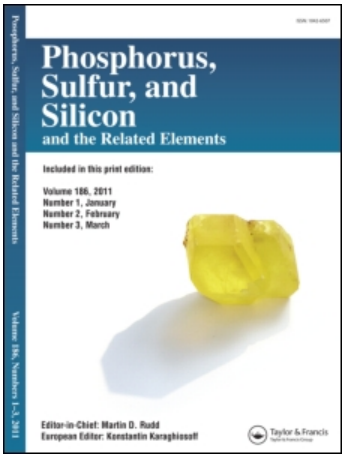

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COMPARISON OF THE CRYSTAL AND MOLECULAR STRUCTURES OF *N,N'*-DIBENZYL-*N*-(5,5-DIMETHYL-2-OXO-1,3,2-DIOXAPHOSPHORINANYL)-THIOUREA AND *N,N'*-DICYCLOHEXYL-*N*-(5,5-DIMETHYL-2-OXO-1,3,2-DIOXAPHOSPHORINANYL)-THIOUREA

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COMPARISON OF THE CRYSTAL AND MOLECULAR STRUCTURES OF *N,N'*-DIBENZYL-*N*-(5,5-DIMETHYL-2-OXO-1,3,2-DIOXAPHOSPHORINANYL)-THIOUREA AND *N,N'*-DICYCLOHEXYL-*N*-(5,5-DIMETHYL-2-OXO-1,3,2-DIOXAPHOSPHORINANYL)-THIOUREA

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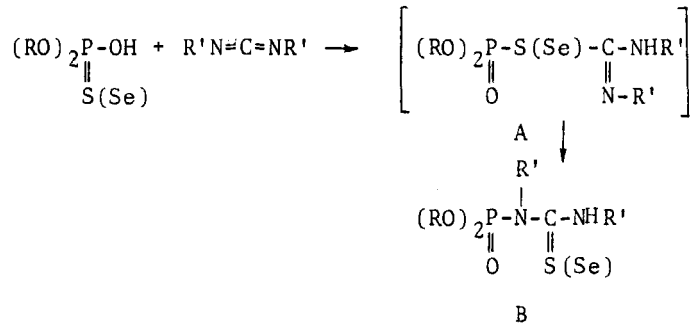
X-Ray analysis of *N,N'*-dibenzyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphoranyl)-thiourea (**1**) and its dicyclohexyl analog (**2**) revealed important structural differences in the solid state. The thiourea moiety in **1** formed by the atoms S, C(1), N(1) and N(2) has been found to be planar. The sulphur and phosphorus atoms in **1** adopt a practically antiperiplanar arrangement around the C(1)—N(1) bond (the torsional angle 159.0(3)°). The molecule of **1** is stabilized by an intramolecular N—H ··· O=P hydrogen bond. In contrast to **1**, compound **2** has a non-planar thiourea skeleton and the sulphur and phosphorus atoms are close to each other (the torsional angle P—N(1)—C(1)—S is 91(1)° and the non-bonding S ··· P distance is equal to 3.73 A). The molecules of **2** form dimeric structures due to intermolecular hydrogen bonds between the NH-protons and PO-groups.

INTRODUCTION

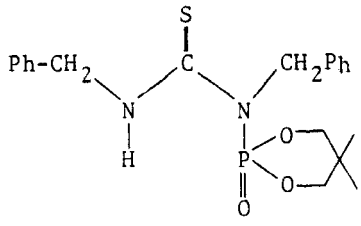
Recently, we have demonstrated by means of ^{31}P NMR spectra that the reaction between O,O-diesters of phosphorothio(seleno)ic acids and carbodiimides affords in the first step S(Se)-phosphorylisothio(seleno)ureas (A) which undergo facile rearrangement to the stable and isolable *N*-phosphorylthio(seleno)ureas (B).[1]

Our further studies revealed important differences in the physical and chemical properties of *N*-phosphorylthio(seleno)ureas depending on the nature of substituents at the nitrogen atom in the starting carbodiimides. Thus, for example, the coupling



constant $^3J_{P,H}$ between P and the benzyl methylene protons in *N*-phosphoryl-*N*,*N'*-dibenzylthioureas was observed to be about 9.5 Hz whereas in the case of *N*-phosphoryl-*N*,*N'*-dicyclohexylthioureas the coupling constant between P and the cyclohexyl CH—N proton was much higher *ca.* 23 Hz. Moreover, we have found that the rearrangement of *S*-phosphoryl-*N*,*N'*-dibenzylisothioureas to *N*-phosphoryl-*N*,*N'*-dibenzylthioureas is irreversible while in the case of the dicyclohexyl analogues the rearrangement is a reversible process which is believed to be responsible for the reaction with the second molecule of phosphorus thio- or selenoacid.

