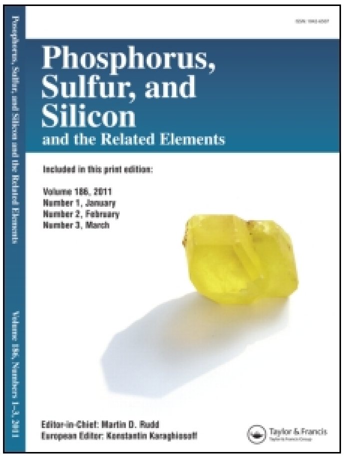

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SYNTHESIS AND X-RAY STRUCTURE OF DIISOPROPYLPHOSPHORYL ALKANEDIYL DIISOTHIOUREA

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SYNTHESIS AND X-RAY STRUCTURE OF DIISOPROPYLPHOSPHORYL ALKANEDIYL DIISOTHIOUREA

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Symmetric organic compounds containing 1-phosphoryl-3-imino groups were prepared by a two phase reaction between the corresponding dialkylphosphite and alkanediyl diisothiourea. The X-ray structure analysis showed that the diisopropylphosphoryl ethylenediisothiourea **IIa** crystallized in the orthorhombic space group Pbca with the cell dimensions a = 16.660(3) Å, b = 8.910(2) Å, c = 17.457(3) Å, Z = 4, at −100°C. The coordination around the phosphorus atom in the molecule is distorted tetrahedrally. The molecule has moieties slightly out of plane around O=P—N—C—N with strong intermolecular hydrogen bonds.

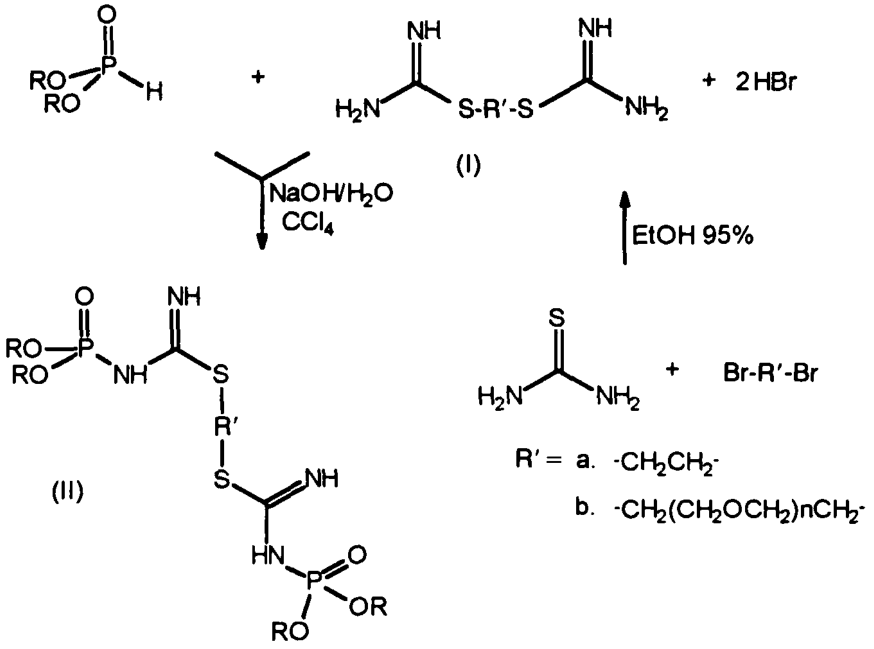
Key words: Reaction of dialkylphosphite with alkylisothiourea; phosphorylation of alkylisothiourea; symmetric diisopropylphosphoryl ethylenediisothiourea; dialkylphosphoryl alkylisothiourea.

INTRODUCTION

Bidentate compounds containing a 1-phosphoryl-3-carbonyl group are known to form colorful complexes with various metal ions.[1] They are powerful extractants for trivalent lanthanides and actinides as well as alkali metal cations.[2,3] An alternation of the molecular structure might improve the extractant properties of these compounds, such as the complexing capacity and the ion selectivity. Recently we have reported the syntheses and preliminary complexation studies of the compounds containing 1-phosphoryl-2-aza-3-thiocarbonyl or imino groups.[4,5] Here the preparation of the symmetric-polydentate ligands containing similar binding sites is described and X-ray structural analysis of **IIa** is reported.

