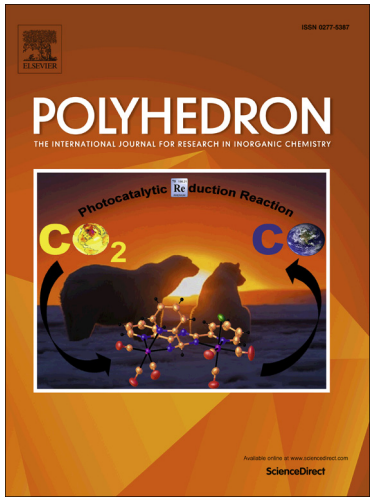


New condensed nitrogen-phosphorus heterocycles

Richard Ševč ík, Jiř í Př íhoda, Marek Nečas

PII: S0277-5387(16)30687-8
DOI: http://dx.doi.org/10.1016/j.poly.2016.12.036
Reference: POLY 12394

To appear in: *Polyhedron*

Received Date: 9 August 2016
Revised Date: 22 December 2016
Accepted Date: 23 December 2016

Please cite this article as: R. Ševč ík, J. Př íhoda, M. Nečas, New condensed nitrogen-phosphorus heterocycles, *Polyhedron* (2016), doi: http://dx.doi.org/10.1016/j.poly.2016.12.036

New condensed nitrogen-phosphorus heterocycles

Richard Ševčík [a], Jiří Příhoda[a,*], Marek Nečas[a, b]

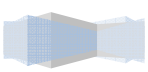
[a] *Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, CZ-61137 Brno, Czech Republic*

[b] *CEITEC - Central European Institute of Technology, Masaryk University, Kamenice 5, CZ-62500 Brno, Czech Republic*

Abstract

To extend our previous study aimed at the reactions of chlorodithiophosphoric acid pyridiniumbetaine (py.PS_2Cl) with thiosemicarbazide derivatives, we performed the reactions of chlorodithiophosphoric acid pyridiniumbetaine with a new group of polyfunctional nucleophiles – symmetrical and nonsymmetrical derivatives of hydrazine-1,2-bis(thiocarboamide) of general formula R(H)N-C(S)N(H)N(H)C(S)-N(H)R (R = methyl, *i*-propyl, ethyl, *t*-butyl, phenyl). In analogy to heterocyclic anions obtained with the thiosemicarbazide derivatives, the hydrazine derivatives were expected to form heterobicyclic dianions from the reactions with py.PS_2Cl. All the reactions were carried out in acetonitrile in the presence of pyridine to keep the same reaction conditions as with the previous experiments. Four new compounds were prepared and characterized by ^{31}P NMR, FTIR, Raman spectroscopy, and single crystal X-ray diffraction. Molecular structures of the products are based on heterobicyclic dianion consisting of two condensed five membered P-N-N-C-N rings, each of them bearing an organic group. Both of the organic groups in heterobicyclic dianion are either identical (Me, ^{i}Pr) or different (Et/^{t}Bu, Et/Ph). The molecular structure of the heterobicyclic dianion with unusual structural features was further examined by quantum chemistry calculations.

∗ Corresponding author. Address: Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, CZ-625 00 Brno, Czech Republic. Tel.: +420 549 49 6690; fax: +420 549 49 2443.
E-mail address: JiriPrihoda@seznam.cz (J. Příhoda).

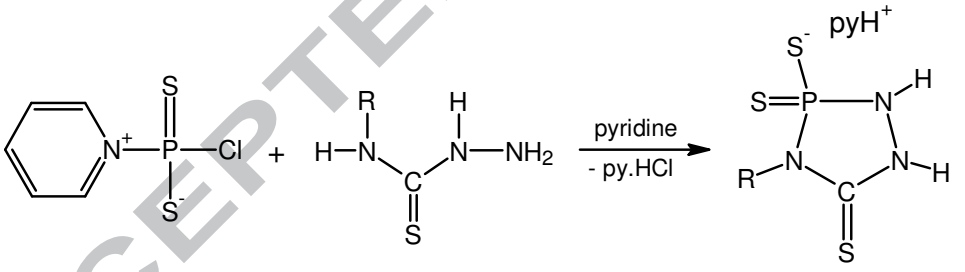


Keywords

chlorodithiophosphoric acid pyridiniumbetaine, polyfunctional nucleophiles, heterocycles, nitrogen-phosphorus compounds, NMR, FTIR, X-ray, DFT

1. Introduction

Recently, we reported on the reactions of chlorodithiophosphoric acid pyridiniumbetaine (py.PS_2Cl, **I**) with a variety of polyfunctional nucleophiles [1-5] yielding mostly heterocyclic compounds featuring a $(PS_2)^-$ group in their structures. Among them the reactions of py.PS_2Cl with thiosemicarbazide and its monoalkyl- and monoarylderivatives [3,4,5] were studied as well. It was found that thiosemicarbazide or its derivatives bearing small organic groups in position 4 (methyl, ethyl, phenyl, 4-nitrophenyl) react with py.PS_2Cl to give analogous products **A** – **E** with five-membered P-N-N-C-N heterocyclic anions bearing the organic groups (Eq. 1).

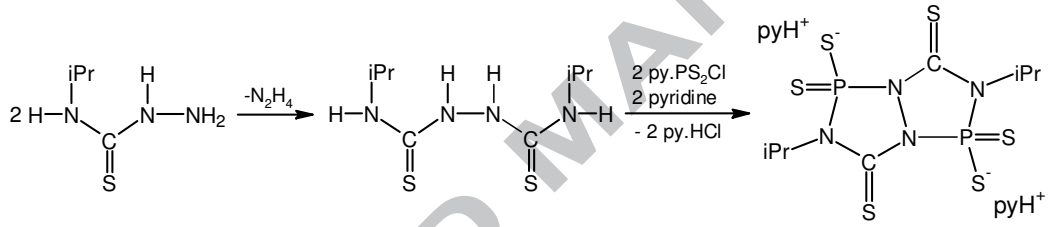


(Eq. 1)

A: R = H; ref. [3]
B: R = Me; ref. [4]
C: R = Et; ref. [4]
D: R = Ph; ref. [5]
E: R = 4-NO_2Ph; ref. [5]

In case of thiosemicarbazide monoalkylderivatives with more bulky substituents (*iso*-propyl, *tert*-butyl), all attempts to prepare analogous P-N-N-C-N heterocyclic rings were not successful, only presumptive evidences (^{31}P NMR) of their formation were obtained and they

were not isolated in a pure form. During the study of the reactions of **I** with 4-*iso*-propylthiosemicarbazide, a new compound with unexpected molecular structure containing a heterobicyclic dianion was obtained when formerly prepared 4-*iso*-propylthiosemicarbazide was used. The formation of this product may be explained if hydrazine-1,2-bis(thiocarbo-*iso*-propylamide) is considered as the reacting polynucleophile instead of 4-*iso*-propylthiosemicarbazide (Eq. 2) as it was previously assumed by Janča [3]; yet there was no evidence for the assumption. The assumed hydrazine derivative possibly arose from two molecules of 4-*iso*-propylthiosemicarbazide through condensation reaction which probably occurred on standing at room temperature or during azeotropic distillation process that was performed to remove the moisture before use.



(Eq. 2)

To confirm our postulate, we prepared hydrazine-1,2-bis(thiocarbo-*iso*-propylamide) and used it as starting nucleophile in the reaction with py.PS_2Cl. Subsequently we prepared a series of symmetrical and nonsymmetrical substituted hydrazine-1,2-bis(thiocarboamide) derivatives and studied their reactivity towards py.PS_2Cl. In this paper we report results of the study and discuss the molecular and crystal structures of the products.

