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The Crystal Structure of N,N'-Dibenzyl-N-diphenoxyphosphorylthiourea

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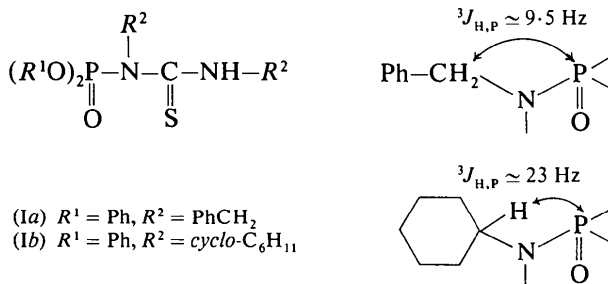Moscow 117312, USSR*

Abstract

Crystals of the title compound are triclinic, space group
$P\bar{1}$, $a = 8·0101$ (8), $b = 11·8192$ (9), $c = 13·5001$ (9)
Å, $\alpha = 97·27$ (9), $\beta = 100·79$ (9), $\gamma = 101·16$ (9)°, $Z =$
2. 2591 intensities were collected on a Syntex
diffractometer. The structure was solved by the direct
method. The positions of all the H atoms were shown
by a Fourier synthesis. The final R value was 0·033.
The positions of the H atoms were refined with
isotropic temperature factors. The non-hydrogen atoms
were refined anisotropically. The atoms forming the
thiourea system are coplanar. There is a hydrogen bond
between the phosphoryl O atom and the secondary N
atom of length 2·702 Å.

Introduction

In connexion with a research programme on the reaction
between carbodiimides and thio- and seleno-acids
(Mikołajczyk, Kiełbasiński & Schiebel, 1976;
Mikołajczyk, Kiełbasiński, Barlow & Russell, 1977;
Mikołajczyk, Kiełbasiński & Goszczyńska, 1977) we

have isolated the 1:1 adducts from the reaction between O,O-dialkylphosphorothioic acids and dicyclohexyl-carbodiimide and dibenzylcarbodiimide (Mikołajczyk, Kiełbasiński & Goszczyńska, 1977). All the spectral data (NMR, IR, MS) of the adducts were consistent with the structure of N-dialkylphosphoryl-N,N'-disubstituted thiourea (I)

$$(R^1O)_2P-N-C-NH-R^2$$

with R^2 on the N, and $\parallel$ O on the P, $\parallel$ S on the C.

$^3J_{H,P} \simeq 9.5$ Hz

Ph—CH$_2$ ... P, N, O structure

(Ia) $R^1 = $ Ph, $R^2 = $ PhCH$_2$
(Ib) $R^1 = $ Ph, $R^2 = cyclo$-C$_6$H$_{11}$

$^3J_{H,P} \simeq 23$ Hz

It is interesting to note that the coupling constant $^3J_{H,P}$, between P and the benzyl methylene protons in (Ia), was observed to be about 9·5 Hz, whereas in the case of (Ib) the coupling constant between P and the proton at C(1) of the cyclohexyl moiety was much higher at ca 23 Hz.

The X-ray analysis of the title compound (Ia) was undertaken to confirm the proposed structure. It was also hoped that by comparing its structure with that of (Ib) a stereochemical basis for the difference in the above discussed coupling constants might be obtained.

Experimental

Crystal data

C$_{27}$H$_{25}$N$_2$O$_3$PS, $M_r = 486$, $F(000) = 492$, triclinic, $a = 8·0101$ (8), $b = 11·8192$ (9), $c = 13·5001$ (9) Å, $\alpha = 97·27$ (9), $\beta = 100·79$ (9), $\gamma = 101·16$ (9)°, $V = 1214·01$ Å^3; $D_m = 1·342$; $D_c = 1·337$ Mg m^{-3}, $Z = 2$, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 0·185$ mm^{-1}, space group $P\bar{1}$.

Approximate cell parameters were determined from oscillation and rotation photographs using Cu $K\alpha$ radiation. These parameters were redetermined on the Syntex $P2_1$ diffractometer using Mo $K\alpha$ radiation. The space group is $P\bar{1}$. The density was measured by flotation.