RESULT AND DISCUSSION

The symmetric alkanediyl diisothiourea hydrobromide (**I**) can be prepared by reacting thiourea and alkanediyl dibromide in 95% ethanol at reflux temperature. This symmetric diisothiourea (**I**) is phosphorylated in a two phase reaction of sodium



hydroxide/water and diisopropylphosphite in carbon tetrachloride solution at 50°C. The synthesized compounds were characterized by conventional methods. The molecular structure of N,N'-diisopropylphosphoryl ethylenediisothiourea (**IIa**) is shown in Figure 1. Final atomic coordinates and equivalent isotropic displacement coefficients are given in Table I. Bond lengths and bond angles are listed in Table II. The coordination of the P atom in the molecule is distorted tetrahedrally: O(3)—P—O(1) and O(3)—P—N(1) angles are increased and O(3)—P—O(2),

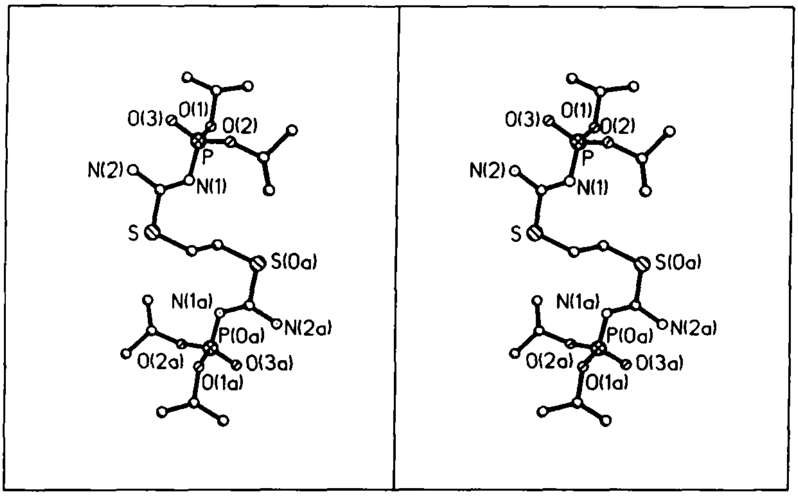


FIGURE 1 ORTEP perspective view of diisopropylphosphoryl ethylenediisothiourea.

TABLE I
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($pm^2 \times 10^{-1}$)

atom	X	Y	Z	U(eq)*
S	5544(1)	4825(1)	8842(1)	38(1)
P	3867(1)	1297(1)	8675(1)	28(1)
0(1)	3054(1)	2124(2)	8518(1)	36(1)
0(2)	3762(1)	210(3)	9378(1)	44(1)
0(3)	4135(1)	374(3)	8021(1)	41(1)
N(1)	4465(2)	2630(3)	8954(1)	29(1)
N(2)	4935(2)	3252(3)	7719(1)	37(1)
C(1)	2406(2)	1314(4)	8120(2)	48(1)
C(2)	2389(3)	1810(7)	7308(2)	95(2)
C(3)	1642(2)	1672(5)	8527(3)	65(2)
C(4)	3442(2)	703(5)	10104(2)	48(1)
C(5)	2774(3)	-391(7)	10294(2)	90(2)
C(6)	4081(2)	709(5)	10699(2)	56(1)
C(7)	4894(2)	3404(3)	8486(2)	27(1)
C(8)	5385(2)	4637(4)	9870(2)	39(1)

* U (eq) =one third of the trace of the orthogonalized U tensor

N(1)—P—O(2) and N(1)—P—O(1) are decreased from the ideal value 109.5° while the O(1)—P—O(2) angle is maintained at its ideal value. The P—N bond length is the range of the corresponding amidophosphates (1.61–171) Å.[6] The bond lengths of P=O(3), P—O(2) and P—O(1) are normal. The bond length of C(7)—N(1) is 1.286(4) Å. It is shorter than a normal C—N single bond (1.47 Å) and is even smaller than a simple C=N (1.30 Å). The bond length of C(7)—N(2), 1.346(4) Å, indicates the double character; sum of the bond angles around C(7) is 360.6°. These data suggest planarity around the C(7) atom. Refinement to see the hydrogen atoms in the X-ray structure was not successful. This information suggests strong resonance between carbon-nitrogen of N(1)—C(7)—N(2). The calculated distance between O(3) . . . N(2) (intramolecular) is 2.938 Å; between O(3) . . . N(2) (intermolecular) is 2.766 Å. This suggests hydrogen bonding of P—O(3) . . . . H—N(2) in the crystal structure and also that the intermolecular bonds are stronger than the intramolecular bonds. The calculated dihedral angle between P—O(3)/C(7)—N(2)