2. Experimental

2.1. Chemicals and synthetic procedures

All chemicals were used as supplied (Aldrich, Lachema). Solvents were dried by standard methods and were distilled prior to use [6]. Chlorodithiophosphoric acid pyridiniumbetaine was prepared according to the known procedure [7]. Hydrazine-1,2-bis(thiocarboamide) derivatives were prepared according to the literature procedure [8] by two-step reactions of hydrazine and particular *iso*-thiocyanate derivatives. In case of symmetrical hydrazine derivatives syntheses were arranged as one-pot reactions, in other cases intermediary thiosemicarbazide derivative was isolated before the second reaction step. In the first step *iso*-thiocyanate derivative reacts with hydrazine intensively at room temperature, the second reaction step mostly necessitates higher temperature (reflux). Basic characteristics of the prepared nucleophiles and syntheses details are given in Table 1.

Table 1. Characteristics of the prepared hydrazine-1,2-bis(thiocarboamide) derivatives

$R_1N(H)C(S)N(H)N(H)C(S)N(H)R_2$		reflux time	yield	color	melting point
R_1	**R_2**	(min)	(%)		(° C)
Me	Me	30	60	white	212-213
i-Pr	*i*-Pr	60	90	white	198-200
Et	*t*-Bu	180	62	white	165-166
Et	Ph	-	85	white	172-173

2.2. Physical measurements

The ^{31}P NMR spectra were measured in acetonitrile using a Bruker AVANCE DRX 300 instrument and were referenced to 85% H_3PO_4. The IR spectra were recorded in nujol mulls on a Bruker IFS 28 spectrometer. The Raman spectra of solid samples were collected in Raman capillaries on a Bruker Equinox X55/S instrument.

2.3. X-Ray measurements

Diffraction data were collected on a KUMA KM-4 κ-axis CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The temperature during data collection was 120(2) K. The intensity data were corrected for Lorentz and polarization effects. All the structures were solved by direct methods and refined by full-matrix least-squares methods using anisotropic thermal parameters for the non-hydrogen atoms. Crystal data and structure refinement parameters are listed in Table 3. The software packages used were Xcalibur CCD system [9] for the data collection/reduction, and SHELXTL [10] for the structure solution, refinement, and drawing preparation (thermal ellipsoids are drawn at the 50% probability level).

2.4. Quantum chemistry calculations

DFT using ADF® 2014 molecular modeling suite [11, 12] was used for computation of optimized structures and properties; the OPBE exchange-correlation functional [13], Slater type basis set TZ2P [14] with small frozen core were used. Analytical normal mode frequencies were calculated. Bonding energies are given w. r. t. spherical spin-restricted neutral atoms used in ADF-package.

2.5. Reactions of py.PS_2Cl with hydrazine-1,2-bis(thiocarboamide) derivatives

All reactions of py.PS_2Cl with hydrazine-1,2-bis(thiocarboamide) derivatives were performed under dry nitrogen atmosphere in anhydrous solvents using conventional Schlenk techniques.

First, a solution of py.PS_2Cl and pyridine in acetonitrile was prepared. Then a suspension of dry hydrazine-1,2-bis(thiocarboamide) derivative in acetonitrile was added into the reaction mixture which was subsequently stirred for specified time at room temperature. At the end of the reaction, precipitated white solids insoluble in acetonitrile were filtered off and dried under vacuum. In case of ethyl/*tert*-butyl derivative, main fraction of the product (soluble in acetonitrile) was obtained from the concentrated solution upon standing at -25 °C overnight. Reaction details and yields are presented in Table 2.

Table 2. Experimental details and reaction yields

product	hydrazine-1,2-bis(thiocarboamide) derivative				py.PS_2Cl		pyridine		CH_3CN	time	yield
	$\mathbf{R_1}$	$\mathbf{R_2}$	(mmol)	(g)	(mmol)	(g)	(mmol)	(ml)	(ml)	(h)	(%)
II	Me	Me	2.24	0.400	4.49	0.941	4.49	0.37	46	48	92
III	*i*-Pr	*i*-Pr	1.28	0.300	2.56	0.537	2.56	0.21	28	48	90
IV	Et	*t*-Bu	1.96	0.460	3.93	0.823	3.93	0.32	40	72	85
V	Et	Ph	1.81	0.460	3.62	0.758	3.62	0.30	36	72	88

2.6. Bis(pyridinium) salt of 2,6-dimethyl-3,7-dithioxotetrahydro-1H,5H-[1,2,4,3]triazaphospholo[2,1-a][1,2,4,3]triazaphosphole-1,5-bis(thiolate)-1,5-disulfide ***(II)***

White powder, yield: 92 % (with respect to **I**). ^{31}P NMR (dimethylformamide): δ = 89.7 ppm, singlet. IR: 3205 vw, 3145 vw, 3127 vw, 3095 vw, 3062 vw, 1635 vw, 1603 w, 1527 w, 1483 m, 1457 w, 1425 w, 1336 vs, 1323 vs (sh), 1256 vw, 1237 vw, 1192 w, 1156 vw, 1115 w, 1057 vw, 1045 vw, 1025 vw, 1006 vw, 988 vw, 865 w, 768 s, 744 w, 697 s, 671 w, 661 w, 608 vw, 566 s, 499 vw. RA: 3089 w, 3053 vw, 3035 vw, 2926 vw, 1634 vw, 1601 vw, 1481

vw, 1311 vw, 1257 sh, 1231 vw, 1192 w, 1155 vw, 1056 vw, 1026 w, 1008 vs, 943 vw, 757 vw, 636 vw, 602 w, 446 w, 397 s, 352 vw, 319 w, 248 vw, 193 w, 166 w, 130 vs, 83 s.

2.7. Bis(pyridinium) salt of 2,6-diisopropyl-3,7-dithioxotetrahydro-1H,5H-[1,2,4,3]triazaphospholo[2,1-a][1,2,4,3]triazaphosphole-1,5-bis(thiolate)-1,5-disulfide ***(III)***

White powder, yield: 90 % (with respect to **I**). ^{31}P NMR (dimethylformamide): δ = 87.8 ppm, singlet. IR: 3221 vw, 3146 vw, 3134 vw, 3061 w, 1633 vw, 1607 vw, 1534 w, 1527 w, 1483 w, 1467 w, 1423 m, 1352 w, 1308 vs, 1293 vs, 1187 w, 1131 w, 1083 w, 1054 vw, 1024 vw, 1006 vw, 982 vw, 894 vw, 852 w, 768 m, 741 w, 694 m, 672 w, 608 vw, 569 s, 483 vw, 462 vw, 437 vw. RA: 3086 w, 2989 vw, 2970 vw, 2938 vw, 2921 vw, 2870 vw, 1631 vw, 1606 vw, 1426 vw, 1277 vw, 1224 vw, 1187 vw, 1160 vw, 1137 vw, 1110 vw, 1064 vw, 1054 vw, 1027 w, 1008 vs, 945 vw, 933 vw, 873 vw, 857 w, 775 vw, 693 vw, 636 vw, 610 sh, 604 w, 484 vw, 441 vw, 398 s, 370 w, 312 vw, 298 m, 240 vw, 205 vw, 178 sh, 161 sh, 127 m, 103 m, 83 m.