The X-ray analysis of the title compounds **1** and **2** was undertaken to compare their solid state structures. It was hoped that this comparison would reveal the structural and/or conformational reasons of the differences discussed above.



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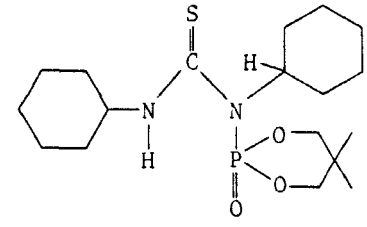

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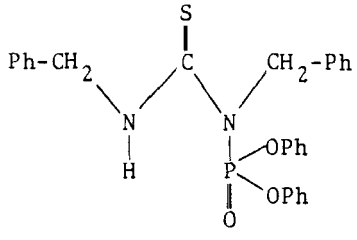

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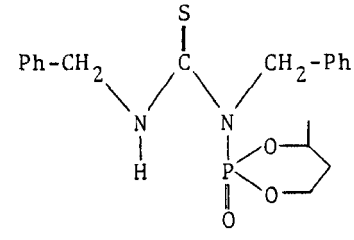

4

In this context we would like to note that we have also reported the X-ray analysis of *N*,*N'*-dibenzyl-*N*-diphenoxyphosphorylthiourea (**3**)[2] and *N*,*N'*-dibenzyl-*N*-(4-methyl-2-oxo-1,3,2-dioxaphosphorinanyl)thiourea (**4**).[3]

RESULTS AND DISCUSSION

The solid state structure of **1** is shown in Figure 1. Figure 2 shows the unit-cell. The molecule of **1** may be considered to consist of three parts: the thiourea moiety, the 1,3,2-dioxaphosphorinane ring and two benzene rings. Similarly as in the case of **3** and **4**, the sulphur and phosphorus atoms in **1** adopt a practically antiperiplanar arrangement around the C(1)—N(1) bond. The torsional angles for this and other selected bonds are given in Table V. The thiourea skeleton formed by the atoms S, C(1), N(1) and N(2) is planar. The atoms bonded to N(1) and N(2) are slightly off this plane. The exact values of these deviations are given in Table VI. Two benzene rings form, with the thiourea plane, the angles of 85.3° and 78.5°, respectively. The 1,3,2-dioxaphosphorinane ring in **1** exists in a chair conformation with the phosphoryl oxygen O(3) and nitrogen N(1) atoms in an axial and equatorial position, respectively. The torsion angles of this ring are collected in Table VI. The mirror-plane asymmetry parameter[4] is $\Delta C_{S(P)} = 0.9°$.

The conformation of the molecule of **1** is stabilized by an intramolecular hydrogen bond N(2)—H(3) · · · O(3). The distance between N(2) and O(3) is 2.684 Å and the sum of the distances N(2)—H(3) and H(3) · · · O(3) is 2.937 Å.

The bond lengths and angles for **1** are not significantly different from those previously observed for the above mentioned trisubstituted thioureas, **3** and **4**. It should be noted that the tertiary nitrogen atom, N(1) bearing the electronegative phosphoryl group forms the bond C(1)—N(1) = 1.421(4) Å which is longer than that in thiourea [1.30(1) Å].[5]

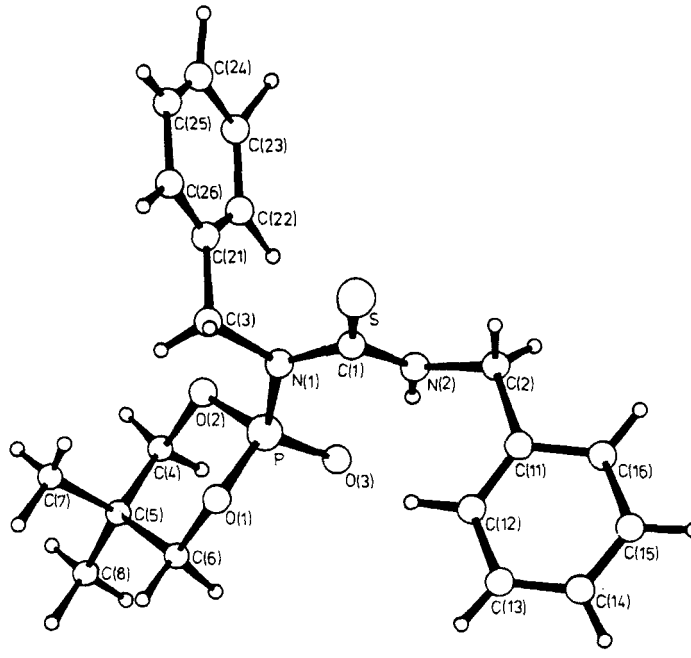

FIGURE 1 Three-dimensional view of *N*,*N'*-dibenzyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)-thiourea (**1**).

