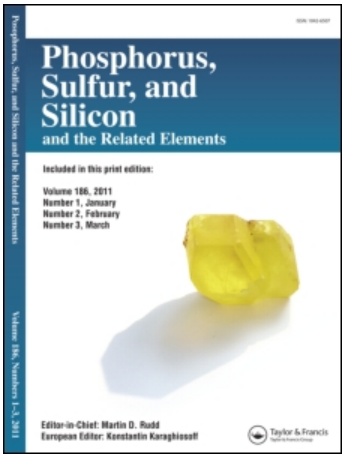

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CRYSTAL AND MOLECULAR STRUCTURE OF TWO N-CHALCOGENOPHOSPHORYL-CHALCOGENOUREAS

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CRYSTAL AND MOLECULAR STRUCTURE OF TWO N-CHALCOGENOPHOSPHORYL-CHALCOGENOUREAS

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Ph(Me)N—C(O)—NH—P(O)$(OPh)_2$, **1**, and Ph(Me)N—C(S)—NH—P(S)$(OPh)_2$, **2**, were synthesized by reaction of N-methyl aniline with $(PhO)_2P(O)NCO$ and $(PhO)_2P(S)NCS$, respectively. X-ray crystal structure analysis shows that **1** crystallizes in space group $Pna2_1$ with two symmetry-independent molecules, **2** in space group $P\bar{1}$. In both compounds **1** and **2** an extended π-delocalization along the P1—N1—C1—N2 sequence is observed. P1—N1 bonds (**1**: 1.646, 1.646 A; **2**:: 1.671 Å), N1—C1 bonds (**1**: 1.406, 1.397 Å; **2**: 1.378 Å) and N2—C1 bonds (**1**: 1.358 Å, 1.360 Å; **2**: 1.354 Å) are remarkably shorter than single bonds. Configurations of the molecules are Z,E′ for **1** and Z,Z′ for **2**. **1** forms in the crystal dimers with NH . . . O hydrogen bonds via phosphoryl oxygen (N . . . O distances 2.863 Å, 2.891 Å).

Keywords: N,N-methylphenyl-N′-diphenoxyphosphoryl-urea; N,N-methylphenyl-N′-diphenoxythiophosphoryl-thiourea; X-ray crystal structure analysis; hydrogen bonds; pi-delocalization.

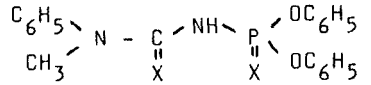
INTRODUCTION

Phosphorus-containing 1,3-dichalcogeno compounds with a μ-NH group, HA, are useful extracting agents for many metal ions M^{n+}. They form stable chelate complexes MA_n. Esters of imidodiphosphoric and imido(thio)diphosphoric acid are investigated intensively.[1–9] The tetraphenyl imidodiphosphate, $(PhO)_2P(O)$—NH—$P(O)(OPh)_2$, exists in the crystal as well as in nonpolar solvents in form of dimers.[4,6] Two molecules are connected by N—H . . . O intermolecular hydrogen bonds. The two phosphoryl oxygen atoms in the molecule are in trans position and only one of them participates in hydrogen bonds.

In connection with structure reactivity studies in metal extraction, N,N-diorganyl substituted N′-diphenoxy(thio)phosphoryl ureas and thioureas were synthesized and investigated.[10,11] N,N-Dipropyl-N′-diphenoxythiophosphoryl-thiourea forms six-membered chelate rings with Ni(II). The Ni atom lies in the centre of symmetry and is coordinated by four S atoms of two molecules of the ligand in a planar arrangement.[11,12]

So far, little is known about the molecular and crystal structure of phosphorylated

and thiophosphorylated ureas and thioureas. N,N-methylphenyl-N'-diphenoxyphosphoryl-urea, $(PhO)_2P(O)$—NH—C(O)N(Me)Ph, **1**, and N,N-methylphenyl-N'-diphenoxythiophosphoryl-thiourea, $(PhO)_2P(S)$—NH—C(S)N(Me)Ph, **2**, form colorless crystals and have been used as representatives for crystal and molecular structure determination.