The intensities of 2591 reflections were measured at room temperature on a Syntex $P2_1$ automatic diffractometer. For 33 reflections the intensities were less than 4σ and therefore 2558 reflections were used for least-squares refinement. Lorentz and polarization corrections were applied. Absorption corrections were not calculated ($\mu = 0·185$ mm^{-1}).

Structure solution and refinement

All calculations were performed on an ODRA 1305 computer using the *SHELX* 76 system of programs (Sheldrick, 1976). The distribution of the E values calculated during the data reduction showed the space group to be $P\bar{1}$. Hence, all subsequent calculations were performed in the centrosymmetric space group.

The phase problem was solved by the automatic centrosymmetric direct-methods program incorporated into the *SHELX* 76 system. Three origin-defining ($\bar{2}13$; $4\bar{1}4$ and $\bar{3}01$) and 12 multisolution reflections were selected automatically and the values of $E \geq 1·2$ were used. The E map computed for the best solution revealed the positions of 11 of the 34 non-hydrogen atoms. At this stage the R value was 0·45. The structure was refined by standard least-squares methods and difference electron density syntheses. Three cycles of full-matrix least-squares refinement using isotropic temperature factors resulted in the R value of 0·105. In two further cycles with all non-hydrogen atoms treated anisotropically R decreased to 0·072. In a subsequent difference Fourier synthesis all H atoms except those belonging to the benzene rings could be located. Therefore, the remaining benzene ring H atoms were generated with C—H constrained to 1·08 Å. The positional and isotropic thermal parameters of the hydrogen atoms, taken initially as those of the C atoms to which they were bonded, were refined. Final refinement converged with conventional $R = 0·0328$, $R_w = (\sum w^{1/2}\Delta/\sum w^{1/2}|F_o|) = 0·0395$ and $R_g = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0·0558$. The weights were $w = k/[\sigma^2(F_o) + gF_o^2]$ where k and g refined to 1·000 and 0·00266, respectively. In the final difference map no significant density was observed.

Description and discussion of the structure

The molecular structure and atomic numbering is shown in Fig. 1. The packing of the molecules in the unit cell is shown in Fig. 2. The bond lengths and angles
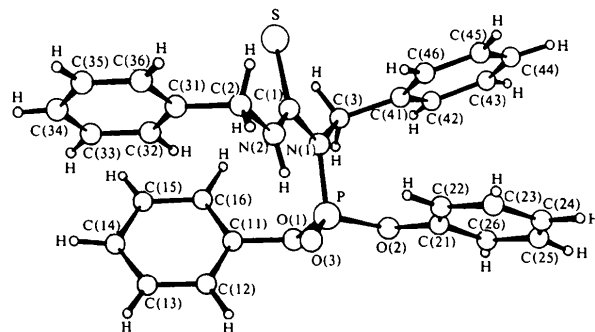

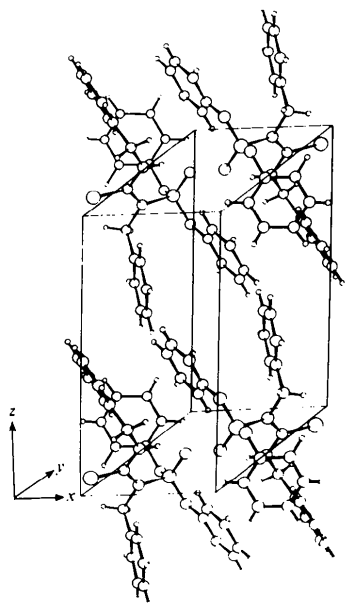Fig. 1. The molecule of N,N'-dibenzyl-N-diphenoxyphosphoryl-thiourea (Ia).

Fig. 2. The packing of the molecules of (I*a*) in the unit cell.

are listed in Tables 1 and 2 respectively. The final atomic coordinates for the non-hydrogen atoms are given in Table 3.* Table 4 contains atomic coordinates and isotropic temperature factors for H atoms. Table 5 lists computed least-squares planes with the distances of various atoms from the planes and angles between the planes.