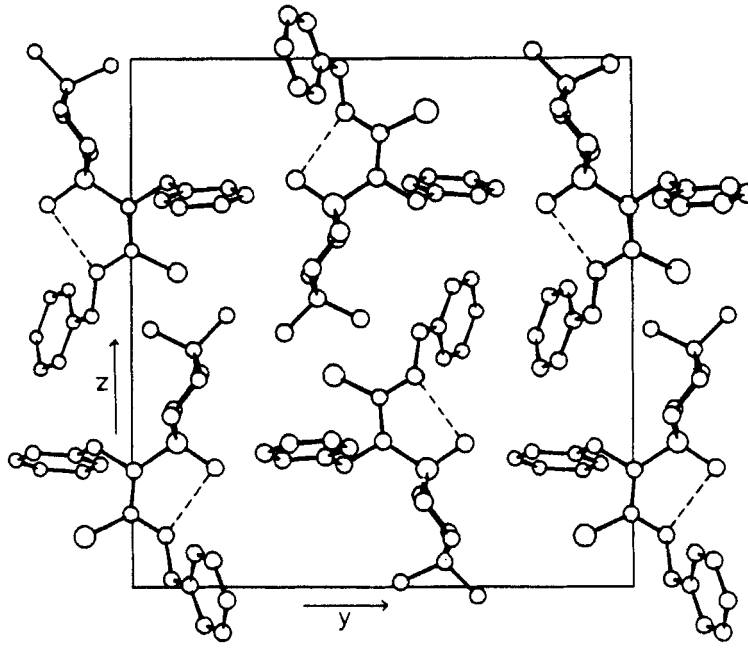

FIGURE 2 Packing of the molecules of **1** in the unit cell.

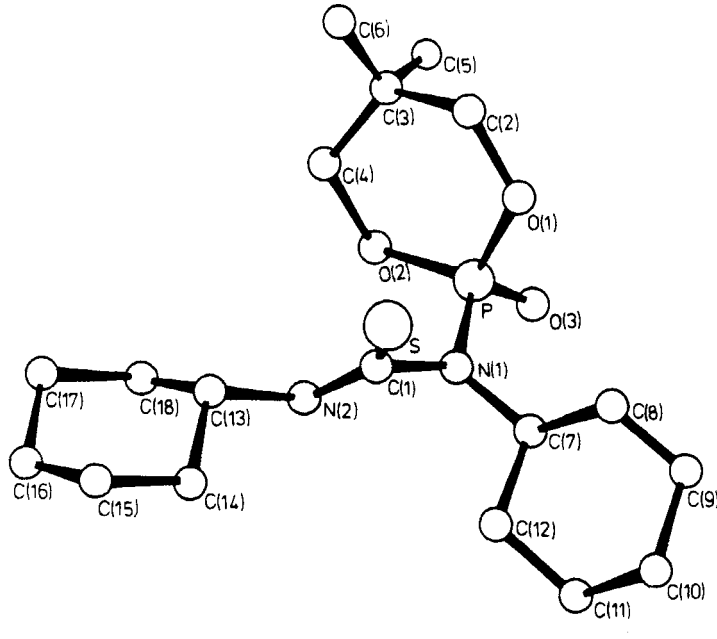

FIGURE 3 Three-dimensional view of *N,N'*-dicyclohexyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)-thiourea (**2**).

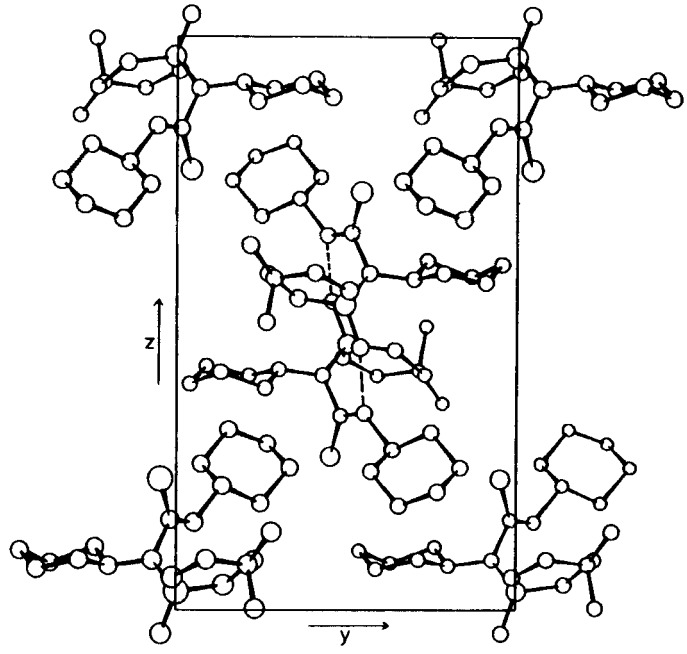

FIGURE 4 Packing of the molecules of **2** in the unit cell.