1: X= O
2: X= S

RESULTS AND DISCUSSION

Structure of N,N-methylphenyl-N'-diphenoxyphosphoryl-urea, 1

The molecular structures of the two symmetry-independent molecules of **1** are shown in Figure 1. Atomic parameters are listed in Table I. Bond lengths, angles, and torsion angles are given in Table II.

Both molecules are not only nearly identical in their distances and angles but also in their configuration. Small differences in the angles and torsion angles may be attributed to intermolecular interactions.

The tautomeric form of **1** in the crystalline state is the keto form where H1 is bonded to N1 and not to O3 or O4. The configuration of the molecules is best described as Z,E'[13] with absolute values of torsion angles $|\omega_1(O3—C1—N1—P1)| = 10.9$ and 8.8° and $|\omega_2(O4—P1—N1—C1)| = 179.4$ and 178.4° for molecule 1 and 2, respectively.

The P—O bonds (1.575–1.580; 1.461; 1.462 Å) show the expected values which are 1.59 Å for P—O—C groups and 1.46 Å for P=O groups.[14]

The P—N bond (1.646; 1.646 Å) is clearly between P—N single (1.77 Å) and double bond (1.57 Å).[14] It is about the same bond length as in the tetraphenyl imidophosphate (1.639; 1.653 Å).[4] This is a hint to π-electron delocalization which occurs along the P—N—C—N sequence of **1**. Especially C1—N2 (1.358; 1.360 Å) is shortened in comparison with a C—N single bond (1.47 Å). For the same reason the C—N bond to the phenyl ring (1.437; 1.434 Å, expected value: 1.43 Å) is shorter than the C—N bond to the methyl group (1.472; 1.481 Å, expected value: 1.47 Å). The length of the C—O bond in the urea fragment (1.213; 1.227 Å) corresponds to a nearly uninfluenced $C(sp^2)$=O bond (1.21 Å).[15] In the crystal structure intermolecular hydrogen bonding of the type N—H . . . O exists between pairs of the two symmetry-independent molecules (Figure 2). Oxygen atoms of phosphoryl groups participate in these hydrogen bonds. The N . . . O distances (2.863; 2.891 Å) are typical for this type of hydrogen bonds (mean value from literature: 2.89 Å)[16] and are somewhat longer than in $[(PhO)_2P(O)NHP(O)(OPh)_2]_2$ (2.747 Å).[4]

Structure of N,N-methylphenyl-N'-diphenoxythiophosphoryl-thiourea, 2

The molecular structure of **2** is shown in Figure 3. Atomic parameters are listed in Table III. Bond lengths, angles, and torsion angles are given in Table IV.

The tautomeric form of **2** in the crystalline state is again the keto form with the