2.8. Bis(pyridinium) salt of 2-tert-butyl,6-ethyl-3,7-dithioxotetrahydro-1H,5H-[1,2,4,3]triazaphospholo[2,1-a][1,2,4,3]triazaphosphole-1,5-bis(thiolate)-1,5-disulfide ***(IV)***

White powder, yield: 85 % (with respect to **I**). ^{31}P NMR (dimethylformamide): δ = 88.6 ppm (triplet 1:2:1, ^{3}J[P-H]= 12 Hz; doublet, ^{3}J[P-P] = 4.6 Hz), δ = 86,9 ppm (doublet, ^{3}J[P-P] = 4.6 Hz). IR: 3206 m, 3139 m, 3127 m, 3081m, 3063 s, 1635 w, 1613 w, 1603 w, 1527 m, 1482 m, 1397w, 1367 m, 1340 s, 1314 vs, 1290 vs, 1224 w, 1206 w, 1190 m, 1158 w, 1104 w, 1081 vw, 1066 vw, 1057 vw, 1046 vw, 980 vw, 858 vw, 799 w, 750 s, 693 s, 636 w, 608 w, 558 s, 516 vw, 505 vw. RA: 3092 vw, 3076 sh, 2956 vw, 2931 vw, 1632 vw, 1602 vw,

1445 vw, 1366 vw, 1344 vw, 1288 vw, 1220 vw, 1189 w, 1154 vw, 1056 vw, 1026 w, 1007 vs, 924 vw, 896 vw, 811 vw, 720 vw, 637 w, 608 vw, 601 sh, 503 vw, 397 m, 379 sh, 308 vw, 286 vw, 251 vw, 221 vw, 166 w, 135 s, 112 s, 97 s, 84 vs.

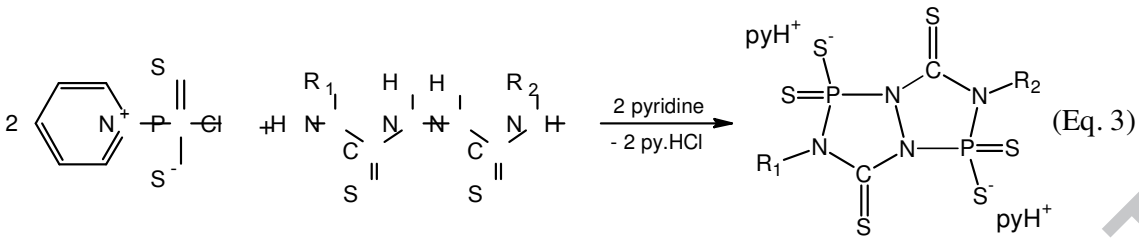
*2.9. Bis(pyridinium) salt of 2-ethyl,6-phenyl-3,7-dithioxotetrahydro-1H,5H-[1,2,4,3]triazaphospholo[2,1-a][1,2,4,3]triazaphosphole-1,5-bis(thiolate)-1,5-disulfide (**V**)*

White powder, yield: 88 % (with respect to **I**). ^{31}P NMR (dimethylformamide): δ = 88.5 ppm (triplet 1:2:1, ^{3}J[P-H]= 12 Hz; doublet, ^{3}J[P-P] = 7.8 Hz), δ = 87,9 ppm (doublet, ^{3}J[P-P] = 7.8 Hz). IR: 3203 vw, 3143 w, 3127 w, 3093 w, 3063 m, 1634 vw, 1601 w, 1527 m, 1482 m, 1456 w, 1439 w, 1376 s, 1368 s, 1342 vs, 1315 vs, 1274 w, 1257 m, 1188 s, 1160 vw, 1148 vw, 1079 vw, 1054 vw, 1045 vw, 1016 vw, 970 w, 927 vw, 873 vw, 808 vw, 774 m, 744 m, 704 s, 674 w, 604 vw, 584 w, 560 s, 506 vw, 424 vw. RA: 3090 vw, 3079 vw, 3066 vw, 3054 vw, 3040 vw, 2963 vw, 2936 vw, 2927 vw, 2866 vw, 1631 vw, 1611 sh, 1601 vw, 1439 vw, 1366 vw, 1324 sh, 1306 vw, 1276 vw, 1254 vw, 1235 vw, 1191 vw, 1159 vw, 1080 vw, 1057 vw, 1026 w, 1007 vs, 931 vw, 897 vw, 728 vw, 636 vw, 604 w, 559 vw, 508 vw, 492 vw, 427 vw, 400 s, 316 w, 287 vw, 267 vw, 238 vw, 191 w, 168 w, 127 s, 104 s, 83 s.

3. Results and discussion

3.1. Products and reaction mechanism

A series of reactions of **I** with hydrazine-1,2-bis(thiocarboamide) derivatives were carried out to yield new compounds with heterobicyclic dianions (Eq. 3). Obtained results confirmed that

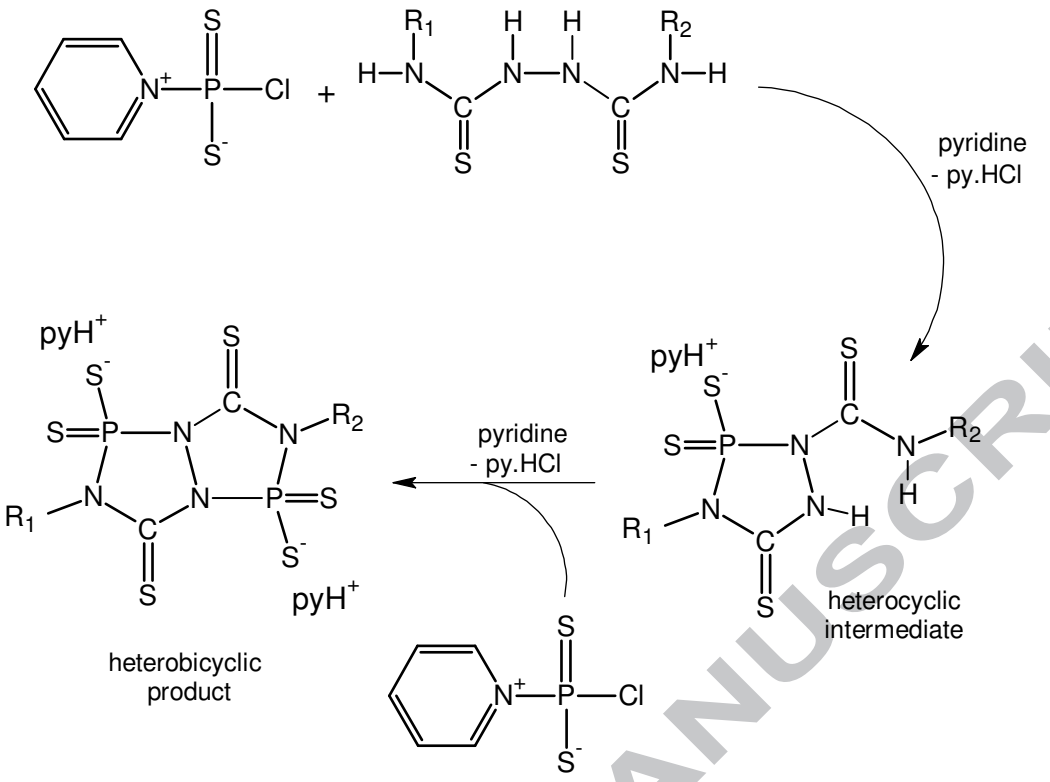


(Eq. 3)