The structure of the thiourea **2** with numbering system is shown in Figure 3. Figure 4 shows the packing of the unit cell. The molecule of **2** contains three six-membered, non-planar rings joined by the thiourea moiety. The torsion angles for two cyclohexyl rings and for the 1,3,2-dioxaphosphorinane ring are given in Table V. As expected, the cyclohexyl rings are in a chair conformation. The six-membered ring with phosphorus has a distorted chair conformation in which the phosphoryl oxygen O(3) and nitrogen N(1) atoms connected to phosphoryl are in an axial and equatorial position, respectively. In contrast to **1**, the deviation of the atoms P and C(7) from the thiourea plane (Table VI, plane 2) is much more accentuated.

In view of the fact that the precision of the structural determination of **2** is not high enough, the detailed discussion of the differences in bond lengths and angles is omitted. It is only worth mentioning that the lengthening of the C(1)—N(1) bond was also observed in **2**.

Of great importance is the finding that the molecule of **2** forms dimers due to intermolecular hydrogen bonds between the amide proton at N(2) and the phosphoryl oxygen atom O(3), of the length 2.80 Å.

After the brief description of general features of both structures **1** and **2** let us consider in detail the most important structural differences between them.

In general, for *N*-phosphoryl-*N*,*N'*-disubstituted thiourea four, possible planar conformations can be considered. They are shown in Figure 5.

The molecule of **1** adopts a conformation a. In a similar conformations exist also thioureas **3** and **4**. However, the conformation of the thiourea skeleton in *N*-phos-

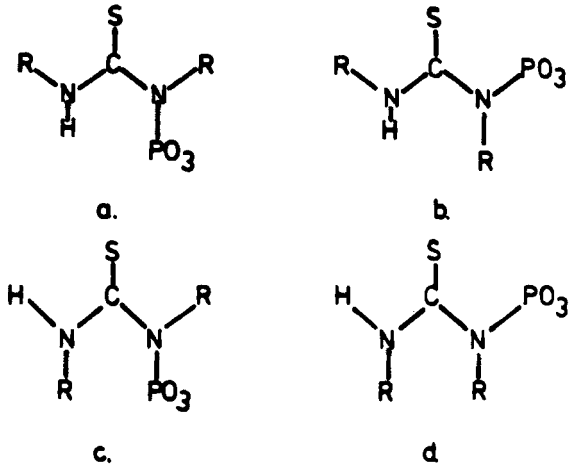

FIGURE 5 The possible planar conformations of *N*-phosphoryl-*N*,*N'*-disubstituted thiourea.

phoryl-*N*,*N'*-dicyclohexylthiourea **2** is quite different. First of all, the presence of two bulky cyclohexyl substituents is destroying the planarity of the thiourea skeleton.[6] The displacement of the phosphorus atom off the plane passing through the atoms S, N(1), N(2) and C(1) is 1.435(4) Å in **2** whereas that in **1** is only 0.490(1) Å. Secondly, there are striking differences in the torsional angles P—N(1)—C(1)—S in both structures under discussion. The value of this angle for **1** is 159.0(3)°. In the non-planar conformation of **2** this angle is much smaller and equal to 91(1)°. Consequently, the S ··· P non-bonding distance in **2** of 3.73 Å is much shorter than that in **1** (4.242 Å). It is comparable with the sum of the van der Waals radii for P and S (3.75 Å). This may be a main factor responsible for the restricted rotation around the C(1)—N(1) bond in **2**. Moreover, the free rotation around the C(7)—N(1) bond in **2** is restricted by the interactions between equatorial H(82) and H(71) and the phosphoryl oxygen atom and in the most favoured conformation the torsional angle H(71)—C(7)—N(1)—P is 38(1)°. In **1** there are two dihedral angles

