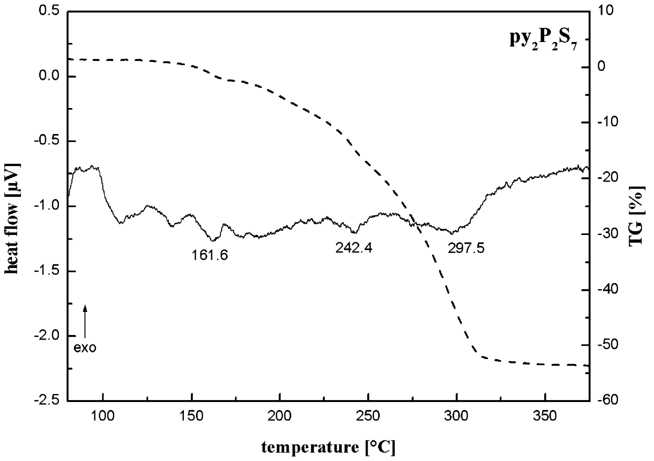


Figure 11. Thermogram of $py_2P_2S_7$ (**4**).

Experimental Section

General Conditions: All reactions were carried out in an inert gas atmosphere using Argon (Messer), purity 4.6 in 50 L steel cylinder) and working with Schlenk techniques. The glass vessels used were stored in a 130 °C drying oven. Before filling they were flame dried in vacuo at 10^{-3} mbar. Elemental sulfur was used as received (Acros Organics). P_4S_{10} and P_4S_3 were commercially obtained (Honeywell Riedel-de Haën). The pyridine used was dried with commonly known methods and freshly distilled before use.

X-ray Crystallography: The single crystal X-ray diffraction data were collected with an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA), Enhance molybdenum K_α radiation source (λ = 71.073 pm), Oxford Cryosystems Cryostream cooling unit, four circle kappa platform and a Sapphire CCD detector. Data collection and reduction were performed with CrysAlisPro.[14] The structures were solved with SIR97[15], refined with SHELXL-97,[16] and checked with PLATON,[17] all integrated into the WinGX software suite.[18] The finalized CIF files were checked with checkCIF.[19] Intra- and intermolecular contacts were analyzed with DIAMOND (version 3.2i), plots are shown with thermal ellipsoids at the 50 % probability level. Details for data collection and structure refinement are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-937614 (**1b**) and CCDC-940974 (**2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

NMR Spectroscopy: NMR spectra were recorded with a Jeol EX 400 Eclipse instrument operating at 161.997 MHz (^{31}P). Chemical shifts are referred to 85 % H_3PO_4 as external standard. All spectra were measured, if not mentioned otherwise, at 25 °C.

DTA/TG: Thermal analytic measurements were carried out with a Thermoanalyzer TG-DTA-92 (Setaram) in an inert gas atmosphere (He). The compound was heated in a corundum melting pot up to a temperature of 750 °C in steps of 5 °C·min^{-1}.

Mass Spectrometry: Mass spectra were obtained with an MStation JMS 700 (Jeol) using the ionization method DEI+/EI+.

IR Spectroscopy: The spectra were recorded with a Perkin-Elmer Spektrum one FT-IR instrument (KBr pellets) equipped with a Diamant-ATR Dura Sampler at 25 °C (neat). Raman spectra were recorded with a Bruker RAMII Raman instrument (λ = 1064 nm, 200 mW, 25 °C) equipped with a D418-T Detector at 200 mW at 25 °C.

py$_2$P$_2$S$_5$ (1a): P_4S_{10} (889.2 mg, 2 mmol) was stirred in pyridine (40 mL) for 1 h. Colorless needles of **1a** crystallized overnight and were separated by filtration and dried in vacuo. (Yield: 1415.4 mg, 93 %). **^{31}P{^{1}H} NMR** (pyridine): δ (ppm) = 104.2 (s). Elemental analysis for py$_2$P$_2$S$_5$: calcd. C 31.57, N 7.36, H 2.65, P 16.28, S 42.14 %; found C 32.92, N 7.69, H 3.30, S 31.78 %. **Mass** (EI+) *m*/*z* = 379.8 ([$C_{10}H_{10}N_2P_2S_5$]$^+$), 347.8 ([M–S]$^+$), 299.9 ([M–py]$^+$), 221.9 ([M–py$_2$]$^+$), 191.9 ([M–py$_2$S]$^+$), 160.0 ([M–py$_2$S$_2$]$^+$), 128.0 ([PS$_3$]$^+$), 96.0 ([PS$_2$]$^+$), 63.0 ([PS]$^+$). **Raman** (200 mW, room temp.): $\tilde{\nu}$ = 3066 (31), 1609 (36), 1567 (29), 2000 (43), 1014 (100), 468 (50), 448 (37) cm^{-1}. **IR** (200 mW, room temp.): $\tilde{\nu}$ = 1087 (s), 3060 (m), 1633 (vw), 1606 (m), 1532 (vw), 1484 (vw), 1471 (vw), 1452 (vs), 1330 (vw), 1262 (vw), 1194 (w), 1154 (vw), 1093 (vw), 1053 (m), 1044 (s), 1011 (m), 762 (m), 734 (vs), 673 (vs), 655 (w), 642 (w), 575 (vs), 461 (w), 454 (w), 423 (w) cm^{-1}.