$R_1 = R_2 =$ Me (comp. **II**) $R_1 =$ Et, $R_2 = {}^t$Bu (comp. **IV**)

$R_1 = R_2 = {}^i$Pr (comp. **III**) $R_1 =$ Et, $R_2 =$ Ph (comp. **V**)

hydrazine-1,2-bis(thiocarboamide) derivatives react with **I** under the formation of compounds with the heterobicyclic dianion, and a two-step reaction mechanism (Eq. 4) was experimentally confirmed for dimethylderivative ($R_1 = R_2 =$ Me). In the first step, **I** reacts with hydrazine-1,2-bis(thiocarboamide) derivative under the formation of a heterocyclic intermediate with a five-membered P-N-N-C-N ring similar to five-membered rings in compounds **A** – **E**. The heterocyclic intermediate with $R_1 = R_2 =$ Me (compound **VI**) was isolated and characterized by single crystal X-ray diffraction. In the next step the heterocyclic intermediate reacts with the second molecule of **I** under the formation of a heterobicyclic dianion. Compound **VI** should be considered only a reaction intermediate since an attempt to prepare **VI** by the reaction of equimolar amounts of **I** and hydrazine-1,2-bis(thiocarbomethylamide) was not successful; only compound **II** was obtained as the main product, although in low yield and purity, while traces of the intermediate **VI** were confirmed only in the reaction mixture by ^{31}P-NMR.



(Eq. 4)

As both the present reaction of **I** with intentionally prepared hydrazine-1,2-bis(thiocarbo-*iso*-propylamide) and the previously studied reaction of **I** with "4-*iso*-propylthiosemicarbazide" yielded the same product **III**, we can conclude that the same nucleophile hydrazine-1,2-bis(thiocarbo-*iso*-propylamide) was employed in both the reactions. The present results thus confirm at least a part of the proposed reaction route (Eq. 2). Although the first step, i.e. proposed condensation 4-*iso*-propylthiosemicarbazide was not studied, it is legitimate to claim that its transformation to hydrazine-1,2-bis(thiocarbo-*iso*-propylamide) occurred on prolonged standing at room temperature or during azeotropic distillation. To avoid the issue with 4-*iso*-propylthiosemicarbazide transformation it is necessary to use freshly prepared derivative which can be dried simply under vacuum.

3.2. Nuclear magnetic resonance

The products are insoluble (**II** and **III**) or slightly soluble (**IV** and **V**) in acetonitrile and are easily isolated from the reaction mixtures. All of the compounds are well soluble in dimethylformamide. In ^{31}P NMR spectra of the compounds **II** and **III**, only singlets are observed. Signal spliting due to P-H or P-N interactions is not observed which is rather unexpected in case of **II** as spliting due to P-H interaction is observed in **B** that contains an analogous P-N-N-C-N ring with methyl group. ^{31}P NMR spectra of nonsymmetrical compounds **IV** and **V** show two doublets due to inequivalence of phosphorus atoms; one of them is split further into a triplet by coupling to CH_2 hydrogens of ethyl group.

3.3. Molecular spectroscopy

Infrared and Raman spectra of compounds **II** – **V** are quite simple but assignment is complicated because of absorption bands overlaps. Nevertheless, the presence of pyridinium cations, and of phenyl group in case of **V**, is clearly seen in the infrared spectra. A band around 3202 cm^{-1} is in all cases assigned to N-H bonding vibration in pyridinium cations, other bands belonging to cations can be found in the region above 3000 cm^{-1} (aromatic C-H bonding vibrations) and at 1500-1650 cm^{-1}. Some of the cation bands are still found in the region of 650-790 cm^{-1} but they are overlapped by bands of PS_2 group. Absorption bands belonging to C=S bonding vibrations were not identified. Vibrations of pyridinium cations are observed in Raman spectra as well, they can be found in the same regions as in infrared spectra, moreover very strong band at ca 1007 cm^{-1} is assigned to pyridinium cation as well. The presence of organic substituents in the molecules of **II** – **V** is evidenced by the bands at 2850-3000 cm^{-1} belonging to aliphatic C-H bonding vibrations, with more bands being observed for the bulkier organic substituents.

3.4. X-ray diffraction analysis

Molecular structures of compounds **II - VI** (Fig. 2 – 6) were definitely confirmed by single crystal X-ray diffraction. The molecules of **II** – **IV** possess heterobicyclic moieties substituted by two hydrocarbon groups, either identical (Me – **II**, ^{i}Pr – **III**) or different (Et/^{t}Bu – **IV**, Et/Ph – **V**) from each other. While in **II** the heterobicyclic moiety is perfectly planar as a result of crystallographically imposed mirror symmetry, in the other compounds the deviation from planarity is less or more pronounced. The r.m.s. deviation of atoms fitted to the ring plane is largest for one of the crystallographically independent molecules in **III** (0.2232 Å). The ring planarity is reflected in tendency of nitrogen atoms towards sp^2 hybridization, as documented by bond valence angles sums on nitrogen atoms which range from 353.4 to 360.0 °. The P–S bond lengths range from 1.939 to 1.975 Å and are significantly longer than in the starting py.PS_2Cl (1.920 Å) [15]. In agreement with the concept of a charge delocalization in the $(PS_2)^-$ moiety [1,2], the respective P–S bond lengths are very similar in the present compounds, although the differences are more significant in case of unsymmetrically substituted dianions (compounds **IV** and **V**). In the crystal structures of the present compounds, pyridinium cations are involved in a network of hydrogen bonds between N–H groups and sulfur atoms, with the exception of **III** for which N–H…Cl bonds to chloride anions are preferred.

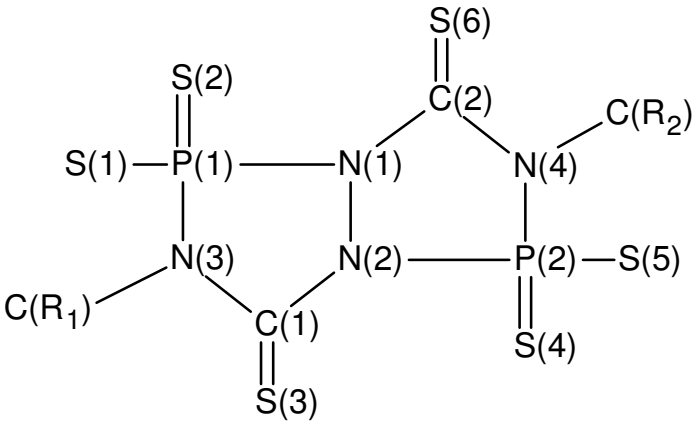


Fig. 1 X-ray diffraction analysis – general numbering scheme for heterobicyclic dianions of **II** – **V** used in the text and Tab. 4 ($C(R_1)$ and $C(R_2)$ represent carbon atoms binding organic substituents to heterobicyclic skeleton, R_1 stands for ethyl group in compounds **IV** and **V**). Intermediate **VI** keeps the same numbering scheme but contains only one P-N-C-N-N ring marked with lower numbers.