Table 2. *Bond angles* (°)

O(2)–P–O(1)	96·8 (1)	O(3)–P–O(2)	116·2 (1)
O(3)–P–O(2)	117·8 (1)	N(1)–P–O(1)	105·7 (1)
N(1)–P–O(2)	105·2 (1)	N(1)–P–O(3)	113·2 (1)
C(11)–O(1)–P	117·9 (1)	C(21)–O(2)–P	126·0 (1)
C(1)–N(1)–P	126·6 (1)	C(3)–N(1)–P	113·9 (1)
C(3)–N(1)–C(1)	118·7 (2)	C(2)–N(2)–C(1)	123·2 (2)
N(1)–C(1)–S	121·3 (2)	N(2)–C(1)–S	122·5 (2)
N(2)–C(1)–N(1)	116·1 (2)	C(31)–C(12)–N(2)	114·6 (2)
C(41)–C(13)–N(1)	115·0 (2)	C(11)–C(16)–C(15)	118·1 (2)
C(14)–C(15)–C(16)	120·9 (2)	C(13)–C(14)–C(15)	119·2 (2)
C(12)–C(13)–C(14)	121·0 (3)	C(11)–C(12)–C(13)	118·1 (2)
C(16)–C(11)–C(12)	122·6 (2)	C(16)–C(11)–O(1)	118·3 (2)
C(12)–C(11)–O(1)	119·1 (2)	C(22)–C(21)–O(2)	123·1 (2)
C(26)–C(21)–O(2)	114·9 (2)	C(26)–C(21)–C(22)	121·9 (2)
C(23)–C(22)–O(21)	118·3 (2)	C(24)–C(23)–C(22)	120·8 (2)
C(25)–C(24)–C(23)	119·8 (2)	C(26)–C(25)–C(24)	120·6 (3)
C(25)–C(26)–C(21)	118·5 (3)	C(32)–C(31)–C(2)	123·7 (2)
C(36)–C(31)–C(2)	118·1 (2)	C(36)–C(31)–C(32)	118·1 (2)
C(33)–C(32)–C(31)	120·6 (3)	C(34)–C(33)–C(32)	120·5 (3)
C(35)–C(35)–C(33)	119·8 (2)	C(36)–C(35)–C(34)	119·9 (3)
C(35)–C(36)–C(31)	121·1 (2)	C(46)–C(41)–C(3)	122·7 (2)
C(46)–C(41)–C(42)	118·7 (2)	C(44)–C(43)–C(42)	120·6 (3)
C(43)–C(42)–C(41)	120·5 (3)	C(45)–C(44)–C(43)	119·1 (2)
C(45)–C(46)–C(41)	120·6 (2)	H(3)–N(2)–C(1)	114 (2)
H(3)–N(2)–C(2)	122 (2)	H(4)–C(2)–N(2)	103 (2)
H(3)–C(2)–C(31)	109 (2)	H(5)–C(2)–N(2)	109 (2)
H(5)–C(2)–C(31)	104 (2)	H(5)–C(2)–H(4)	116 (3)
H(1)–C(3)–N(1)	109 (2)	H(1)–C(3)–C(41)	108 (2)
H(2)–C(3)–N(1)	110 (2)	H(2)–C(3)–C(41)	108 (2)
H(2)–C(3)–H(1)	105 (2)	H(16)–C(16)–C(15)	120 (2)
H(1)–C(16)–C(11)	121 (2)	H(15)–C(15)–C(16)	121 (3)
H(15)–C(15)–C(14)	117 (3)	H(14)–C(14)–C(15)	115 (2)
H(14)–C(14)–C(13)	125 (3)	H(13)–C(13)–C(14)	116 (2)
H(13)–C(13)–C(12)	122 (3)	H(12)–C(12)–C(13)	121 (3)
H(12)–C(12)–C(11)	120 (2)	H(22)–C(22)–C(21)	120 (2)
H(22)–C(22)–C(23)	121 (3)	H(23)–C(23)–C(22)	120 (3)
H(23)–C(23)–C(24)	119 (2)	H(24)–C(24)–C(23)	119 (3)
H(24)–C(24)–C(25)	121 (3)	H(25)–C(25)–C(24)	127 (3)
H(25)–C(25)–C(26)	111 (3)	H(26)–C(26)–C(21)	121 (2)
H(26)–C(26)–C(25)	120 (2)	H(32)–C(32)–C(31)	120 (2)
H(32)–C(32)–C(33)	119 (3)	H(33)–C(33)–C(32)	120 (3)
H(33)–C(33)–C(34)	119 (2)	H(34)–C(34)–C(33)	117 (3)
H(34)–C(34)–C(35)	122 (3)	H(35)–C(35)–C(34)	113 (3)
H(35)–C(35)–C(36)	126 (3)	H(42)–C(42)–C(41)	118 (2)
H(42)–C(42)–C(43)	120 (3)	H(43)–C(43)–C(42)	119 (3)
H(43)–C(43)–C(44)	120 (3)	H(44)–C(44)–C(43)	120 (3)
H(44)–C(44)–C(45)	120 (3)	H(45)–C(45)–C(44)	120 (2)
H(45)–C(45)–C(46)	119 (3)	H(46)–C(46)–C(41)	120 (2)
H(46)–C(46)–C(45)	119 (3)		

