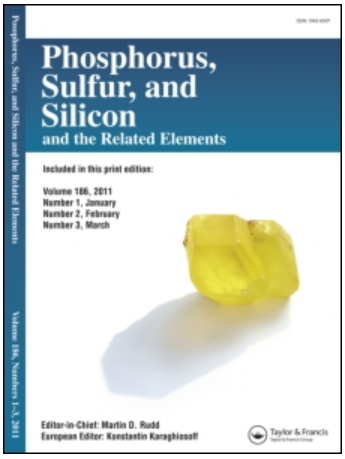

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE CRYSTAL AND MOLECULAR STRUCTURE OF *N,N'* DICYCLOHEXYL-*N*-DINEOPENTOXYPHOSPHORYL-THIOUREA

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To cite this Article Karolak-wojciechowska, Janina , Mikołajczyk, Marian , Kiesinski, Piotr and Sut, Anna(1984) 'THE CRYSTAL AND MOLECULAR STRUCTURE OF *N,N'* DICYCLOHEXYL-*N*-DINEOPENTOXYPHOSPHORYL-THIOUREA', Phosphorus, Sulfur, and Silicon and the Related Elements, 21: 2, 221 — 225
To link to this Article: DOI: 10.1080/03086648408077660
URL: http://dx.doi.org/10.1080/03086648408077660

Phosphorus and Sulfur, 1984, Vol. 21, pp. 221–225
0308-664X/84/2102–0221/$10.00/0

THE CRYSTAL AND MOLECULAR STRUCTURE OF *N,N'*-DICYCLOHEXYL-*N*-DINEOPENTOXYPHOSPHORYL-THIOUREA

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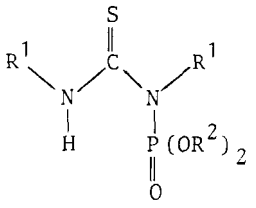
(*Received May 23, 1984*)

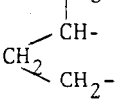
The crystal structure of the title compound was determined by X-ray diffraction technique from diffractometer intensity measurements; $C_{23}H_{45}O_3NPS$, monoclinic, space group $P2_1/c$, a = 11.225(2), b = 11.567(2), c = 21.423(5) Å, β = 100.92(4)°, 2954 reflections, R = 0.069. The thiourea moiety in this compound was found to be non-planar. In contrast to other *N,N*-disubstituted *N*-phosphorylthioureas, no hydrogen bonds of the type NH · · · O=P were found in the title compound.

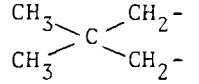
INTRODUCTION

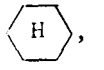
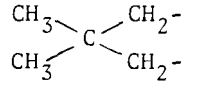
In the course of our studies[1,2] on the reaction between carbodiimides and phosphorothioic and phosphoroselenoic acids we have found that *N*-phosphorylthio(seleno)ureas formed as the reaction intermediates exhibit different physical and chemical properties depending on the nature of substituents bonded to the nitrogen atoms. To understand the reasons for these differences we decided to determine the solid state structures of some selected *N*-phosphorylthioureas. Till now we have reported the X-ray analysis of *N*-phosphorylthioureas **1**, **2**, **3** and **4**.[3–5]

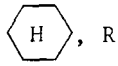


1, R^1=PhCH$_2$, R^2=Ph

2, R^1=PhCH$_2$, R^2+ R^2= 

3, R^1=PhCH$_2$, R^2+ R^2= 

4, R^1=  , R^2+ R^2= 

5, R^1=  , R^2 = $(CH_3)_3CCH_2$

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It was found that the thioureas **1**, **2** and **3** containing *N*-benzyl substituents have a planar conformation with the sulphur and phosphorus atoms in an antiperiplanar arrangement around the C(1)–N(1) bond. However, in the case of the thiourea **4** derived from *N*, *N'*-dicyclohexylcarbodiimide the thiourea skeleton was found to be non-planar and the sulphur and phosphorus atoms were close to each other. Unfortunately, the accuracy of the structural determination of **4**[5] was not high enough (R = 0.113) to discuss in detail the differences in structural parameters, especially between **3** and **4**. Therefore, we have determined the crystal structure of *N*,*N'*-dicyclohexyl-*N*-dineopentoxyphosphorylthiourea (**5**) which contains also the cyclohexyl groups at nitrogens and additionally two bulky neopentoxy groups bonded to the phosphorus atom.