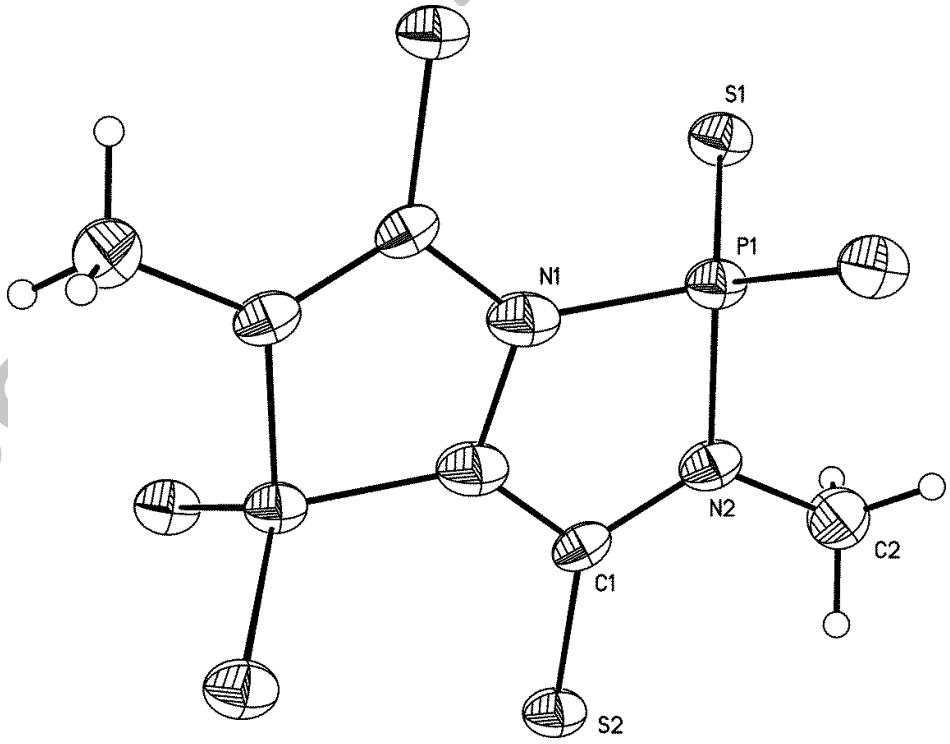


Fig. 2 The ORTEP drawing of anionic part of compound **II**.

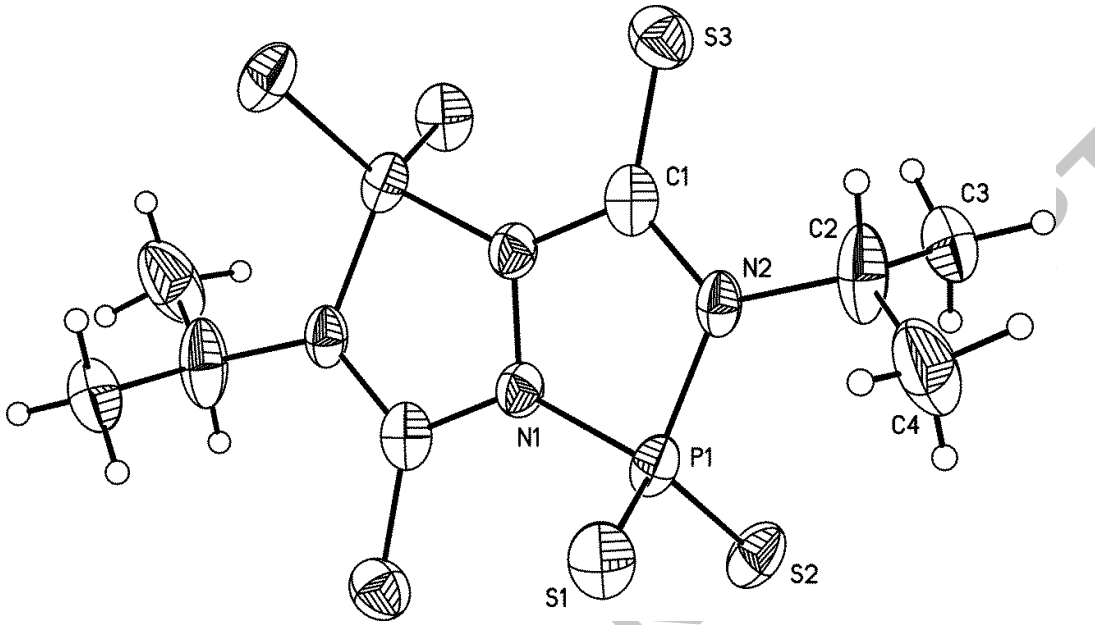


Fig. 3 The ORTEP drawing of anionic part of compound **III**.

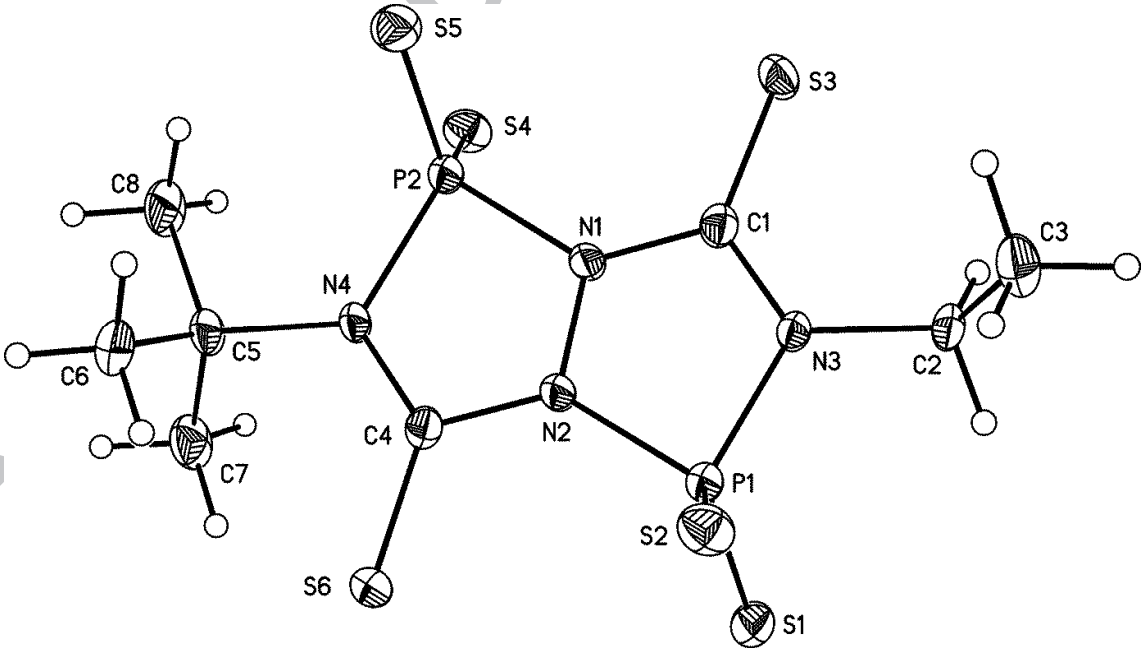


Fig. 4 The ORTEP drawing of anionic part of compound **IV**.