Table 1. *Bond lengths* (Å)

P–O(1)	1·577 (2)	P–O(2)	1·563 (1)
P–O(3)	1·453 (2)	N(1)–P	1·676 (2)
C(11)–O(1)	1·418 (2)	C(21)–O(2)	1·407 (2)
C(1)–S	1·666 (2)	C(1)–N(1)	1·413 (3)
C(3)–N(1)	1·491 (3)	C(1)–N(2)	1·328 (3)
C(2)–N(2)	1·457 (3)	C(31)–C(2)	1·517 (3)
C(41)–C(3)	1·512 (3)	C(15)–C(16)	1·379 (3)
C(11)–C(16)	1·370 (3)	C(14)–C(15)	1·376 (4)
C(13)–C(14)	1·383 (4)	C(12)–C(13)	1·371 (3)
C(11)–C(12)	1·376 (3)	C(22)–C(21)	1·372 (3)
C(26)–C(21)	1·366 (3)	C(23)–C(22)	1·387 (3)
C(24)–C(23)	1·367 (4)	C(25)–C(24)	1·365 (5)
C(26)–C(25)	1·392 (3)	C(32)–C(31)	1·383 (4)
C(36)–C(31)	1·379 (3)	C(32)–C(33)	1·380 (3)
C(34)–C(33)	1·369 (4)	C(35)–C(34)	1·365 (4)
C(36)–C(35)	1·384 (3)	C(3)–C(41)	1·512 (3)
C(46)–C(41)	1·374 (3)	C(42)–C(41)	1·368 (3)
C(43)–C(42)	1·384 (4)	C(44)–C(43)	1·366 (4)
C(44)–C(45)	1·367 (4)	C(46)–C(45)	1·386 (3)
H(3)–N(2)	0·92 (2)	H(4)–C(2)	0·99 (2)
H(5)–C(2)	0·94 (3)	H(1)–C(3)	0·99 (2)
H(2)–C(3)	0·94 (2)	H(16)–C(16)	1·04 (3)
H(15)–C(15)	0·84 (2)	H(14)–C(14)	0·96 (2)
H(13)–C(13)	0·90 (3)	H(12)–C(12)	0·96 (2)
H(22)–C(22)	0·95 (2)	H(23)–C(23)	1·01 (3)
H(24)–C(24)	1·04 (2)	H(25)–C(25)	0·93 (3)
H(26)–C(26)	1·02 (3)	H(32)–C(32)	0·97 (3)
H(33)–C(33)	1·10 (3)	H(34)–C(34)	0·95 (2)
H(35)–C(35)	0·90 (3)	H(36)–C(36)	0·92 (3)
H(42)–C(42)	0·96 (3)	H(43)–C(43)	0·97 (3)
H(44)–C(44)	0·97 (2)	H(45)–C(45)	0·99 (3)
H(3)···O(3)	1·86	H(46)–C(46)	0·94 (3)
N(2)···O(3)	2·70		