RESULTS AND DISCUSSION

The solid state structure of the thiourea **5** with numbering system is shown in Figure 1. The bond lengths and angles for **5** are listed in Table I and II, respectively.

It was found that both cyclohexyl rings in **5** adopt a chair conformation with the nitrogen atoms N(1) and N(2) occupying equatorial positions. The torsion angles for the cyclohexyl rings are in the range between 55.5° and 60°.

The atoms N(1), N(2), C(1) and S form the basic thiourea plane. The maximum deviation from it (0.009Å) was found for the C(1) atom. Table III shows also deviations of the neighbouring atoms from this plane. An inspection of the data in Table III shows that the P and C(12) atoms bonded to N(1) are deviated more from this plane than the atoms C(18) and H(2) connected with the nitrogen atom N(2). Thus, the plane through the atoms P,N(1) and C(12) is twisted more than that passing through the atoms C(18), N(2) and H(2) with respect to the basic thiourea plane. This different degree of twisting may be expressed quantitatively by the dihedral angles for both the above mentioned planes equal to 47.9 and 14°,

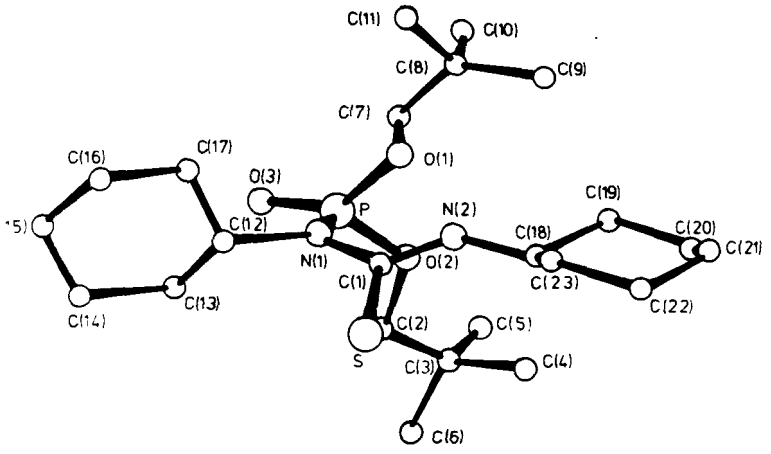

FIGURE 1. Three-dimensional view of *N*,*N'*-dicyclohexyl-*N*-dineopentoxyphosphorylthiourea **5**.

TABLE I

Bonds lengths (Å) in **5**

P—O(1)	1.560(4)	P—O(2)	1.568(3)
P—O(3)	1.455(3)	P—N(1)	1.674(3)
O(1)—C(71)	1.360(10)	O(1)—C(7)	1.539(11)
O(2)—C(2)	1.443(6)	C(2)—C(3)	1.519(6)
C(3)—C(4)	1.527(7)	C(3)—C(5)	1.512(8)
C(3)—C(6)	1.530(7)	C(8)—C(9)	1.506(8)
C(8)—C(71)	1.542(11)	C(8)—C(111)	1.563(18)
C(8)—C(101)	1.590(15)	C(8)—C(7)	1.516(12)
C(8)—C(10)	1.553(13)	C(8)—C(11)	1.591(14)
C(1)—S	1.651(4)	C(1)—N(1)	1.415(5)
C(1)—N(2)	1.339(5)	N(1)—C(12)	1.497(5)
N(2)—C(18)	1.458(5)	C(12)—C(13)	1.518(7)
C(12)—C(17)	1.520(5)	C(13)—C(14)	1.538(7)
C(14)—C(15)	1.517(7)	C(15)—C(16)	1.522(9)
C(16)—C(17)	1.537(7)	C(18)—C(19)	1.534(7)
C(19)—C(20)	1.541(6)	C(20)—C(21)	1.507(8)
C(21)—C(22)	1.510(8)	C(22)—C(23)	1.529(6)
C(23)—C(18)	1.511(6)		