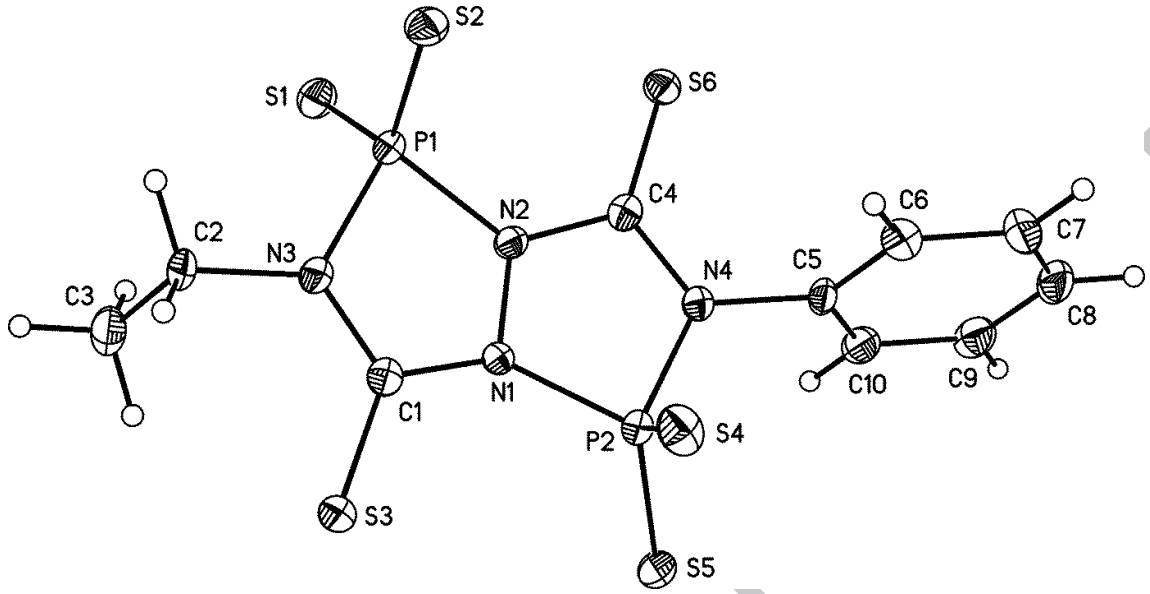


Fig. 5 The ORTEP drawing of anionic part of compound **V**.

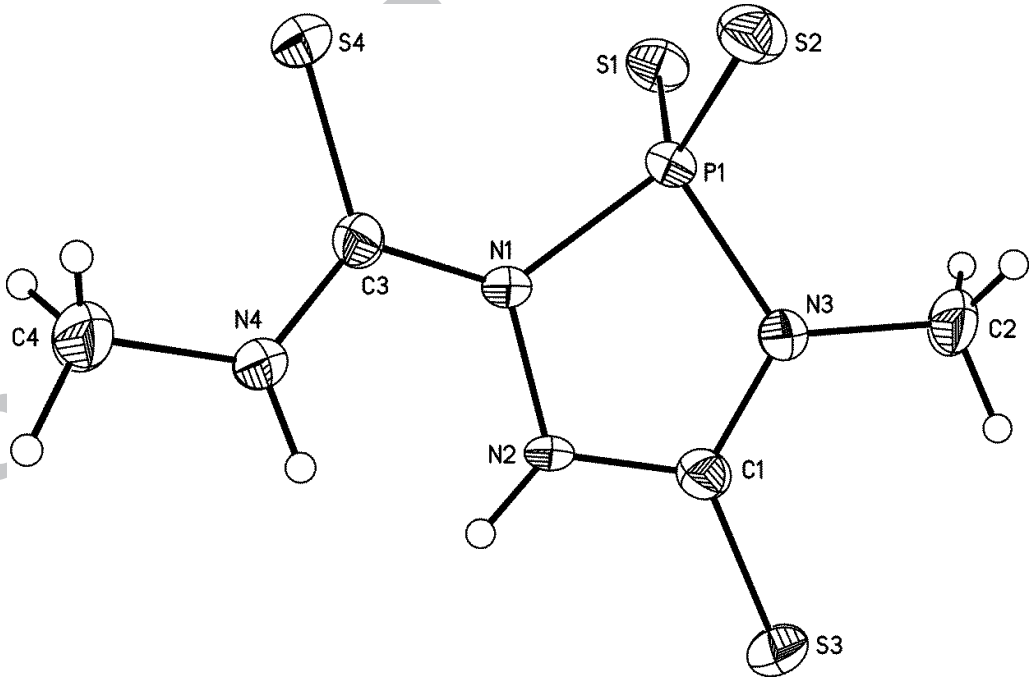


Fig. 6 The ORTEP drawing of anionic part of intermediate **VI**.

3.5. Quantum chemistry calculation

Tendency of nitrogen atoms of heterobicyclic dianions of **II** – **V** to possess rather sp^2 hybridization was further examined by quantum chemistry calculations. Optimized structure and properties of the dianion $C_4H_6N_4P_2S_6^{2-}$ (symmetry D_{2h}) of compound **II** with its perfect planar geometry was calculated via DFT. Calculated bond lengths (Fig. 7) are mostly in good agreement with the experimental ones, although with the exception of P(1)-N(1) bond they are more or less shorter. The largest difference can be found for exocyclic bonds C(1)-S(3)/C(2)-S(6) (0.027 Å) and N(3)-C(R_1)/N(4)-C(R_2) (0.033 Å) and especially for endocyclic N(1)-N(2) bond (0.039 Å) but as we can see in case of two crystallographically independent molecules of **III,** lengths of the N(1)-N(2) bond can differ even more (0.049 Å). The distribution of the electron density - contour map, Hirshfeld charges [16] and Voronoi deformation density [17] - in the dianion was calculated. The extent of π-conjugation in the dianion is clearly seen from the Fig. 8 showing two bonding π-orbitals $2A_u$ and $3B_g$. Except for the two phosphorus atoms all atoms in plane are engaged; the role of the phosphorus d-orbitals in bonding is qualitatively negligible as usual. Bond order analysis in the Nalewajski-Mrozek approach [18] shows that the C-S and P-S bonds have a biggest share of a partial double bond. Results of the DFT computation are thus in compliance with experimental data of the single crystal X-ray diffraction and confirm presumptive π-electron conjugation in the heterobicyclic dianion.

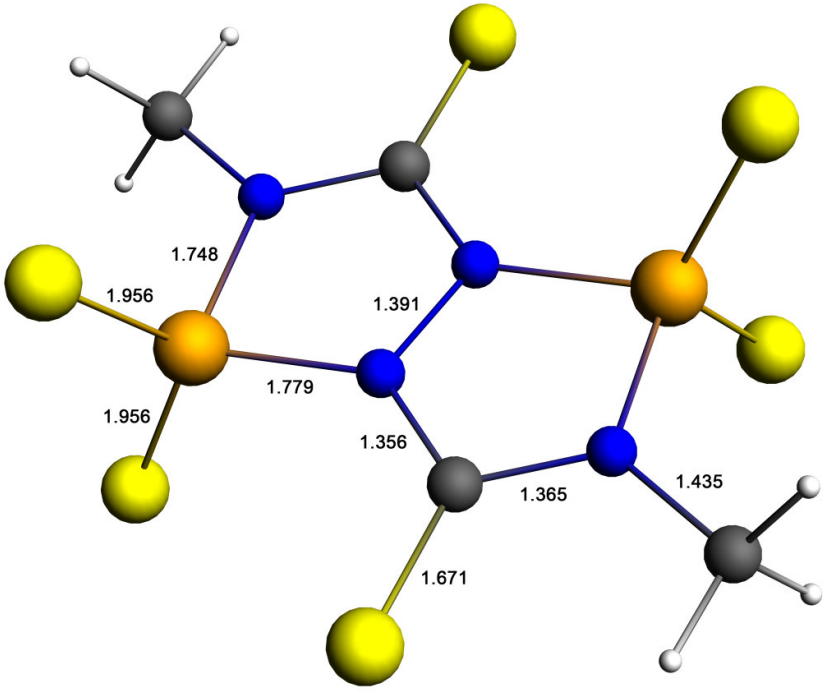


Fig. 7 Bond lenghts (Å) in anionic part of compound **II** calculated via DFT.