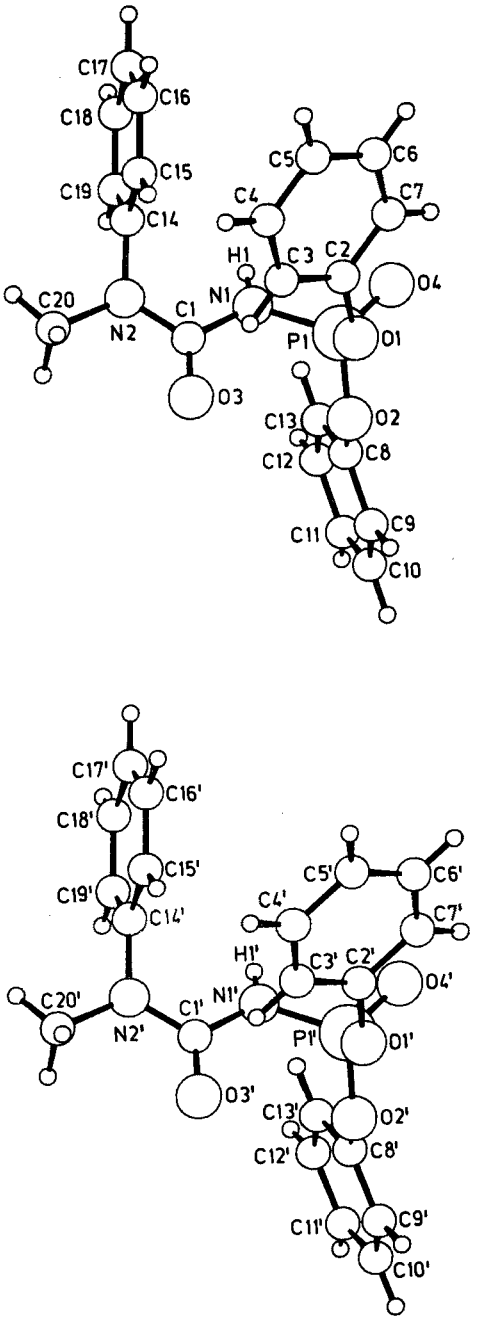


FIGURE 1 Molecular structure and atomic numbering scheme of **1** (Molecule 1 and 2).

TABLE I

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of N,N-methylphenyl-N′-diphenoxyphosphoryl-urea, **1**

	x	y	z	U_{eq} **
Molecule 1				
P1	1581(1)	5642(2)	2500	16(1)
O1	1640(2)	4944(5)	1702(2)	17(1)
O2	1952(2)	7066(5)	2310(2)	21(1)
O3	728(2)	7572(5)	1636(2)	22(1)
O4	1796(2)	4742(5)	3116(2)	20(1)
N1	882(2)	6044(6)	2633(3)	16(1)
N2	-54(2)	6848(6)	2334(3)	18(2)
C1	526(2)	6880(7)	2153(3)	17(2)
C2*	1302(2)	3727(4)	1512(2)	18(2)
C3	859(2)	3921(4)	987(2)	25(2)
C4	516(2)	2719(4)	766(2)	35(3)
C5	616(2)	1322(4)	1070(2)	35(3)
C6	1060(2)	1128(4)	1595(2)	32(2)
C7	1403(2)	2331(4)	1816(2)	25(2)
C8*	2095(2)	8168(5)	2797(2)	21(2)
C9	2531(2)	9142(5)	2556(2)	25(2)
C10	2710(2)	10309(5)	3008(2)	30(2)
C11	2453(2)	10501(5)	3702(2)	39(3)
C12	2017(2)	9527(5)	3944(2)	35(2)
C13	1838(2)	8360(5)	3491(2)	23(2)
C14*	-306(2)	5627(5)	2733(2)	17(2)
C15	-422(2)	4306(5)	2362(2)	25(2)
C16	-680(2)	3123(5)	2738(2)	36(3)
C17	-821(2)	3262(5)	3486(2)	31(2)
C18	-704(2)	4583(5)	3857(2)	27(2)
C19	-447(2)	5765(5)	3481(2)	23(2)
C20	-466(3)	7723(8)	1882(4)	30(2)
H1	743(24)	5820(69)	3062(33)	23(17)
Molecule 2				
P1'	5992(1)	-62(2)	4839(1)	16(1)
O1'	5937(2)	-823(5)	5623(2)	18(1)
O2'	5616(2)	1342(5)	5058(2)	20(1)
O3'	6829(2)	1736(5)	5762(2)	23(2)
O4'	5773(2)	-911(5)	4209(2)	20(1)
N1'	6687(2)	377(6)	4708(3)	18(2)
N2'	7618(2)	1248(6)	5018(3)	18(2)
C1'	7039(2)	1157(7)	5208(3)	15(2)
C2*	6237(2)	-2127(4)	5786(2)	17(2)
C3'	6717(2)	-2048(4)	6267(2)	25(2)
C4'	6999(2)	-3340(4)	6496(2)	23(2)

TABLE I (*Continued*)