TABLE II
Bond lengths (Å) and bond angles (deg) for compound **IIa**

bond lengths			
S-C(7)	1.778(3)	S-C(8)	1.821(3)
P-0(1)	1.566(2)	P-0(2)	1.574(2)
P-0(3)	1.476(2)	P-N(1)	1.625(3)
0(1)-C(1)	1.472(4)	0(2)-C(4)	1.443(4)
N(1)-C(7)	1.286(4)	N(2)-C(7)	1.346(4)
C(1)-C(2)	1.484(6)	C(1)-C(3)	1.493(5)
C(4)-C(5)	1.516(6)	C(4)-C(6)	1.487(5)
C8()-C(8A)	1.506(6)		
Bond angles			
C(7)-S-C(8)	101.0(1)	0(1)-P-0(2)	109.3(1)
0(1)-P-0(3)	112.9(1)	0(2)-P-0(3)	107.1(1)
0(1)-P-N(1)	103.9(1)	0(2)-P-N(1)	106.5(1)
0(3)-P-N(1)	117.0(1)	P-0(1)-C(1)	119.1(2)
P-0(2)-C(4)	122.6(2)	P-N(1)-C(7)	122.9(2)
0(1)-C(1)-C(2)	108.6(3)	0(1)-C(1)-C(3)	107.2(3)
C(2)-C(1)-C(3)	112.0(4)	0(2)-C(4)-C(5)	105.5(3)
0(2)-C(4)-C(6)	110.5(3)	C(5)-C(4)-C(6)	112.0(3)
S-C(7)-N(1)	119.9	S-C(7)-N(2)	112.9(2)
N(1)-C(7)-N(2)	127.2(3)	S-C(8)-C(8A)	112.4(3)

is 32.9°. The strong resonance between N(1)—C(7)—N(2) would lead to the planarity of this side of the molecule while the lack of double bond character between P—N(1) would make the rotation around the P—N(1) bond easy. Rotation around the P—N(1) bond would cause loss of planarity in this part of molecule and thus reduce the intramolecular hydrogen bonding. Figure 2 shows the stereoscopic view of the the content of the unit cell of computed **IIa** with only H-bridges between different molecules indicated.

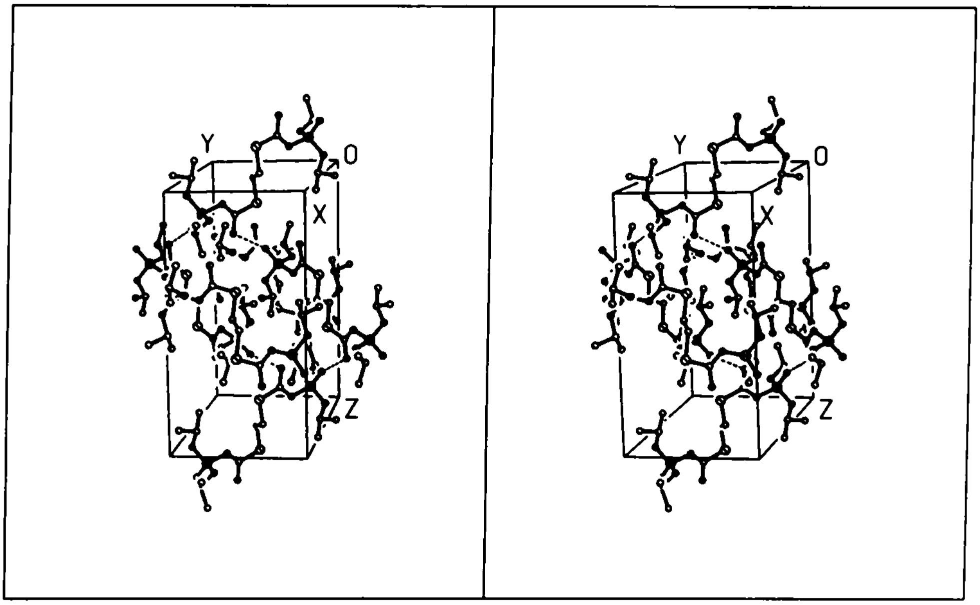


FIGURE 2 Stereoscopic view of the content of the unit cell of compound **IIa**.