The molecule of (I*a*) may be described in terms of the following planes: the thiourea residue and four benzene rings. The plane passing through the atoms P, S, N(1), N(2), C(1), C(2), C(3) and H(3) may be used as a base of the molecule. The four benzene rings form angles of 61·6, 79·3, 89·7 and 78·0° with the base plane. It is expected from other known thiourea structures that the atoms of the thiourea grouping, *i.e.* P, S, N(1), N(2), C(1), C(2), C(3) and H(3), would be coplanar. For the atoms of this group |Table 5; plane (*e*)| the maximum and mean deviations from the best plane are 0·142 (P atom) and 0·076 Å, respectively. The O(3) atom, bonded to P, is 0·045 Å out of this plane. The best plane is defined by the atoms: N(1), C(1), N(2) and S |Table 5, plane (*f*)|.

P and H(3) at N(2) are *trans* oriented with respect to S. Most probably the configuration with *cis* H(3) is sterically inhibited. On the other hand, the *trans* position of the phosphoryl group should stabilize the structure by the formation of the intramolecular hydrogen bond N(2)—H(3)···O(3) of 2·70 Å. The sum of distances N(2)—H(3) = 0·92 Å and H(3)··· O(3) = 1·86 Å is 2·78 Å. This hydrogen bond closes a six-membered ring formed by the atoms O(3), P, N(1), C(1), N(2) and H(3). The N(2)···O(3) distance of 2·70 Å is short for this type of hydrogen bond for which corresponding distances have been found to be in the range 2·64–3·18 Å (Corbridge, 1974, p. 252).

The C(1)=S double bond of 1·666 (2) Å in (I*a*) is shorter than the value 1·70 (1) Å found for thiourea (Truter, 1967) and 1·709 (4) Å for *N*-(4-imidazol-4-yl-butyl)-*N'*-methylthiourea (Kamenar, Prout & Ganellin, 1973). The C—N bonds in thiourea are 1·3Ɔ (1) Å and in the *N,N'*-disubstituted thiourea (Kamenar, Prout & Ganellin, 1973) 1·326 (5) and 1·336 (5) Å. The C(S)—N bonds in our compound, which is a three-substituted thiourea, also differ. The bond distance between C(1) and the secondary N atom, N(2), is 1·328 (3) Å whereas that between C(1) and the tertiary N atom, N(1), is 1·413 (3) Å. The P—N(1) bond length of 1·676 (2) Å is substantially shorter than the generally accepted single P—N bond length of 1·77 Å (Cruickshank, 1961). It is longer, however, than the P—N bonds of 1·52, 1·60 Å found in cyclo-triphosphazenes (Corbridge, 1974) where strong d_π–p_π conjugation between P and N is assumed. The shortening of the C(1)=S and P—N(1) bonds as well as the lengthening of the C(1)—N(1) bond in (I*a*) may be rationalized on the same basis.

Table 4. *Hydrogen atom positional parameters with isotropic temperature factors* ($\text{Å}^2 \times 10^3$)