C5'	6801(2)	-4713(4)	6245(2)	20(2)
C6'	6322(2)	-4793(4)	5764(2)	19(2)
C7'	6040(2)	-3500(4)	5535(2)	22(2)
C8'*	5454(2)	2487(5)	4591(2)	15(2)
C9'	4986(2)	3359(5)	4836(2)	19(2)
C10'	4801(2)	4569(5)	4416(2)	26(2)
C11'	5084(2)	4907(5)	3753(2)	32(2)
C12'	5552(2)	4034(5)	3508(2)	36(2)
C13'	5737(2)	2825(5)	3928(2)	23(2)
C14'*	7888(2)	181(5)	4539(2)	19(2)
C15'	8015(2)	-1233(5)	4805(2)	28(2)
C16'	8276(2)	-2277(5)	4341(2)	31(2)
C17'	8411(2)	-1907(5)	3611(2)	26(2)
C18'	8284(2)	-493(5)	3345(2)	28(2)
C19'	8023(2)	551(5)	3809(2)	23(2)
C20'	8023(3)	2082(8)	5506(4)	31(2)
H1'	6805(22)	220(62)	4295(28)	5(14)

* refinement of the phenyl rings C2-C7, C8-C13, C14-C19, C2'-C7', C8'-C13', C14'-C19' as fixed groups

**U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE II

Distances, angles, and selected torsion angles in **1**

Intramolecular distances (Å)			
Molecule 1		Molecule 2	
P1-O1	1.580(4)	P1'-O1'	1.580(4)
P1-O2	1.575(4)	P1'-O2'	1.579(4)
P1-O4	1.462(4)	P1'-O4'	1.461(4)
P1-N1	1.646(5)	P1'-N1'	1.646(5)
O1-C2	1.384(6)	O1'-C2'	1.394(5)
O2-C8	1.369(6)	O2'-C8'	1.385(6)
O3-C1	1.213(7)	O3'-C1'	1.227(7)
N1-C1	1.406(8)	N1'-C1'	1.397(8)
N1-H1	0.86(6)	N1'-H1'	0.81(5)
N2-C1	1.358(7)	N2'-C1'	1.360(7)
N2-C14	1.437(6)	N2'-C14'	1.434(6)
N2-C20	1.472(8)	N2'-C20'	1.481(8)
all phenyl ring distances 1.395			

TABLE II (*Continued*)

Intramolecular angles (°)

Molecule 1		Molecule 2	
O1-P1-O2	94.7(2)	O1'-P1'-O2'	94.7(2)
O1-P1-O4	116.4(2)	O1'-P1'-O4'	116.3(2)
O2-P1-O4	116.2(2)	O2'-P1'-O4'	115.7(2)
O1-P1-N1	107.6(2)	O1'-P1'-N1'	108.1(2)
O2-P1-N1	111.6(3)	O2'-P1'-N1'	111.2(3)
O4-P1-N1	109.5(2)	O4'-P1'-N1'	109.9(2)
P1-O1-C2	119.8(3)	P1'-O1'-C2'	121.3(3)
P1-O2-C8	125.6(3)	P1'-O2'-C8'	126.2(3)
P1-N1-C1	125.6(4)	P1'-N1'-C1'	125.3(4)
P1-N1-H1	116(4)	P1'-N1'-H1'	114(4)
C1-N1-H1	118(4)	C1'-N1'-H1'	120(4)
C1-N2-C14	121.6(5)	C1'-N2'-C14'	121.6(5)
C1-N2-C20	118.1(5)	C1'-N2'-C20'	118.7(5)
C14-N2-C20	116.0(4)	C14'-N2'-C20'	115.9(4)
O3-C1-N1	122.3(5)	O3'-C1'-N1'	121.3(5)
O3-C1-N2	124.3(5)	O3'-C1'-N2'	123.8(5)
N1-C1-N2	113.4(5)	N1'-C1'-N2'	114.9(5)
O1-C2-C3	118.0(2)	O1'-C2'-C3'	118.1(2)
O1-C2-C7	122.0(2)	O1'-C2'-C7'	121.7(2)
O2-C8-C9	115.3(2)	O2'-C8'-C9'	115.6(2)
O2-C8-C13	124.7(2)	O2'-C8'-C13'	124.4(2)
N2-C14-C15	119.3(2)	N2'-C14'-C15'	119.7(2)
N2-C14-C19	120.7(2)	N2'-C14'-C19'	120.3(2)
all phenyl ring angles 120.0			