EXPERIMENTAL

The NMR spectra (^1H, ^{13}C and ^{31}P) were recorded on a Bruker AC300 spectrometer. All chemical shifts are reported with respect to TMS or H_3PO_4. IR spectra were obtained on a Perkin-Elmer Model 1710 spectrometer. Mass spectra were taken on a Varian MAT 8500 (70eV) spectrometer. The X-ray structure analysis was carried out on a Siemens P4 diffractometer.

Preparation of alkanediyl diisothiourea (**I**). Thiourea (0.8 mol) in 300 ml of 95% ethanol was heated to reflux. Then the alkanediyl dibromide (0.4 mol) was added in one portion and the resulting mixture was kept at 50°C for 4 hours. A precipitate or an oil was formed during this reaction period. The product was separated and recrystallized from 95% ethanol to give the desired pure compound.

Preparation of diisopropylphosphoryl alkanediyl diisothiourea (**II**).

General procedure. Alkanediyl diisothiourea dihydrobromide (**I**) (0.01 mol) and sodium hydroxide (0.02 mol) were dissolved in a mixture of 10 ml of water and 2 ml of ethanol. This solution was cooled in 0°C and a solution of diisopropylphosphite (0.01 mol) in 10 ml of carbon tetrachloride was added dropwise at this temperature. The mixture was stirred at 50°C for 4 hours. After the reaction, 10 ml of water and chloroform (1:1) were added. The organic layer was separated and the aqueous solution was extracted three times with 5 ml of chloroform each. The organic layers were combined, washed once with 5 ml of water and dried over anhydrous magnesium sulphate. The solvent was removed in vacuum to give the crude product.

Diisopropylphosphoryl ethylenediisothiourea (**IIa**). Recrystallization from 95% ethanol; colorless crystal; m.p. 180–182°C; 86% yield; IR (KBr plate) cm^{-1}; 3360 (NH), 3270, 3100, 2960, 1630 (C═N), 1560, 1380, 1320, 1200, 1100 (P═O), 1000, 890; ^1H-NMR ($CDCl_3$) δ: 1.25–1.35 (m, 24H, CH_3 of i-Pr), 3.16 (broad s, 4H, CH_2—S), 4.45–4.54 (m, 4H, CH—O); ^{31}P-NMR: −0.015; ^{13}C-NMR: 23.8 (Me), 30.7 (S—CH_2), 71.0, 71.1 (O—CH), 168.4 (C═N); MS (m/e): 507 (M^+ + 1).

Crystal data for **IIa**: Molecular formula: $C_{16}H_{36}N_4O_6P_2S_2$; molecular weight: 506.5; crystal system: orthorhombic; radiation: MoKα (λ = 0.71073 Å); Space group: Pbca; crystal size (mm): 0.30 × 0.30 × 0.40; cell dimension: a = 16.660(3) Å, b = 8.910(2) Å, c = 17.457(3) Å; volume: 2591.2(2) $Å^3$; Z: 4; density (calc.): 1.298 Mg/m^3; temperature, 173 K; 2θ range, $2.0° < 2\theta < 50.0°$; number of measured reflections: 3379; number of unique data: 2286; number of observed data: 2286 ($F > 0.0\sigma(F)$); number of refined parameters: 137; absorption coefficient, 0.365 mm^{-1}; R: 0.0657; wR: 0.0425; the structure was solved by direct methods and refined by full-matrix least-squares techniques.

Diisopropylphosphoryl 3-oxapentanediyl diisothiourea (**IIb**). Light yellow oil; 62% yield; IR cm^{-1}: 3390 (NH), 3170, 2970, 1628 (C=N), 1560, 1200, 1100 (P=O), 1000; ^{1}H-NMR δ: 1.2–1.35 (m, 24H, Me of i-Pr), 2.80–3.00 (m, 4H, $\mathrm{S{-}CH_2}$), 3.60–3.72 (m, 4H, $\mathrm{O{-}CH_2}$), 4.44–4.59 (m, 4H, O—CH); ^{31}P-NMR: 2.35; ^{13}C-NMR: 23.7, 23.8 (Me), 30.7 ($\mathrm{S{-}CH_2}$), 69.0 ($\mathrm{O{-}CH_2}$), 70.8 (O—CH), 168.5 (C=N); MS (m/e): 548 ($M^+ - 2$).

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