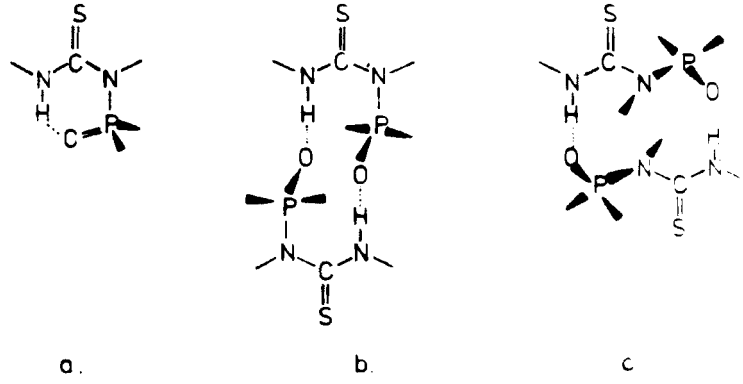

FIGURE 6 The possible hydrogen bond systems in *N*-phosphoryl-*N*,*N'*-disubstituted thiourea: (a) intramolecular (b) and (c) intermolecular with different modes of pairing of the molecules.

H(5)—C(3)–N(1)—P of 8.7(3)° and H(4)—C(3)—N(1)—P of 125.2(4)° and a free rotation around the C(3)—N(1) bond can take place.

Finally, it is necessary to point out that the two different conformations of thioureas, **1** and **2** are stabilized in a different way by hydrogen bonds. Whereas the structure of **1**, as well as of other *N,N'*-dibenzyl-substituted thioureas, is stabilized by an intramolecular N—H ··· O=P hydrogen bond (see Figure 6a), similar N—H ··· O=P hydrogen bonds are formed in **2** intermolecularly which results in the formation of dimeric structures. Of the two modes of pairing of thiourea molecules shown in Figures 6b and c the latter is preferred since it leads to a more compact spatial structure. The structural differences between **1** and **2** found in the solid state provide a good basis for the rationalisation of different spectroscopic features for both compounds. This point will be discussed in detail elsewhere.

EXPERIMENTAL

Single crystals of thioureas **1** and **2** were obtained by slow evaporation of their ethereal solutions. Good quality crystals of **1** were needle-shaped. However, the crystals of **2** were obtained in the form of very soft, thin twinned plates. The space groups and approximate cell parameters were determined from

TABLE I

Positional parameters ($\times 10^4$) and equivalent U values ($\times 10^3$) for the nonhydrogen atoms $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ for *N,N'*-dibenzyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)-thiourea (**1**)

	X	Y	Z	U_{eq}
P	−608(2)	−5918(1)	−2755(1)	24(0)
O(1)	1138(4)	−5800(2)	−3253(1)	27(1)
O(2)	−2162(4)	−5852(2)	−3379(1)	27(1)
O(3)	−637(5)	−6678(1)	−2273(1)	39(1)
C(4)	−1963(7)	−6403(2)	−4077(2)	29(1)
C(5)	−224(7)	−6257(2)	−4512(2)	28(1)
C(6)	1344(7)	−6353(2)	−3948(2)	34(1)
C(7)	−189(7)	−5391(2)	−4897(2)	34(2)
C(8)	−47(8)	−6923(2)	−5159(2)	40(2)
S	−105(2)	−4063(1)	−980(1)	33(0)
N(1)	−807(5)	−5047(2)	−2229(2)	24(1)
N(2)	−740(5)	−5685(2)	−994(2)	29(1)
C(1)	−555(6)	−4981(2)	−1396(2)	23(1)
C(2)	−242(7)	−5786(2)	−161(2)	33(1)
C(3)	−1097(7)	−4261(2)	−2676(2)	29(1)
C(11)	1571(7)	−6155(2)	−53(2)	29(1)
C(12)	2775(8)	−6257(2)	−658(2)	33(2)
C(13)	4437(8)	−6625(2)	−518(2)	39(2)
C(14)	4857(8)	−6904(2)	238(3)	41(2)
C(15)	3645(8)	−6816(2)	847(2)	43(2)
C(16)	1994(8)	−6441(2)	709(2)	36(2)
C(21)	−2910(7)	−3890(2)	−2529(2)	25(1)
C(22)	−4373(8)	−4377(2)	−2352(2)	30(2)
C(23)	−6023(7)	−4023(3)	−2215(2)	37(2)
C(24)	−6240(8)	−3165(3)	−2267(2)	39(2)
C(25)	−4796(9)	−2677(2)	−2444(2)	37(2)
C(26)	−3101(8)	−3025(2)	−2574(2)	32(2)

TABLE II

Positional parameters ($\times 10^4$) and equivalent U values ($\times 10^3$) for the nonhydrogen atoms
$U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$
for *N,N'*-dicyclohexyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)-thiourea (**2**)