Torsion angles (°)

Molecule 1		Molecule 2	
O2-P1-O1-C2	-169.5(3)	O2'-P1'-O1'-C2'	-174.9(3)
O4-P1-O1-C2	68.1(4)	O4'-P1'-O1'-C2'	63.4(4)
N1-P1-O1-C2	-55.1(4)	N1'-P1'-O1'-C2'	-60.7(4)
O1-P1-O2-C8	-177.4(4)	O1'-P1'-O2'-C8'	-176.1(4)
O4-P1-O2-C8	-54.9(5)	O4'-P1'-O2'-C8'	-53.8(4)
N1-P1-O2-C8	71.6(4)	N1'-P1'-O2'-C8'	72.5(4)
O1-P1-N1-C1	-52.0(6)	O1'-P1'-N1'-C1'	-50.5(6)
O2-P1-N1-C1	50.6(6)	O2'-P1'-N1'-C1'	52.2(6)
O4-P1-N1-C1	-179.4(5)	O4'-P1'-N1'-C1'	-178.4(5)
P1-N1-C1-O3	-10.9(9)	P1'-N1'-C1'-O3'	-8.8(9)
P1-N1-C1-N2	170.1(4)	P1'-N1'-C1'-N2'	173.0(4)
C14-N2-C1-O3	154.9(5)	C14'-N2'-C1'-O3'	157.7(5)
C14-N2-C1-N1	-26.1(7)	C14'-N2'-C1'-N1'	-24.1(8)
C20-N2-C1-O3	-0.8(9)	C20'-N2'-C1'-O3'	0.5(9)
C20-N2-C1-N1	178.1(5)	C20'-N2'-C1'-N1'	178.7(5)

Intermolecular distances (Å)			
H1 ... O4'[-1/2+x,1/2-y,z]	2.08	N1 ... O4'[-1/2+x,1/2-y,z]	2.863
H1'... O4 [1/2+x,1/2-y,z]	2.13	N1'... O4 [1/2+x,1/2-y,z]	2.891
Intermolecular angles (°)			
N1-H1...O4'[-1/2+x,1/2-y,z]	151	N1'-H1'...O4[1/2+x,1/2-y,z]	157

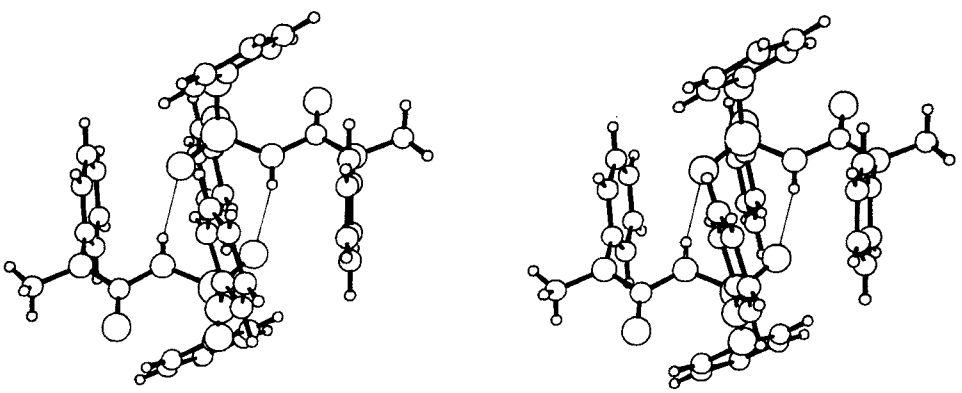


FIGURE 2 Pair of symmetry-independent molecules in **1** with NH . . . O hydrogen bonds (stereo pair).