TABLE II

Bond angles (°) in **5**

O(2)—P—O(1)	98.7(2)	O(3)—P—O(1)	115.5(2)
O(3)—P—O(2)	115.9(2)	N(1)—P—O(1)	106.4(2)
N(1)—P—O(2)	105.9(2)	N(1)—P—O(3)	113.0(2)
C(71)—O(1)—P	137.7(2)	C(7)—O(1)—P	109.1(4)
C(2)—O(2)—P	118.9(3)	C(3)—C(4)—C(5)	108.7(4)
C(6)—C(3)—C(4)	110.9(4)	C(6)—C(3)—C(5)	110.6(4)
C(2)—C(3)—C(4)	110.3(4)	C(2)—C(3)—C(5)	111.1(4)
C(2)—C(3)—C(6)	105.1(4)	C(5)—C(5)—C(4)	108.7(4)
C(71)—C(8)—C(9)	109.0(5)	C(111)—C(8)—C(9)	108.7(7)
C(111)—C(8)—C(71)	110.7(8)	C(101)—C(8)—C(9)	113.8(7)
C(101)—C(8)—C(71)	105.7(7)	C(101)—C(8)—C(111)	109.0(9)
C(7)—C(8)—C(9)	118.0(5)	C(10)—C(8)—C(9)	108.8(6)
C(10)—C(8)—C(9)	107.1(7)	C(11)—C(8)—C(9)	107.9(6)
C(11)—C(8)—C(7)	110.9(7)	C(11)—C(8)—C(10)	103.0(7)
C(3)—C(2)—O(2)	109.8(4)	N(1)—C(1)—S	122.8(3)
N(2)—C(1)—S	123.9(3)	N(2)—C(1)—N(1)	113.2(3)
C(1)—N(1)—P	119.1(3)	C(12)—N(1)—P	121.9(2)
C(12)—N(1)—C(1)	117.5(3)	C(18)—N(2)—C(1)	124.7(3)
C(13)—C(12)—N(1)	113.9(3)	C(17)—C(12)—N(1)	109.9(3)
C(17)—C(12)—C(13)	113.5(3)	C(14)—C(13)—C(12)	110.0(4)
C(15)—C(14)—C(13)	111.0(5)	C(16)—C(15)—C(14)	111.8(5)
C(17)—C(16)—C(15)	110.6(4)	C(16)—C(17)—C(12)	109.7(4)
C(19)—C(18)—N(2)	107.4(3)	C(23)—C(18)—N(2)	114.3(3)
C(23)—C(18)—C(19)	110.0(4)	C(20)—C(19)—C(18)	109.4(4)
C(21)—C(20)—C(19)	111.1(4)	C(22)—C(21)—C(20)	111.3(4)
C(23)—C(22)—C(21)	110.8(4)	C(22)—C(23)—C(18)	109.5(4)

TABLE III

Deviation of atoms from the thiourea moiety plane in **5**

N(2)*	−0.003	C(1)*	0.009
N(1)*	−0.003	S*	−0.003
C(18)	−0.338	C(12)	0.846
P	−1.188	H(2)	0.18

The plane equation for atoms with asterisks 6.7005X + 8.8633Y + 2.5784Z = 9.0464.

respectively. In conclusion, the structure of **5** like that of **4** has a non-planar thiourea skeleton though the deviation from the planarity is smaller in the former case.

The bond distances and angles in **5** are very similar to the corresponding values found for the thioureas **1–4**. In comparison with **1**, **2** and **3**, only two bonds in **5** are slightly different: (i) C(1)—S of 1.651(4) Å is shorter and (ii) N(2)–C(1) of 1.339(5) Å is longer. However, these differences are not significant. It may be of interest to note that a similar tendency for these two bonds has been observed for **4**.

The most interesting observation is that the thiourea **5** does not form hydrogen bonds. The contact forces between neighbouring molecules of **5** are weak and belong to van der Waals forces. The N(2)H · · · O(3) distance, which is smallest among all the intermolecular distances, is equal to 3.246 Å and it is too long for the hydrogen bond to be formed (the sum of the van der Waals radii for the nitrogen and oxygen atoms is 3.05 Å).[6] This finding is very surprising in view of the fact that the molecules of **1**, **2** and **3** are stabilized by an intramolecular NH · · · O=P hydrogen bond. On the other hand, in the case of the thiourea **4** containing also the N-cyclohexyl substituents there are two intermolecular NH · · · O=P hydrogen bonds resulting in the formation of dimeric crystal structures.