	X	Y	Z	U_{eq}
P	2221(3)	36(5)	337(2)	53(1)
O(1)	3750(7)	−106(9)	582(4)	58(3)
O(3)	1893(7)	−427(9)	−395(3)	60(4)
O(2)	1855(7)	1420(5)	453(4)	58(4)
C(2)	4626(13)	912(14)	887(9)	107(9)
C(6)	4985(20)	2765(21)	1407(13)	199(13)
C(5)	4339(16)	2333(21)	24(9)	123(9)
C(3)	4149(11)	2117(13)	802(6)	54(5)
C(4)	2771(12)	2293(15)	884(9)	122(9)
C(7)	1158(14)	−1972(18)	787(9)	107(8)
C(8)	2210(16)	−2854(26)	894(13)	139(12)
C(9)	1938(14)	−4114(21)	728(10)	95(8)
C(10)	676(14)	−4588(16)	1033(10)	107(9)
C(11)	−452(17)	−3675(28)	814(12)	144(13)
C(12)	−86(16)	−2375(21)	1097(11)	104(9)
C(13)	−51(12)	1356(17)	2181(7)	74(7)
C(14)	−1019(18)	761(17)	2577(10)	118(9)
C(15)	−1325(25)	1571(22)	3193(11)	162(13)
C(16)	−1903(13)	2682(19)	2935(7)	81(7)
C(17)	−984(22)	3336(24)	2515(14)	173(14)
C(18)	−695(21)	2485(22)	1867(11)	135(11)
N(1)	1384(8)	−691(10)	887(4)	51(4)
N(2)	209(9)	554(10)	1543(4)	54(4)
C(1)	1269(10)	−168(15)	1588(4)	70(6)
S	2361(3)	−445(6)	2306(2)	125(3)

TABLE III

Bond lengths (Å)

(a) *N,N'*-dibenzyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)-thiourea (**1**)

O(1)—P	1.568(3)	O(2)—P	1.575(3)
O(3)—P	1.468(2)	N(1)—P	1.664(3)
C(6)—O(1)	1.479(4)	C(4)—O(2)	1.480(4)
C(5)—C(4)	1.515(7)	C(6)—C(5)	1.520(6)
C(7)—C(5)	1.537(5)	C(8)—C(5)	1.535(5)
C(1)—S	1.669(3)	C(1)—N(1)	1.421(4)
C(3)—N(1)	1.489(4)	C(1)—N(2)	1.325(4)
C(2)—N(2)	1.464(4)	C(11)—C(2)	1.495(7)
C(21)—C(3)	1.506(7)		

The average values of the C—C bonds for the benzene rings are 1.389(5) and 1.391(5) Å.[9]

(b) *N,N'*-dicyclohexyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)-thiourea (**2**)

O(1)—P	1.555(7)	O(3)—P	1.464(7)
O(2)—P	1.595(8)	N(1)—P	1.635(10)
C(2)—O(1)	1.495(17)	C(4)—O(2)	1.495(16)
C(3)—C(2)	1.417(21)	C(3)—C(6)	1.500(24)
C(3)—C(5)	1.521(20)	C(4)—C(3)	1.434(17)
N(1)—C(7)	1.441(23)	N(2)—C(13)	1.543(18)
C(1)—N(1)	1.459(15)	C(1)—N(2)	1.327(16)
S—C(1)	1.648(10)		

The average values of the C—C bonds for the cyclohexyl rings are 1.51(2) and 1.50(2) Å.[9]

TABLE IV

Bond angles (°)

(a) *N,N'*-dibenzyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)-thiourea (**1**)

O(2)—P—O(1)	104.6(1)	O(3)—P—O(1)	114.2(2)
O(3)—P—O(2)	114.5(2)	N(1)—P—O(1)	105.0(2)
N(1)—P—O(2)	103.5(2)	N(1)—P—O(3)	113.8(1)
C(6)—O(1)—P	116.0(3)	C(4)—O(2)—P	114.6(3)
C(5)—C(4)—O(2)	112.3(3)	C(6)—C(5)—C(4)	110.4(3)
C(7)—C(5)—C(4)	111.1(4)	C(7)—C(5)—C(6)	110.1(3)
C(8)—C(5)—C(4)	108.1(3)	C(8)—C(5)—C(6)	107.8(4)
C(8)—C(5)—C(7)	109.3(3)	C(5)—C(6)—O(1)	110.6(3)
C(1)—N(1)—P	125.3(2)	C(3)—N(1)—P	117.3(2)
C(3)—N(1)—C(1)	117.2(2)	C(2)—N(2)—C(1)	124.0(3)
N(1)—C(1)—S	120.5(2)	N(2)—C(1)—S	124.2(2)
N(2)—C(1)—N(1)	115.3(3)	C(11)—C(2)—N(2)	113.1(3)
C(21)—C(3)—N(1)	112.6(3)	C(12)—C(11)—C(2)	123.8(3)
C(16)—C(11)—C(2)	116.6(4)	C(22)—C(21)—C(3)	122.0(3)
C(26)—C(21)—C(3)	118.5(4)		