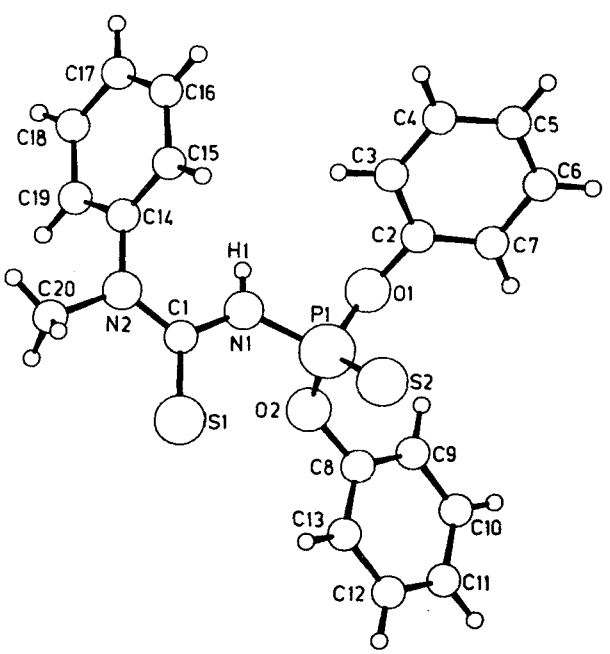


FIGURE 3 Molecular structure and atomic numbering scheme of **2**.

TABLE III

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of N,N-methylphenyl-N′-diphenoxythiophosphoryl-thiourea, **2**

	x	y		U_{eq}*
P1	3895(2)	6668(1)	7162(1)	40(1)
S1	2798(2)	6292(1)	9528(1)	54(1)
S2	2267(2)	7798(1)	7035(1)	53(1)
O1	4436(5)	6158(2)	5984(2)	45(2)
O2	5724(5)	7158(2)	8057(2)	45(2)
N1	3447(6)	5302(2)	7496(2)	38(2)
N2	2528(6)	3897(2)	8481(2)	41(2)
C1	2917(7)	5107(3)	8460(3)	38(3)
C2	3403(8)	5980(3)	4823(3)	40(2)
C3	2171(8)	4961(3)	4352(3)	55(3)
C4	1318(9)	4711(4)	3167(4)	63(3)
C5	1690(10)	5480(6)	2483(4)	69(4)
C6	2893(10)	6503(6)	2967(4)	79(4)
C7	3808(9)	6771(4)	4156(3)	62(3)
C8	6595(8)	8378(3)	8266(3)	43(3)
C9	7513(9)	8653(4)	7536(4)	60(3)
C10	8445(10)	9818(5)	7807(5)	84(4)
C11	8390(10)	10690(4)	8813(5)	83(4)
C12	7475(9)	10394(4)	9534(4)	65(3)
C13	6512(8)	9220(3)	9259(3)	51(3)
C14	2513(7)	2852(3)	7532(3)	39(3)
C15	1361(8)	2670(3)	6434(3)	46(3)
C16	1362(8)	1624(3)	5562(3)	56(3)
C17	2474(8)	786(3)	5793(4)	57(3)
C18	3614(8)	968(3)	6888(4)	60(3)
C19	3643(8)	2011(3)	7766(3)	50(3)
C20	2096(8)	3599(3)	9529(3)	61(3)
H1	3456(72)	4721(37)	7007(35)	65(15)

* U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE IV

Distances, angles, and selected torsion angles in **2**

Intramolecular distances (Å)			
P1-S2	1.895(2)	C4-C5	1.359(8)
P1-O1	1.591(3)	C5-C6	1.357(9)
P1-O2	1.582(3)	C6-C7	1.394(6)
P1-N1	1.671(3)	C8-C9	1.345(8)
S1-C1	1.664(3)	C8-C13	1.374(5)

TABLE IV (*Continued*)

O1-C2	1.402(4)	C9-C10	1.372(7)
O2-C8	1.413(4)	C10-C11	1.395(8)
N1-C1	1.378(6)	C11-C12	1.341(10)
N1-H1	0.78(4)	C12-C13	1.390(6)
N2-C1	1.354(4)	C14-C15	1.381(5)
N2-C14	1.445(4)	C14-C19	1.382(7)
N2-C20	1.476(6)	C15-C16	1.393(5)
C2-C3	1.366(6)	C16-C17	1.369(7)
C2-C7	1.370(6)	C17-C18	1.374(6)
C3-C4	1.379(6)	C18-C19	1.389(5)