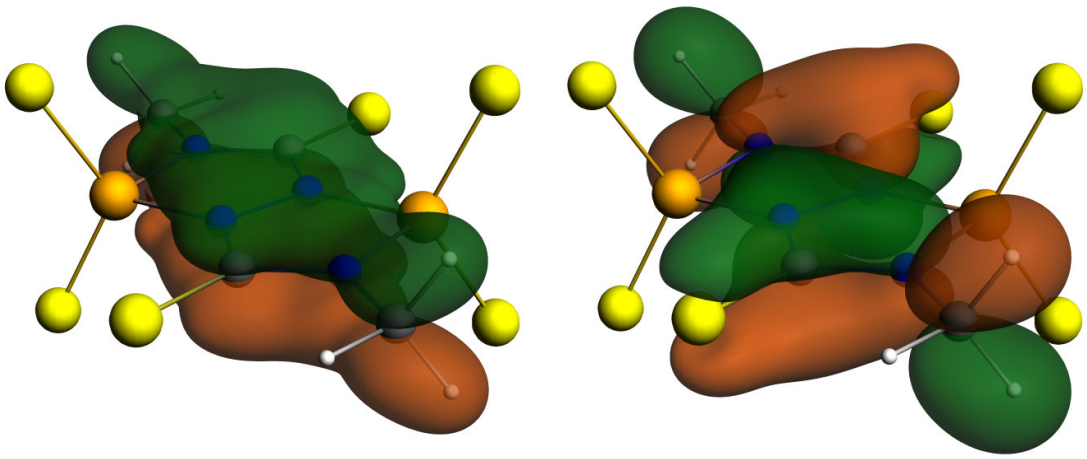


Fig. 8 Bonding π-orbitals $2A_u$ (left) and $3B_g$ (right) in anionic part of compound **II** calculated via DFT.

Conclusion

We have studied the reactions of py.PS_2Cl with disubstituted derivatives of hydrazine-1,2-bis(thiocarboamide) and prepared four new heterobicyclic compounds with two condensed P-N-N-C-N rings in high yields. Some details about the mechanism of their formation were obtained through isolation of an intermediate heterocyclic compound. DFT calculations show an extensive conjugation of π-electron density leading to preferred planar geometry of the heterobicyclic dianions, which was fully confirmed by single crystal X-ray diffraction.

Appendix A. Supplementary data

CCDC 1494069 - 1494073 contain the supplementary crystallographic data for compounds **II** - **VI**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

We would like to thank to Pavel Kubáček for his valuable contribution dealing with DFT computations.

References

1. V. Novoměstská, J. Marek, J. Příhoda, *Polyhedron* 18 (1999), 2723.

2. M. Janča, M. Nečas, Z. Žák, J. Příhoda, *Polyhedron* 20 (2001), 2823.

3. M. Janča, Dissertation, Masaryk University Brno, 2002.

4. R. Ševčík, J. Příhoda, M. Nečas, *Polyhedron* 24 (2005), 1855.

5. R. Ševčík, J. Příhoda, *Polyhedron* 85 (2015), 161.

6. D. D. Perrin, W. L. F. Armarego, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1988.

7. M. Meisel, H. Grunze, *Z. Anorg. Allg. Chem.* 360 (1968) 277.

8. M. Busch, H. Lotz, *J. Prakt. Chem*., (2) 90 (1914) 260.

9. Oxford Diffraction Ltd., XCALIBUR CCD System, CrysAlis Software System, Version 1.168. Oxford, England, 2001.

10. G. M. Sheldrick, *Acta Cryst*. A64 (2008) 112.

11. C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, Towards an order-N DFT method, *Theor. Chim. Acta* (1998), 99, 391.

12. G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, Chemistry with ADF, *J. Comput. Chem.* (2001), 22, 931.

13. M. Swart, A. W. Ehlers, L. Koop, Performance of the OPBE exchange-correlation functional, *Mol. Phys*. (2004), 102, 2467.

14. E. van Lenthe and E. J. Baerends, Optimized Slater-type basis sets for the elements 1-118, *J. Comput. Chem.* (2003) 24, 1142.

15. M. T. Averbuch-Pouchot, M. Meisel, *Acta Cryst.* C45 (1989), 1937.

16. F. L. Hirshfeld, Bonded-atom fragments for describing molecular charge densities, *Theor. Chim. Acta* (1977) 44, 129.

17. C. Fonseca Guerra, J.-W. Handgraaf, E. J. Baerends and F. M. Bickelhaupt, Voronoi Deformation Density (VDD) charges. Assessment of the Mulliken, Bader, Hirshfeld, Weinhold and VDD methods for Charge Analysis, *J. Comput. Chem.* (2004) 25, 189.

18. R. F. Nalewajski, J. Mrozek and G. Mazur, Quantum chemical valence indices from the one-determinantal difference approach, *Can. J. Chem.* (1996) 74, 1121.

Table 3. Crystal data and details of the structure determination.

	II	**III**	**IV**	**V**	**VI**
Empirical formula	$C_{14}H_{18}N_6P_2S_6$	$C_{33}H_{44}Cl_3N_9P_2S_6$	$C_{18}H_{26}N_6P_2S_6$	$C_{22.5}H_{25}Cl_{0.5}N_{6.5}P_2S_6$	$C_{14}H_{20}ClN_6PS_4$
Formula weight	524.64	927.42	580.75	658.52	467.02
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	*C*2/*m*	*P*-1	*P*-1	*C*2/*c*	$Pca2_1$
a (Å)	17.335(4)	9.7991(3)	9.3401(19)	28.5583(4)	25.969(2)
b (Å)	7.0873(14)	9.9585(3)	10.441(2)	15.4755(2)	9.4719(8)
c (Å)	9.3398(19)	26.9346(8)	15.566(3)	14.3913(2)	8.8065(9)
α (°)	90	100.410(2)	106.85(3)	90	90
β (°)	97.97(3)	90.300(2)	91.28(3)	110.326(2)	90
γ (°)	90	118.5930(10)	113.48(3)	90	90
Volume ($Å^3$)	1136.4(4)	2257.01(12)	1316.0(5)	5964.24(14)	2166.2(3)
Z	2	2	2	8	4
Calculated density (Mg/m^3)	1.533	1.365	1.466	1.467	1.432
μ (mm^{-1})	0.757	0.587	0.662	0.637	0.648
Measured / unique reflections	4340 / 1126	23011 / 7911	9963 / 4782	34354 / 5244	21814 / 3196
Data / restraints / parameters	1126 / 0 / 83	7911 / 96 / 478	4782 / 0 / 293	5244 / 0 / 339	3196 / 1 / 235
Final R indices [$I>2\sigma(I)$]	0.0856 / 0.2229	0.0561 / 0.1360	0.0343 / 0.0749	0.0323 / 0.0837	0.0336 / 0.0782
Final R indices [all data]	0.0952 / 0.2486	0.1190 / 0.1433	0.0523 / 0.0797	0.0486 / 0.0921	0.0382 / 0.0803
GooF	1.099	1.023	0.937	1.110	1.061
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ ($e.A^{-3}$)	2.071 / -0.711	0.724 / -0.440	0.630 / -0.282	0.582 / -0.266	0.357 / -0.379

Table 4. Selected bond lengths (Å) and angles (°).