The average angles for the benzene rings are 120.0(2) and 120.1(4)°.[9]

(b) *N,N'*-dicyclohexyl-*N*-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl)-thiourea (**2**)

O(3)—P—O(1)	109.1(4)	O(2)—P—O(1)	107.2(5)
O(2)—P—O(3)	115.9(5)	N(1)—P—O(1)	110.0(5)
N(1)—P—O(3)	110.8(5)	N(1)—P—O(2)	103.6(5)
C(2)—C(1)—P	123.1(8)	C(4)—O(2)—P	123.7(7)
C(3)—C(2)—O(1)	119.4(1.1)	C(6)—C(3)—C(2)	102.5(1.2)
C(5)—C(3)—C(2)	99.8(1.3)	C(5)—C(3)—C(6)	121.5(1.4)
C(4)—C(3)—C(2)	115.7(1.3)	C(4)—C(3)—C(6)	107.7(1.3)
C(4)—C(3)—C(5)	109.7(1.1)	C(3)—C(4)—O(2)	112.9(1.2)
N(1)—C(7)—C(12)	111.2(1.5)	N(1)—C(7)—C(8)	123.3(1.4)
N(2)—C(13)—C(18)	106.6(1.2)	N(2)—C(13)—C(14)	109.6(1.4)
C(7)—N(1)—P	119.1(9)	C(1)—N(1)—P	119.4(9)
C(1)—N(1)—C(7)	118.4(1.1)	C(1)—N(2)—C(13)	121.3(9)
N(2)—C(1)—N(1)	110.3(8)	S—C(1)—N(1)	122.6(9)
S—C(1)—N(2)	127.1(9)		

The average angles for the cyclohexyl rings are 115(2)° and 109(1)°.[9]

Weissenberg photographs using Cu-K_α radiation. A small single crystal was mounted on A Syntex $P2_1$ diffractometer and the cell dimensions were refined using Mo-K_α radiation at −120°C.

Crystal data. For **1**: $C_{20}H_{25}N_2O_3PS$. M = 404.5. Orthorombic a = 7.504(2), b = 16.079(3), c = 16.860(3) Å, V = 2034.27 Å^3, Z = 4, F(OOO) = 856, (Mo-K_α) = 0.71069 Å at −120°C, μ = 2.14 cm^{-1}, space group $P2_12_12_1$. For **2**: $C_{18}H_{33}N_2O_3PS$. M = 388.56. Monoclinic, a = 10.091(2), b = 11.047(3), C = 18.813(4) Å, β = 98.05(3)°, V = 2076.52 Å^3, Z = 4. F(OOO) = 840, (Mo-K_α) = 0.71069 Å at −120°C, μ = 2.08 cm^{-1}, space group $P2_1/n$.

Integrated data for both structures were collected at −120°C with monochromatic Mo-K_α radiation at a scan rate of 2°/min, 3 standard reflections being checked for alignment and crystal stability. There was no evidence of crystal decay during the time of data collection. Data collection was limited to the range $\theta < 2\theta < 50°$. The data were corrected for Lorentz-polarization effect but not for absorption.

Structure solution and refinement. Of 1829 collected reflections for **1**, 1601 had $F \geqslant 4\delta(F)$ and were classified as observed. The structure of **1** was solved by direct methods. The entire molecule was visible in the first E-map. After two cycles of unweighted isotropic refinement the agreement factor R was 0.096. Further full-matrix least-squares anisotropic refinement reduced R to 0.069. After including hydrogen atoms (temperature factors of H-atoms were refined only in the last cycle) and weighting scheme $w = k/[\sigma^2(Fo) + gFo^2]$ where k = 1.7014 and g = 0.000792 the R value was reduced to 0.0385 and

TABLE V

Torsional angles (°)
(a) In thiourea skeleton

1		2	
C(3)—N(1)—C(1)—S	14.7(2)	C(7)—N(1)—C(1)—S	69(1)
C(3)—N(1)—C(1)—N(2)	164.1(3)	C(7)—N(1)—C(1)—N(2)	−110(1)
P—N(1)—C(1)—S	159.0(3)	P—N(1)—C(1)—S	−91(0.5)
P—N(1)—C(1)—N(2)	−22.2(2)	P—N(1)—C(1)—N(2)	89(1)
C(2)—N(2)—C(1)—S	−12.4(2)	C(13)—N(2)—C(1)—S	8(1)
C(2)—N(2)—C(1)—N(1)	168.9(3)	C(13)—N(2)—C(1)—N(1)	−172(1)