Intramolecular angles (°)

S2-P1-O1	115.2(1)	C3-C4-C5	120.2(5)
S2-P1-O2	117.9(1)	C4-C5-C6	120.0(4)
S2-P1-N1	120.8(2)	C5-C6-C7	121.4(6)
O1-P1-O2	100.0(2)	C2-C7-C6	117.2(5)
O1-P1-N1	98.5(2)	O2-C8-C9	119.8(3)
O2-P1-N1	100.7(2)	O2-C8-C13	117.0(4)
P1-O1-C2	126.2(4)	C9-C8-C13	123.1(4)
P1-O2-C8	124.1(3)	C8-C9-C10	118.6(4)
P1-N1-C1	127.5(2)	C9-C10-C11	119.5(6)
P1-N1-H1	114(3)	C10-C11-C12	120.9(5)
C1-N1-H1	118(4)	C11-C12-C13	119.9(4)
C1-N2-C14	124.1(3)	C8-C13-C12	117.9(5)
C1-N2-C20	119.2(3)	N2-C14-C15	121.1(4)
C14-N2-C20	116.7(3)	N2-C14-C19	118.1(3)
S1-C1-N1	121.5(2)	C15-C14-C19	120.8(3)
S1-C1-N2	122.9(3)	C14-C15-C16	118.8(4)
N1-C1-N2	115.6(3)	C15-C16-C17	120.6(4)
O1-C2-C3	119.9(3)	C16-C17-C18	120.4(4)
O1-C2-C7	117.7(4)	C17-C18-C19	119.8(5)
C3-C2-C7	121.9(3)	C14-C19-C18	119.6(4)
C2-C3-C4	119.2(4)		

Torsion angles (°)

S2-P1-O1-C2	-30.4(3)	O2-P1-N1-C1	76.9(5)
O2-P1-O1-C2	-157.9(3)	P1-N1-C1-S1	-5.1(6)
N1-P1-O1-C2	99.6(3)	P1-N1-C1-N2	175.7(4)
S2-P1-O2-C8	-36.7(4)	C14-N2-C1-S1	175.8(4)
O1-P1-O2-C8	89.0(4)	C14-N2-C1-N1	-5.0(7)
N1-P1-O2-C8	-170.3(4)	C20-N2-C1-S1	-4.5(7)
S2-P1-N1-C1	-55.0(4)	C20-N2-C1-N1	174.7(4)
O1-P1-N1-C1	178.8(4)		

atom H1 bonded to N1 and not to S1 or S2. The configuration, on the other hand, is different from **1**. It is best described as Z,Z′ with absolute values of torsion angles $|\omega_1$(S1—C1—N1—P1)| = 5.1° and $|\omega_2$(S2—P1—N1—C1)| = 55.0°. The P—S bond (1.895 Å) is best described as a double bond (1.92 Å) whereas the P—O bond lengths (1.591; 1.582 Å) are in good agreement with the value for a P—O single bond (1.59 Å).

The P—N bond (1.671 Å) is halfway between P—N single (1.77 Å) and double bond (1.57 Å). The C—S bond (1.664 Å) is somewhat longer than a C—S double bond (1.61 Å).

As in **1** the other bonds in **2** show an extended π-electron delocalization.