	x	y	z	U
H(1)	0·295 (4)	0·073 (3)	1·078 (2)	392
H(2)	0·104 (5)	0·084 (3)	1·067 (3)	392
H(3)	0·264 (5)	0·382 (3)	0·938 (3)	420
H(4)	0·082 (5)	0·491 (3)	0·881 (3)	460
H(5)	−0·078 (5)	0·407 (3)	0·916 (3)	460
H(16)	0·196 (5)	−0·025 (3)	0·881 (3)	483
H(15)	0·083 (5)	−0·077 (3)	0·704 (3)	612
H(14)	0·183 (5)	−0·006 (3)	0·580 (3)	584
H(13)	0·443 (5)	0·138 (3)	0·627 (3)	556
H(12)	0·585 (5)	0·206 (3)	0·800 (3)	445
H(22)	0·496 (4)	0·465 (3)	1·138 (3)	475
H(23)	0·601 (5)	0·619 (3)	1·282 (3)	616
H(24)	0·797 (5)	0·594 (3)	1·429 (3)	642
H(25)	0·885 (5)	0·404 (3)	1·416 (3)	680
H(26)	0·783 (4)	0·257 (3)	1·283 (2)	542
H(32)	0·061 (4)	0·215 (3)	0·769 (2)	520
H(33)	−0·071 (5)	0·119 (3)	0·595 (3)	672
H(34)	−0·265 (5)	0·213 (3)	0·503 (3)	659
H(35)	−0·342 (5)	0·372 (3)	0·573 (3)	662
H(36)	−0·216 (4)	0·462 (3)	0·746 (2)	508
H(42)	0·325 (4)	0·022 (3)	1·240 (2)	561
H(43)	0·371 (4)	0·073 (3)	1·418 (2)	660
H(44)	0·314 (4)	0·249 (3)	1·490 (2)	631
H(45)	0·199 (4)	0·370 (3)	1·381 (2)	587
H(46)	0·164 (4)	0·317 (3)	1·205 (2)	474

Table 3. *Positional parameters for the non-hydrogen atoms*

	x	y	z		x	y	z
P	0·4544 (1)	0·2547 (0)	1·0144 (0)	C(22)	0·5777 (3)	0·4550 (2)	1·1963 (2)
O(1)	0·4815 (2)	0·1359 (1)	0·9561 (1)	C(23)	0·6395 (4)	0·5425 (2)	1·2814 (2)
O(2)	0·5768 (2)	0·2571 (1)	1·1168 (1)	C(24)	0·7537 (4)	0·5271 (2)	1·3649 (2)
O(3)	0·4890 (2)	0·3551 (1)	0·9605 (1)	C(25)	0·8065 (4)	0·4240 (3)	1·3652 (2)
S	−0·0931 (1)	0·2135 (1)	0·9966 (1)	C(26)	0·7457 (3)	0·3345 (2)	1·2811 (2)
N(1)	0·2517 (2)	0·2249 (1)	1·0319 (1)	C(31)	−0·0657 (3)	0·3493 (2)	0·7744 (2)
N(2)	0·1478 (2)	0·3584 (2)	0·9380 (1)	C(32)	−0·0237 (3)	0·2497 (2)	0·7298 (2)
C(1)	0·1096 (3)	0·2695 (2)	0·9870 (1)	C(33)	−0·0996 (4)	0·2003 (2)	0·6293 (2)
C(2)	0·0164 (3)	0·4112 (2)	0·8832 (2)	C(34)	−0·2174 (4)	0·2493 (3)	0·5722 (2)
C(3)	0·2184 (3)	0·1279 (2)	1·0912 (2)	C(35)	−0·1617 (4)	0·3470 (3)	0·6152 (2)
C(16)	0·2529 (3)	0·0112 (2)	0·8253 (2)	C(36)	−0·1870 (3)	0·3963 (2)	0·7162 (2)
C(15)	0·1765 (4)	−0·0259 (2)	0·7230 (2)	C(41)	0·2458 (3)	0·1661 (2)	1·2054 (1)
C(14)	0·2473 (4)	0·0232 (2)	0·6489 (2)	C(42)	0·3071 (4)	0·0952 (2)	1·2692 (2)
C(13)	0·3976 (4)	0·1108 (2)	0·6779 (2)	C(43)	0·3293 (4)	0·1249 (3)	1·3741 (2)
C(12)	0·4761 (1)	0·1494 (2)	0·7791 (2)	C(44)	0·2925 (4)	0·2262 (3)	1·4158 (2)
C(11)	0·4006 (3)	0·0991 (2)	0·8511 (2)	C(45)	0·2319 (4)	0·2978 (2)	1·3525 (2)
C(21)	0·6319 (3)	0·3519 (2)	1·1986 (2)	C(46)	0·2081 (3)	0·2677 (2)	1·2474 (2)

Table 5. *Deviations of atoms (Å) from the least-squares planes and angles between the planes*

(a) Plane through the atoms of benzene ring (1)
$$-5.8011X + 9.6405Y + 0.7967Z = -0.6971$$

C(11)	0.007	C(13)	−0.001	C(15)	−0.000
C(12)	−0.004	C(14)	0.003	C(16)	−0.004

The e.s.d. (σ) of the above distances is 0.004.