(b) In 1,3,2-dioxaphosphorinane rings

1		2	
P—O(1)—C(6)—C(5)	57.2(2)	P—O(1)—C(2)—C(3)	−20(0.7)
O(1)—P—O(2)—C(4)	51.8(2)	O(1)—P—O(2)—C(4)	−13(1)
O(2)—P—O(1)—C(6)	−53.0(2)	O(2)—P—O(1)—C(2)	5(1)
P—O(2)—C(4)—C(5)	−56.6(2)	P—O(2)—C(4)—C(3)	37(0.7)
O(2)—C(4)—C(5)—C(6)	55.6(3)	O(2)—C(4)—C(3)—C(2)	−45(1)
C(4)—C(5)—C(6)—O(1)	−54.3(3)	C(4)—C(3)—C(2)—O(1)	37(1)

(c) In cyclohexyl rings of **2** (E.s.d's are 1°)

C(8)—C(7)—C(12)—C(11)	−50	C(13)—C(14)—C(15)—C(16)	63
C(7)—C(12)—C(11)—C(10)	60	C(14)—C(15)—C(16)—C(17)	−59
C(12)—C(11)—C(10)—C(9)	−58	C(15)—C(16)—C(17)—C(18)	57
C(11)—C(10)—C(9)—C(8)	50	C(16)—C(17)—C(18)—C(13)	−60
C(10)—C(9)—C(8)—C(7)	−48	C(17)—C(18)—C(13)—C(14)	64
C(9)—C(8)—C(7)—C(12)	47	C(18)—C(13)—C(14)—C(15)	−64

TABLE VI

Least-squares planes of thiourea skeleton (the atoms denoted by asterisks have been used for calculated mean plane)

S*	−0.002(1)	S*	−0.001(7)
N(1)*	−0.002(4)	N(1)*	−0.001(9)
N(2)*	−0.003(4)	N(2)*	−0.002(9)
C(1)*	0.007(4)	C(1)*	0.004(20)
C(2)	0.237(5)	C(13)	0.185(20)
C(3)	−0.356(4)	C(7)	−1.180(20)
P	0.490(1)	P	1.435(4)

I. $7.378X - 2.8511Y - 1.8744Z = 1.2672$. II. $5.9371X + 8.6078Y - 5.5750Z = -0.2690$

$R_w = 0.0399$. At this stage of refinement the changes in all parameters, except of temperature factors for H-atoms, became less than 1/20 of their respective e.s.d's. No significant density was observed in the final difference map of **1**.

In the case of **2** the 1328 independent reflections from the total number of 2217 were considered as observed on the basis of criterion $F \geqslant 4\sigma(F)$. The structure of **2** was solved by direct methods using the phase program for centrosymmetric structure. All the non-hydrogen atoms in **2** were visible on the E-map. The full-matrix least-squares refinement with anisotropic thermal parameters reduced R only to 0.123. The different Fourier synthesis showed the position of hydrogen atoms. The last two cycles of refinement have been taken with unit weights and with blocked hydrogen atom position (the thermal parameters for hydrogen atoms were kept as for their parent-atoms) and the agreement factor R was 0.113. In view of the small changes in all parameters the refinement of the structure **2** was finished at this stage. It is evident that the high value of the agreement factor R is due to an imperfection and disorder of the crystals which

made solution and refinement particularly difficult. However, the precision of the structural determination is quite sufficient for the comparison purposes.

All calculations were carried out by SHEL-X76.[8] The atomic parameters for structure **1** and **2** are given in Tables I and II, respectively. Bond distances and angles are listed in Tables III and IV. The bond lengths have been not corrected for thermal motion.

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6. It should be noted that a similar non-planar conformation of urea moiety was found in 1-pyroglutamyl-*N*,*N'*-dicyclohexylurea.[7]
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9. The average values of the bond lengths and angles and e.s.d's have been calculated by means of the equations:

$$\bar{b} = \sum_{i=1}^{6} \frac{b_1}{\sigma_i^2} \Big/ \sum_{i=1}^{6} \frac{1}{\sigma_i^2}$$

$$\sigma(\bar{b}) = \left\{ \frac{1}{5} \left[\sum_{i=1}^{6} (b_i - \bar{b})^2 \frac{1}{\sigma_i^2} \Big/ \sum_{i=1}^{6} \frac{1}{\sigma_i^2} \right] \right\}^{1/2}$$

where b_i and σ_i are the values of the bond length or angle and their e.s.d's; $\bar{b}$ and $\sigma(b)$ are the average values of e.s.d's.