TABLE V

Crystal data and details of structure determination

	PhMeNCONHPO(OPh)$_2$	PhMeNCSNHPS(OPh)$_2$
	A. Crystal data	
Formula	$C_{20}H_{19}N_2O_4P$	$C_{20}H_{19}N_2O_2PS_2$
Formula weight	382.36	414.49
Habit	needles	plates
m.p. (°C)	111–112	93
Space group	$Pna2_1$	P1
a (Å)	22.706(4)	8.136(2)
b (Å)	9.035(2)	11.049(2)
c (Å)	18.079(3)	11.989(2)
α (°)	90	101.66(2)
β (°)	90	104.22(2)
γ (°)	90	94.85(2)
V (Å^3)	3709.14	1012.90
Z	8	2
Dcalc. (g · cm^{-3})	1.37	1.36
F(000)	1600	432
$\mu_{MoK\alpha}$ (cm^{-1})	1.7	3.5
	B. Data collection	
Temperature (°C)	−160	22
2 θ range (°)	3 . . . 56	3 . . . 56
Scan type	ω scan	ω scan
Indices scanned: h, k, l	0 → 30,0 → 11,0 → 23	−4 → 4, −14 → 14,0 → 16
Independent reflections	3568	2447
Observed reflections	2907 with F ≥ 4 σ(F)	1967 with F ≥ 2.5 σ(F)
	C. Solution and refinement	
Structure solution	direct methods	direct methods
Refinement	full-matrix LS	full-matrix LS
Parameters	427	248
Reflections/parameter	6.8	7.9
Weighting scheme	$1/(\sigma_F^2 + 0.0003F^2)$	$1/(\sigma_F^2 + 0.0009F^2)$
H atoms	calc., H1/H1′ ref.	calc., H1 ref.
Max. shift/sigma	0.03	0.06
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.36, −0.38	0.19, −0.20
Final R value	0.057	0.039
	0.078 for all data	0.053 for all data
Final wR value	0.054	0.065
	0.056 for all data	0.068 for all data
Final S value	1.70	1.73

Clear differences are observed for the angles at P1 in **1** and **2**, obviously caused by the substitution of the relatively small O atom by the larger S atom and by the different configuration of the molecules.

In the crystal structure, no intermolecular distances exist that are smaller than the sum of van der Waals radii.

Comparing the molecular structure of **2** with the structure of the nickel complex $Ni[(PhO)_2P(S)NC(S)NPr_2]_2$ it is clearly evident that the complex formation leads to a shortening in P—N (1.574 Å) and C—N (1.321 Å) bonds as well to a lengthening of P—S (1.978 Å) and C—S (1.745 Å) bonds.[11,12]

EXPERIMENTAL

N,N-Methylphenyl-N′-diphenoxyphosphoryl-urea, $(C_6H_5O)_2P(O)—NH—C(O)—N(CH_3)C_6H_5$, **1**, was prepared by dissolving 8.9 g (0.03 mol) diphenoxyphosphorylisocyanate in 20 cm^3 of dry diethylether and adding 0.03 mol N-methyl aniline. A white crystalline precipitate occurs. After stirring for 2 hours the precipitate was isolated by filtration and washed with petrol ether. After recrystallization from ether, crystals of sufficient quality were obtained. m.p. 111–112°C.

$\delta(^{31}P) = -10.3$ ppm. Elemental analysis: 62.82 (calcd. 62.76); H 4.97 (5.07); N 7.33 (7.30); P 8.12 (8.25).

N,N-Methylphenyl-N′-diphenoxythiophosphoryl-thiourea, $(C_6H_5O)_2P(S)—NH—C(S)—N(CH_3)C_6H_5$, **2** was synthesized in a similar way. 0.65 cm^3 (6.6 mmol) N-methyl aniline in 10 cm^3 diethylether were added to a solution of 1.84 g (6.0 mmol) of $(C_6H_5O)_2P(S)NCS$. After stirring for two hours ether was evaporated until white crystals appeared. The precipitation was completed by the addition of pentane. **2** was recrystallized from ether. m.p. 93°C.

$\delta(^{31}P) = 51.9$ ppm. Elemental analysis: C 58.14 (calcd. 57.97); H 4.65 (4.59); N 6.85 (6.76); P 8.13 (7.49); S 15.91 (15.46).

Unit cell dimensions and intensity data were measured on a Syntex-$P2_1$ diffractometer using a graphite monochromator and MoKα radiation (α = 0.71069 Å). Lorentz and polarization corrections were applied, but no absorption correction. Crystal and diffraction data for **1** and **2** are given in Table V. Both structures were solved and refined with the program system SHELXTL-PLUS.[17] The drawings were made with PLUTO78.[18]

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