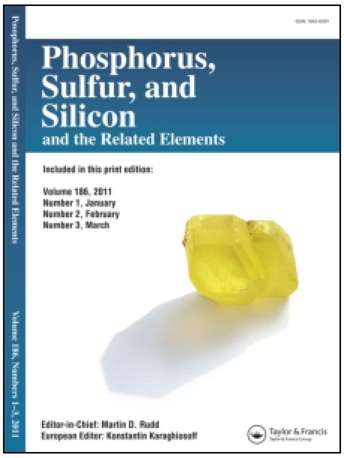

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Syntheses of New Intramolecular Stabilized Dithiometaphosphoric Acid Amides and their Reaction Potentials

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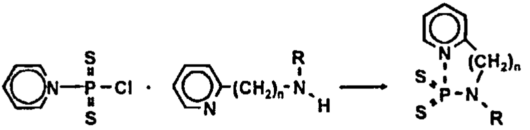
From the reaction of Py→PS_2Cl **1** with aminoalkyl pyridines intramolecular stabilized dithiophosphoric acid amides **3**, containing five- and six-membered rings, are isolated. Methanolysis of **3** leads to intramolecular pyridinium salts **4**. The reaction of **1** with bipyridine (bipy) gives (bipy)$PS_2^+PS_2Cl_2^-$ **9**.

Keywords: Phosphaheterocycles; intramolecular stabilization; aminoalkyl pyridines; dithioxophosphoranes

Reactions of Py→PS_2Cl (Py: pyridine) with primary and secondary aminoalkyl pyridines

The donor stabilized dithiometaphosphoric acid chloride Py→PS_2Cl **1** easily can be synthesized in high yield from P_4S_{10}, $PSCl_3$, and pyridine [1]. The reaction potential of this interesting building block versus protic nucleophiles intensively has been studied in the last two decades [2].

Here we present the reaction of Py→PS_2Cl **1** with various aminoalkyl pyridines **2**. These reactions give the intramolecular stabilized products **3a,b** in moderate yield (45-70%).



1

2a: R = Me; n = 2
2b: R = H; n = 1
2c: R = Me; n = 0

3a: R = Me; n = 2
3b: R = H; n = 1

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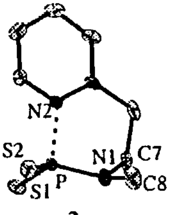
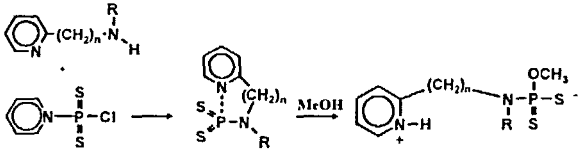


3a

Compound **3a** crystallizes from methylenchloride in the monoclinic system. The skeleton of **3a** forms a six-membered ring. The phosphorus atom is pyramidal, the sum of angles in the N-PS$_2$-plane is 346°. The donor bond between the pyridine nitrogen and phosphorus is 189.5 pm, which is markedly longer than in **1** (184.9 pm). The P-S-distances (196.0/194.8 pm) are typical for P=S-double bonds, the nitrogen center N$_1$ is pyramidal and all distances are normal within the limits of errror. The structure of **3a** is also in good agreement to other dimethylamino stabilized metadithiophosphoryl compounds[3].

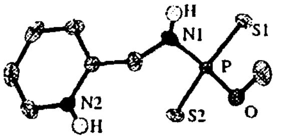
Reactivity versus methanol as nucleophilic reagent

On the reactions of the intramolecular stabilized metadithiophosphoric amides **3** with methanol the intramolecular salts **4** are found in high yield (65-84%). The products are completely characterized.



2a: R = Me; n = 2
2b: R = H; n = 1

4a: R = Me; n = 2
4b: R = H; n = 1



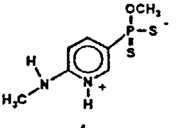
4b

Surprisingly, in **4b** we found the distance P$_1$-N$_1$ to be 165.1 pm, which is distinctly shorter than a normal P-N single bond (169-175 pm)[4]. The surroundings of the nitrogen atom N$_1$ are planar (sum of the bond angles: **4b** 359.1°). This demonstrates a high participation of the corresponding phospha-imin structure, R-HN$^+$=PS$_2^-$OMe. The basicity of the phosphorus-bonded nitrogen experimentally can be valued. Tab. 1 shows the pK$_a$ of various amines[5]. From the protonation of the pyridine-N it can be concluded that the pK$_a$ of N$_1$ has to be less than 5.2.