(b) Plane through the atoms of benzene ring (2)
$$-6.4567X - 3.2871Y + 8.1652Z = 4.5470$$

C(21)	0.003	C(23)	0.004	C(25)	−0.000
C(22)	−0.004	C(24)	−0.001	C(26)	−0.001

The e.s.d. (σ) of the above distances is 0.003.

(c) Plane through the atoms of the benzene ring (3)
$$-5.7344X - 5.6911Y + 7.1028Z = 3.8967$$

C(31)	−0.007	C(33)	0.004	C(35)	−0.001
C(32)	−0.002	C(34)	−0.004	C(36)	0.007

The e.s.d. (σ) of the above distances is 0.005.

(d) Plane through the atoms of the benzene ring (4)
$$6.9844X + 3.6468Y - 2.5841Z = -0.7916$$

C(41)	−0.001	C(43)	−0.004	C(45)	0.002
C(42)	0.004	C(44)	0.001	C(46)	−0.002

The e.s.d. (σ) of the above distances is 0.003.

(e) Plane passing through the atoms P, S, N(1), N(2), C(1), C(2), C(3), H(3)
$$-0.8802X + 6.3835Y + 10.0926Z = 11.5758$$

P	−0.142	N(2)	0.049	C(3)	0.061
S	−0.073	C(1)	0.009	H(3)	0.094
N(1)	0.053	C(2)	−0.051		

The e.s.d. (σ) of the above distances is 0.076.

(f) Plane passing through the atoms S, N(1), N(2), C(1)
$$-1.2627X + 6.2706Y + 10.3115Z = 11.7318$$

S	0.001	N(2)	0.001	
N(1)	0.001	C(1)	−0.003	

The e.s.d. (σ) of the above distances is 0.002.

Angles between the planes (°)

(a)–(b)	72.9	(b)–(d)	26.3
(a)–(c)	84.6	(b)–(e)	79.3
(a)–(d)	72.9	(c)–(d)	23.7
(a)–(e)	61.6	(c)–(e)	89.7
(b)–(c)	13.3	(d)–(e)	78.0

Table 6. *Librational corrections (Å) and corrected bond lengths (Å) for benzene rings*

C(11)–C(16)	0.023	1.394	C(21)–C(22)	0.048	1.420
C(15)–C(16)	0.019	1.398	C(21)–C(26)	0.048	1.413
C(14)–C(15)	0.024	1.399	C(22)–C(23)	0.041	1.427
C(13)–C(14)	0.023	1.406	C(23)–C(24)	0.048	1.416
C(12)–C(13)	0.019	1.390	C(24)–C(25)	0.047	1.412
C(12)–C(11)	0.024	1.399	C(25)–C(26)	0.041	1.432

The configuration at the P atom is described as a distorted tetrahedron and only the O(2)—P—O(1) angle of 96.8 (1)° is smaller than normal. An examination of space-filling models shows that a decrease of the O(2)—P—O(1) angle would be caused by steric interactions of both benzene rings attached to the O(1) and O(2) atoms and the two benzyl groups bonded to the N atoms.

The other bond distances in (Ia) are normal. Only the bond lengths in the benzene rings are slightly (up to 10σ) shorter than expected which is undoubtedly due to the thermal motion of these groups. We have calculated librational corrections to the bond lengths in the benzene rings, using the method of Schomaker & Trueblood (1968). The librational analysis for both phenoxy groups gave a good correction of the bond lengths. The results of the calculations are summarized in Table 6. The librational corrections of bond lengths in these rings are above $+10\sigma$.

It is reasonable to assume that the molecular conformation of N,N'-dibenzyl-N-diphenoxyphosphorylthiourea (Ia) in the crystal state is determined by the intermolecular repulsions of the benzene rings and the intermolecular hydrogen bond N(2)—H(3)···O(3).

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