

## Molecular structure of (diethyldithiocarbomoyl)diphenylthiophosphinate

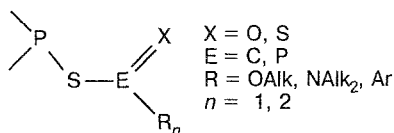
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X-Ray study of (diethyldithiocarbomoyl)diphenylthiophosphinate was carried out. A *Z*-conformation of the diethyldithiocarbomoyl ligand, which results in a short nonvalent intramolecular P...S contact (3.315 Å), is realized in the molecule. Steric hindrances in the molecule increase the P—S—C bond angle to 106.39°.

**Key words:** dithiophosphonic acid, dithiocarbamates, mixed anhydrides, nonvalent interactions, X-ray analysis, conformational analysis.

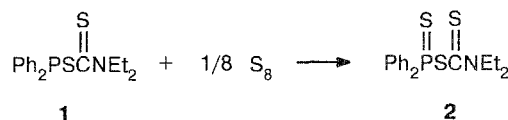
Compounds in a series of derivatives of acids of three-valent phosphorus, in particular, mixed anhydrides of P<sup>III</sup> thio acids and thioorganic acids (dithiocarbamic, xanthogenic, thiocarboxylic, and dithiophosphonic), have been synthesized previously.<sup>1–3</sup> Their structural peculiarity is short intramolecular 1,4-contacts of unbound heteroatoms, one of which is the P<sup>III</sup> atom. In these molecules, intramolecular distances between atoms of thionic sulfur of acid residues and the tricoordinated phosphorus atom are 2.95–3.15 Å, while the sum of van der Waals radii of sulfur and phosphorus atoms is equal to 3.75 Å (see Ref. 4).



The analysis of data performed in terms of modern views of structural chemistry allows one to draw the conclusion that the short contact of 1,4-type between the phosphorus atom and the terminal X atom (X = S, O) is an important peculiarity of mixed anhydrides of thio acids of three-valent phosphorus, which is realized independently of the number and type of thio acid moieties at the three-valent phosphorus atom.<sup>3</sup>

A question arises about the possibility of this type intramolecular contacts of heteroatoms in derivatives of five-valent tetracoordinated phosphorus. To solve this problem, we tried to oxidize or add sulfur to one of the compounds already studied.<sup>1–3</sup> However, the majority of them are inert toward sulfur, and their oxidation results in the formation of difficultly separated complex mixtures. The addition of element sulfur in boiling toluene was successful only in the case of diethyldithio-

carbomoyldiphenylphosphinite (**1**). This reaction results in the formation of (diethyldithiocarbomoyl)diphenylthiophosphinate (**2**), which is a mixed diethylthiocarbamate and diphenyldithiophosphinate:



X-ray study of compound **2** showed that the dithiocarbamoyl moiety of its molecule, as in molecule **1**, has a planar *Z*-conformation (torsion angle P—S(1)—C—S(2) is 8.7°). Unlike the similar compound of tricoordinated phosphorus **1**, the turn of the moieties around the P—S bond is considerably increased in molecule **2**: torsion angle LEP—P—S(1)—C in **1** is equal to 34.6°, S=P—S(1)—C angle in **2** is equal to 63.1°. Bond lengths of P—S(1) in molecules of **1** and **2** are almost equal: 2.123(1) and 2.122(1) Å, respectively. In molecule **2**, the S(1)—C bond is somewhat lengthened (1.790(3) Å) (in **1**, 1.777(3) Å) and the P—S(1)—C bond angle is noticeably increased (to 106.39(9)°) compared to that in **1** (101.9(1)°). As a result, the P...S(2) distance in molecule **2** is increased to 3.315(1) Å compared to that in **1** (3.179(1) Å), which is, nevertheless, 0.4 Å lower than the sum of the van der Waals radii of phosphorus and sulfur.<sup>4</sup> It is likely that these effects are predominantly caused by steric factors: the S atom occupies the region of localization of the LEP of the S(2) atom: the S...S(2) distance is 3.702(1) Å, which is equal to the doubled van der Waals radius of the sulfur atom, but when the conformation found in a molecule of **1** is retained, this contact would be considerably shorter. However, it has been mentioned in our previous works that observed conformations of the

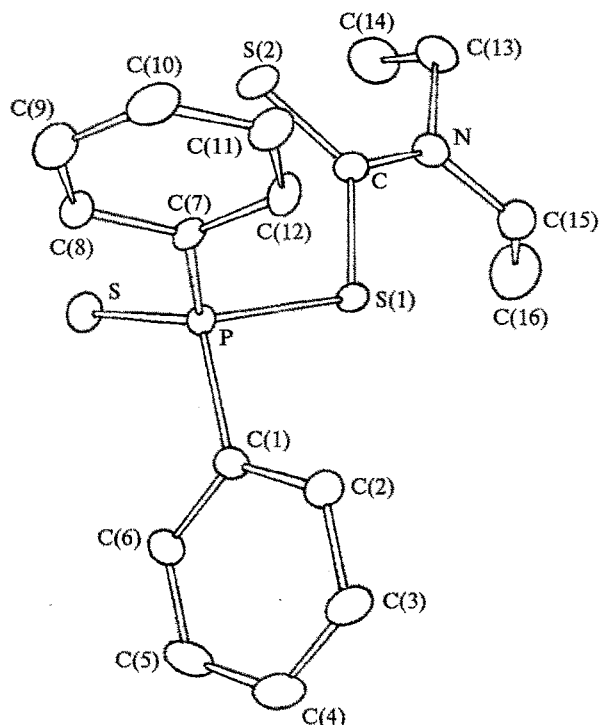


Fig. 1. Geometry of molecule 2 in crystal. H atoms are not shown.