In Table IV some structural parameters are summarized which may be useful in a further discussion on the geometry of the thioureas **1–5** investigated. Let us consider at first the torsional angle P—N(1)—C(1)—S. In *N*,*N*′-dibenzyl-*N*-phosphoryl-thioureas **1**, **2** and **3** having a planar conformation of the thiourea skeleton its value is close to 160°.[3–5] For the thiourea **4** with a non-planar conformation of the thiourea moiety the discussed angle has a value 91°.[5] The value of 125.7° found for the thiourea **5** represents a mean value between both extreme cases. Most probably such a value of the torsion angle P—N(1)—C(1)—S does not allow the formation of an intramolecular hydrogen bond between H(2) and the phosphoryl oxygen atom. Moreover, the steric hindrance around the phosphorus atom due to the presence of two bulky neopentoxy groups in **5** prevents the formation of dimers due to intermolecular hydrogen bonds. It should be noted that in **5** the rotation around the C(12)–N(1) bond is restricted by the interaction between the axial hydrogen atoms H(13) and H(17) and the phosphoryl oxygen atom. The second torsional angle P—N(1)—C(12)—H(12), interesting with regard to the coupling constant, $^3J_{P-H}$,[1,2] has a value of 179.0°.

The deviation of the phosphorus atom from the thiourea moiety plane and the non-bonding distance between phosphorus and sulphur are also useful parameters for comparison of the geometry of *N*,*N*′-disubstituted *N*-phosphorylthioureas which clearly point to a specific geometry of the thiourea **5**.

TABLE IV

Comparison of some structural parameters of *N,N'*-disubstituted *N*-phosphoryl-thioureas

Compound	Torsion angle P—N(1)—C(1)—S (°)	P ··· S distance (Å)	Deviation of P-atom from thiourea plane (Å)	N(2)H ··· O distance	Type of H-bond
1	169.2	4.278	0.279	2.700	intramol.
2	159.0	4.162	0.421	2.684	intramol.
3	162.3	4.242	0.490	2.623	intramol.
4	91.0	3.73	1.43	2.80	intermol.
5	125.7	4.028	1.188	3.246	no bond

EXPERIMENTAL

The crystals of **5** were obtained by slow evaporation of the benzene solution. The appropriate crystals selected for experiment were sealed into a Lindeman glass capillary tube. The space group and approximate cell parameters were determined photographically using Cu-Kα radiation. About 3450 reflections were collected up to $\theta = 55°$ with Syntex P$\bar{1}$ diffractometer using Cu-Kα radiation (λ = 1.54178 Å). A Lorentz polarization correction but no absorption correction was applied. The intensities of standard reflections showed no significant fluctuation during the time of data collection. From 3447 reflections measured, 2954 were classified as observed using criterion $|Fo| > 4\sigma |Fo|$ and used in final refinement of the structure.

Crystal data: $C_{23}H_{45}O_3NPS$, M = 460.78, monoclinic, space group $P2_1/c$, a = 11.225(2), b = 11.567(2), c = 21.423(5) Å, β = 100.92(4)°, V = 2731.19 Å^3, Z = 4, D_x = 1.126 g · cm^{-3}, λ(Cu-Kα) = 1.54178 Å, μ = 16.90 cm^{-1}, F(000) = 1008.

The structure was solved by direct automatic method for centrosymmetric structures using SHELX-76 system of programs. The initial coordinates of 15 atoms were obtained from the E-map. The remaining non-hydrogen atoms were obtained from the successive Fourier difference maps. One of the two neopentoxy groups is partly disordered. The site occupation factor for its three carbon atoms was established at 0.5. The refinement for three pairs of atoms (s.o.f. 0.5) [C(7)—C(71), C(10)—C(101) and C(11)—C(111)] was continued to the end isotropically and the H-atoms bonded to them were not located. The atomic coordinates for other non-hydrogen atoms were refined by blocked full-matrix least-squares with anisotropic thermal parameters. The positions of all H-atoms were found from the subsequent different map. The refinement was stopped at R = 0.069 with units weights. The thermal parameters of H-atoms were kept as 1.5 of the isotropic temperature factors of the parent atoms. The atomic parameters and temperature factors are given in Tables V, VI and VII. (Available on request from the Director of the Cambridge Crystallographic Data Centre (see Note).

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6. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

Note: The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 IEW. Any request should be accompanied by the full literature citation for this communication.