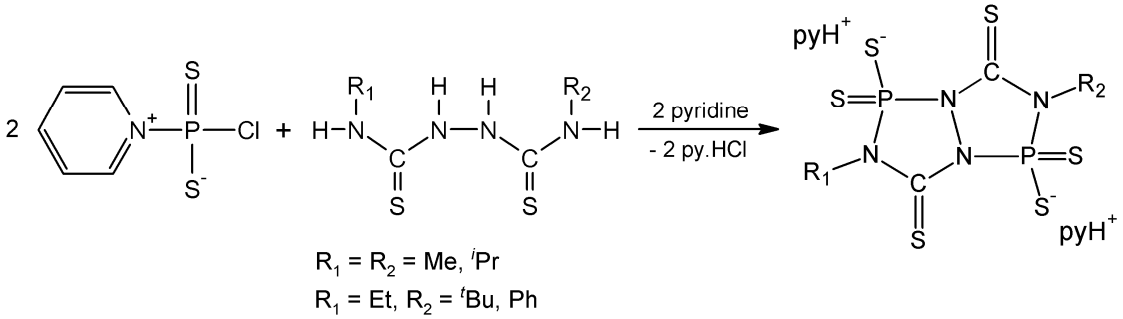
	II ($R_1 = R_2 =$ Me)	**III** ($R_1 = R_2 = {}^{i}$Pr)	**IV** (R_1 = Et, $R_2 = {}^{t}$Bu)	**V** (R_1 = Et, R_2 = Ph)	**VI**
P(1)-S(1)	1.9750 (12)	1.944 (2); 1.9509 (19)	1.9551 (10)	1.9561 (8)	1.9382 (14)
P(1)-S(2)	1.9750 (12)	1.950 (2); 1.9564 (19)	1.9513 (10)	1.9403 (8)	1.9476 (14)
P(2)-S(4)	1.9750 (12)	1.950 (2); 1.9564 (19)	1.9650 (10)	1.9506 (8)	
P(2)-S(5)	1.9750 (12)	1.944 (2); 1.9509 (19)	1.9389 (10)	1.9406 (8)	
P(1)-N(1)	1.755 (6)	1.738 (4); 1.752 (4)	1.739 (2)	1.7626 (18)	1.727 (2)
P(2)-N(2)	1.755 (6)	1.738 (4); 1.752 (4)	1.737 (2)	1.7497 (18)	
P(1)-N(3)	1.750 (5)	1.749 (4); 1.732 (4)	1.726 (2)	1.733 (2)	1.719 (3)
P(2)-N(4)	1.750 (5)	1.749 (4); 1.732 (4)	1.758 (2)	1.7426 (19)	
N(2)-C(1)	1.362 (8)	1.372 (6); 1.358 (6)	1.354 (3)	1.364 (3)	1.342 (4)
N(1)-C(2)	1.362 (8)	1.372 (6); 1.358 (6)	1.367 (3)	1.362 (3)	1.360 (4)
N(3)-C(1)	1.368 (8)	1.377 (6); 1.372 (6)	1.361 (3)	1.351 (3)	1.347 (4)
N(4)-C(2)	1.368 (8)	1.377 (6); 1.372 (6)	1.371 (3)	1.360 (3)	1.328 (4)
C(1)-S(3)	1.698 (5)	1.649 (6); 1.675 (6)	1.673 (2)	1.670 (2)	1.671 (3)
C(2)-S(6)	1.698 (5)	1.649 (6); 1.675 (6)	1.670 (2)	1.669 (2)	1.675 (3)
N(3)-C(R_1)	1.468 (8)	1.495 (6); 1.496 (6)	1.479 (3)	1.479 (3)	1.458 (4)
N(4)-C(R_2)	1.468 (8)	1.495 (6); 1.496 (6)	1.532 (3)	1.445 (3)	1.445 (5)
N(1)-N(2)	1.430 (10)	1.450 (8); 1.401 (7)	1.403 (3)	1.424 (3)	1.422 (3)
S(1)-P(1)-S(2)	120.29 (9)	120.65 (10); 120.33 (9)	118.59 (5)	120.95 (4)	119.35 (5)
S(4)-P(2)-S(5)	120.29 (9)	120.65 (10); 120.33 (9)	119.95 (5)	119.73 (4)	
N(1)-P(1)-N(3)	86.1 (2)	87.0 (2); 86.60 (19)	86.31 (10)	85.76 (9)	87.35 (12)
N(2)-P(2)-N(4)	86.1 (2)	87.0 (2); 86.60 (19)	87.07 (10)	85.79 (9)	
C(1)-N(3)-C(R_1)	122.8 (5)	119.9 (5); 119.5 (4)	122.01 (19)	122.47 (19)	123.9 (3)
C(2)-N(4)-C(R_2)	122.8 (5)	119.9 (5); 119.5 (4)	121.94 (19)	121.43 (19)	122.8 (3)
C(1)-N(3)-P(1)	117.6 (4)	116.5 (3); 116.2 (3)	117.45 (16)	117.57 (15)	116.3 (2)
C(2)-N(4)-P(2)	117.6 (4)	116.5 (3); 116.2 (3)	115.27 (16)	117.56 (15)	
N(2)-N(1)-P(1)	113.0 (5)	111.3 (4); 111.6 (4)	113.13 (15)	112.36 (13)	112.13 (18)
N(1)-N(2)-P(2)	113.0 (5)	111.3 (4); 111.6 (4)	112.85 (15)	112.97 (13)	
C(1)-N(2)-N(1)	113.1 (6)	112.3 (5); 113.3 (5)	113.24 (19)	112.33 (17)	112.4 (2)
C(2)-N(1)-N(2)	113.1 (6)	112.3 (5); 113.3 (5)	113.52 (19)	112.82 (17)	119.3 (2)
N(3)-C(1)-N(2)	110.2 (5)	109.8 (5); 110.0 (4)	109.8 (2)	110.51 (19)	111.2 (3)
N(4)-C(2)-N(1)	110.2 (5)	109.8 (5); 110.0 (4)	110.5 (2)	109.84 (19)	115.8 (3)
N(3)-C(1)-S(3)	126.1 (4)	127.6 (4); 127.2 (4)	126.46 (18)	126.07 (17)	126.2 (3)
N(4)-C(2)-S(6)	126.1 (4)	127.6 (4); 127.2 (4)	131.07 (18)	127.19 (17)	124.3 (3)
N(2)-C(1)-S(3)	123.8 (5)	122.6 (4); 122.8 (4)	123.73 (19)	123.39 (16)	122.6 (2)
N(1)-C(2)-S(6)	123.8 (5)	122.6 (4); 122.8 (4)	118.41 (19)	122.94 (16)	119.9 (2)

Symmetry codes (**II**): (i) $-x, -y, -z+2$; (ii) $x, -y, z$.

Symmetry codes (**III**): (i) $-x, -y, -z+1$; (ii) $-x+2, -y+2, -z$.

Synopsis

Reactions of chlorodithiophosphoric acid pyridiniumbetaine with symmetrical and nonsymmetrical derivatives of hydrazine-1,2-bis(thiocarboamide) of general formula R(H)N-C(S)N(H)N(H)C(S)-N(H)R (R = methyl, *i*-propyl, ethyl, *t*-butyl, phenyl) were studied. Syntheses were carried out in acetonitrile in the presence of pyridine and four new compounds with heterobicyclic dianions were prepared and characterized.



$R_1 = R_2 =$ Me, ^{i}Pr

$R_1 =$ Et, $R_2 = {}^t$Bu, Ph