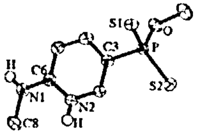
Compound	pK$_a$
NH_3	9.25
$MeNH_2$	10.66
Me_2NH	10.73
Me_3N	9.81
Aniline	4.63
Pyridine	5.20

Tab. 1

In contrary to the reactions of **1** with the amines **2a,b**, the use of 2-methylaminopyridine **2c** after methanolysis gives the electrophilic substitution product **4c**.

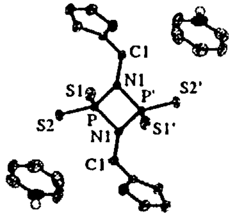


4c

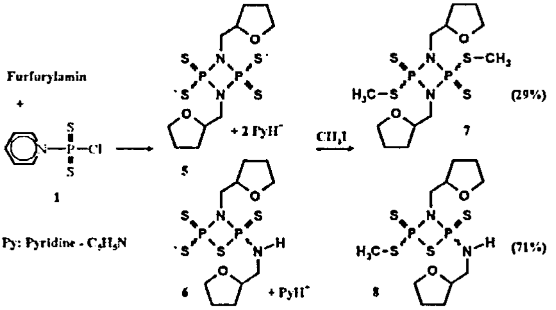


Reaction of 1 with furfurylamine

The reaction of **1** with furfurylamine was expected to form a five-membered ring, containing oxygen as electron pair donating atom. Instead, a mixture of the diazadiphosphetidine **5** and the azathiadiphosphetidine **6** has been isolated in high yield (90%). The X-Ray structure of **5** shows a planar four-membered ring system with pyramidal coordinated nitrogen atoms N_1 and N_1', respectively. Reaction of the mixture **5**/**6** with methyliodide quantitatively leads to the corresponding methylesters **7**/**8**. By ^{31}P-NMR the ratio **7**:**8** is determined to be 29:71. The compounds **7** and **8** are obtained as mixtures of their cis-/trans-isomers, which is proved by nmr.

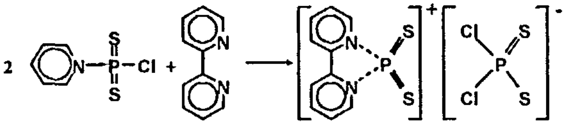


5

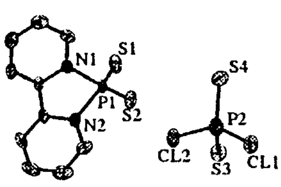


Reaction between 1 and 2,2'-bipyridine (bipy)

The bipyridyl stabilized (bipy)→PS_2^+-cation, synthesized by the reaction of Py→PS_2Cl with an excess of bipyridine, is another example for phosphorus containing ring systems. The structure of compound **9** is proved by X-Ray structure determination at 180 K. ^{31}P-NMR spectroscopy demonstrates that in acetonitrile there is only one signal at $\delta = 83.5$ ppm, probably resulting from rapid exchange between the stabilized PS_2^+-cation and the $PS_2Cl_2^-$-anion at room temperature. For $(C_5H_5N)_2PS_2I$ and $(C_5H_5N)_2PS_2Br$ a ^{31}P-NMR signal at $\delta = 104.7$ ppm is found[6]. For the $PS_2Cl_2^-$-anion $\delta = 81.8$ ppm (in acetonitrile) is described[7].



9



9

The bond distances between the bipyridine nitrogen atoms N_1, N_2 and the phosphorus atom P_1 are 181.9 and 183.1 pm. This is in the same region as has been found for $(C_5H_5N)_2PS_2Br$ (176.8/187.4)[6] and $(C_5H_5N)_2PS_2I$ (183.1/183.1)[6]. The thioxo bonds in the cation are typical for double bonds (P_1-S_1: 191.2 - P_1-S_2: 192.1 pm). In comparison to $(C_5H_5N)_2PS_2Br/(C_5H_5N)_2PS_2I$ the angle N_1-P_1-N_2 in **9** is reduced to 84.6°. In the anion there is nothing unusual. The surroundings of the phosphorus atom P_2 in **9** are distorted tetrahedral and the angles are 103.8-115.6°.

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