py$_2$P$_2$S$_5$·0.5 py (1b): 1a (380.5 mg, 1 mmol) was dissolved in refluxing pyridine (40 mL) for 2 h. The yellow reaction mixture turned orange when cooling down to ambient temperature and the formation of a colorless crystalline precipitate consisting of py$_2$P$_2$S$_5$ could be observed. The needles were separated and dried in vacuo (Yield: 363.1 mg, 83 %). **^{31}P{^{1}H} NMR** (pyridine): δ (ppm) = 104.3 (s). Elemental analysis for (py$_2$P$_2$S$_5$)$_2$·py: calcd. C 35.76, N 8.35, H 3.00, P 14.77, S 38.12 %; found C 32.92, N 7.74, H 2.86, S 40.76 %. **Mass** (EI+) *m*/*z* = 379.8 ([$C_{10}H_{10}N_2P_2S_5$]$^+$), 347.9 ([M–S]$^+$), 299.9 ([M–py]$^+$), 221.9 ([M–py$_2$]$^+$), 191.9 ([M–py$_2$S]$^+$), 160.0 ([M–py$_2$S$_2$]$^+$), 128.0 ([PS$_3$]$^+$), 63.0 ([PS]$^+$). **Raman** (200 mW, room temp.): $\tilde{\nu}$ = 3068 (63), 1610 (23), 1565 (5), 1202 (25), 1012 (100), 465 (37), 448 (14), 417 (30) cm^{-1}. **IR** (200 mW, room temp.): $\tilde{\nu}$ = 3094 (w), 3044 (w), 1610 (m), 1577 (vw), 1476 (vw), 1452 (vs), 1431 (m), 1342 (vw), 1262 (vw), 1199 (vw), 1156 (vw), 1091 (ww), 1057 (m), 1045 (s), 1014 (m), 843 (vw), 763 (vw), 748 (w), 739 (s), 720 (vs), 668 (vs), 642 (vw), 565 (vs), 468 (vw), 457 (s), 421 (w) cm^{-1}.

py$_2$P$_2$S$_{4.34}$O$_{0.66}$ (2): P_4S_3 (1 mmol, 220.1 mg) was refluxed and dissolved in pyridine (10 mL) in the presence of traces of water. Afterwards sulfur (192.4 mg, 0.75 mmol) was added to the yellow reaction mixture and refluxed for 1 h at a temperature of 120 °C. Colorless crystals of py$_2$P$_2$S$_{4.34}$O$_{0.66}$ were obtained while cooling the solution to ambient temperature. The precipitate was separated from the solution and dried in vacuo (Yield: 299.4 mg, 43 %). **^{31}P{^{1}H} NMR** (pyridine): δ (ppm) = 104.3 (s). Elemental analysis (py$_2$P$_2$S$_{4.34}$O$_{0.66}$): calcd. C 32.49, N 7.58, H 2.73, S 37.57 %; found C 32.60, N 8.48, H 3.61, S 33.74 %. **Mass** (DEI+) *m*/*z* = 379.8 (M_S = [$C_{10}H_{10}N_2P_2S_5$]$^+$), 363.6 (M_O = [$C_{10}H_{10}N_2P_2S_4O$]$^+$), 347.9 ([M_S–S]$^+$), 299.9 ([M_S–py]$^+$), 284.7 ([M_O–py]$^+$), 252.8 ([M_O–pyS]$^+$), 221.9 ([M–py$_2$]$^+$), 188.8 ([M_O–pyPS$_2$]$^+$), 128.0 ([PS$_3$]$^+$), 63.0 ([PS]$^+$). **Raman** (200 mW, room temp.): $\tilde{\nu}$ = 3068 (25), 1604 (46), 1182 (53), 1031 (55), 1015 (100), 472 (84) cm^{-1}. **IR** (200 mW, room temp.): $\tilde{\nu}$ = 3009 (w), 2510 (w), 2124 (w), 1629 (w), 1602 (m), 1596 (w), 1517 (m), 1484 (m), 1476 (s), 1447 (s), 1390 (w), 1323 (w), 1252 (w), 1187 (m), 4481 (m), 1159 (m), 1129 (m), 1051 (m), 1023 (w), 1041 (m), 1014 (m), 998 (m), 896 (br., vs), 767 (m), 743 (s), 731 (m), 718 (m), 675 (vs) cm^{-1}.

py$_2$P$_2$S$_4$O (4): To $KMnO_4$ (41.7 mg, 0.264 mmol) a solution of **1** (46.8 mg) in pyridine (5 mL) was added and stirred for 48 h at room temperature. The precipitate was filtered and the solvent was removed from the yellow solution in vacuo (Yield: 44 mg, 98 %). **^{31}P{^{1}H} NMR** (pyridine): δ (ppm) = 98.0 (s). Elemental analysis for py$_2$P$_2$S$_4$O: calcd. C 32.96, N 7.69, H 2.77, S 35.20 %; found C 37.42, N 8.71, H 3.48, S 28.24 %. **Mass** (EI+) *m*/*z* = 363.9 ([$C_{10}H_{10}N_2P_2S_4O$]$^+$), 331.9 ([M–S]$^+$), 284.7 ([M–py]$^+$), 252.9 ([M–pyS]$^+$), 205.0 ([M–py$_2$]), 190.0 ([M–pyS$_2$]$^+$), 173.0 ([M–pyPS$_2$O]$^+$), 128.0 ([PS$_3$]$^+$), 63.0 ([PS]$^+$). **Raman** (200 mW, room temp.): $\tilde{\nu}$ = 3062 (49), 1615 (48), 1016 (100), 470 (60), 385 (52) cm^{-1}. **IR** (200 mW, room temp.): $\tilde{\nu}$ = 3056 (vw), 2397 (w), 1631 (w), 1593 (w), 1532 (w), 1484 (m), 1444 (w), 1385 (vw), 1248 (w), 1211 (w), 1151 (w), 1051 (w), 1033 (vw), 1021 (vw), 998 (w), 868 (br., vs), 743 (s), 680 (vs), 666 (s) cm^{-1}.

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