molecules of type 1 can be additionally stabilized due to  $n-\sigma^*$ -interaction between the orbital of the thio sulfur and the antibonding orbital of the opposite bond, because the S atom in these molecules is located just on its continuation. It is noteworthy that the difference in bond lengths of P—C is observed both in molecule 1 and molecule 2: P—C(1) 1.822(2), P—C(7) 1.805(2) Å in molecule 2 and P(1)—C(6) 1.843(2), P(1)—C(12) 1.827(2) Å in molecule 1. The S(2) atoms are arranged approximately on a continuation of the longer P—C bonds (the S(2)—P(1)—C(6) angles are 157.1(1)° in molecule 1, and S(2)—P—C(1) are 155.1(1)° in 2). Such peculiarities can be caused by hypervalent interaction of the  $n(S)-\sigma^*(P-C)$  type.

It is of interest that a hindered conformation with the LEP of the phosphorus atom or the P=S bond is observed along the lengthened C(Ph)—P bonds, while the second Ph substituent has a *gauche*-conformation.

Thus, study of the structure of 2 allows us to conclude that the established regularities of the spatial structure of molecules of mixed anhydrides of thio acids of three-valent phosphorus can be extended to similar compounds of five-valent tetracoordinated phosphorus *i.e.*, a short contact between the  $P^V$  atom and the thio sulfur atom of the dithiocarbamoyl residue in compound 2 is conformationally forced and primarily caused by the planar *Z*-configuration and the peculiarities of the *gauche*-orientation along P—S(1) bonds.

Table 1. Coordinates of nonhydrogen atoms of the structure of 2, equivalent isotropic temperature parameters of nonhydrogen

atoms  $B_{iso}^{eq} = \sum_{i=1}^3 \sum_{j=1}^3 (a_i^* a_j^*) B(i, j)$ , and isotropic factors of hydrogen atoms  $B_{iso}$

Atom	x	y	z	$B/\text{\AA}^2$
S	0.282	0.0915(5)	0.100	1.64(1)
S(1)	0.06510(6)	0.05992(4)	0.24752(5)	1.207(9)
S(2)	0.03438(7)	-0.11091(5)	0.09950(6)	2.05(1)
P	0.26278(6)	0.05518(4)	0.23026(5)	0.960(9)
N	-0.1683(2)	-0.0283(2)	0.1545(2)	1.61(4)
C	-0.0360(2)	-0.0315(2)	0.1612(2)	1.32(4)
C(1)	0.3324(2)	0.1494(2)	0.3287(2)	1.14(4)
C(2)	0.3245(3)	0.1358(2)	0.4270(2)	1.44(4)
C(3)	0.3762(3)	0.2103(2)	0.5003(2)	1.87(5)
C(4)	0.4363(3)	0.2967(2)	0.4763(2)	2.10(5)
C(5)	0.4452(3)	0.3093(2)	0.3796(2)	2.09(5)
C(6)	0.3934(2)	0.2359(2)	0.3055(2)	1.47(4)
C(7)	0.3433(2)	-0.0617(2)	0.2840(2)	1.06(3)
C(8)	0.4570(2)	-0.0932(2)	0.2565(2)	1.43(4)
C(9)	0.5318(3)	-0.1765(2)	0.3037(2)	1.97(4)
C(10)	0.4945(3)	-0.2287(2)	0.3771(2)	1.88(5)
C(11)	0.3802(3)	-0.1991(2)	0.4029(2)	1.78(4)
C(12)	0.3048(2)	-0.1161(2)	0.3570(2)	1.47(4)
C(13)	-0.2667(3)	-0.0949(2)	0.0813(2)	1.96(5)
C(14)	-0.3075(4)	-0.0552(3)	-0.0274(3)	2.93(6)
C(15)	-0.2245(3)	0.0350(2)	0.2193(2)	2.24(5)
C(16)	-0.3081(4)	0.1232(3)	0.1640(4)	4.19(8)
H(2)	0.293(4)	0.073(3)	0.443(3)	0.9(7)
H(3)	0.373(2)	0.197(2)	0.569(2)	2.0(4)
H(4)	0.478(3)	0.347(3)	0.529(2)	1.1(6)
H(5)	0.489(3)	0.366(2)	0.367(2)	0.1(5)
H(6)	0.409(4)	0.245(3)	0.247(4)	3.1(9)
H(8)	0.493(4)	-0.055(3)	0.204(3)	2.2(8)
H(9)	0.607(4)	-0.202(3)	0.282(3)	2.1(8)
H(10)	0.537(4)	-0.280(3)	0.398(3)	2.9(9)
H(11)	0.349(4)	-0.229(3)	0.448(3)	2.9(8)
H(12)	0.237(3)	-0.095(2)	0.373(2)	0.8(5)
H(13.1)	-0.348(5)	-0.103(3)	0.097(4)	3.2(9)
H(13.2)	-0.226(4)	-0.166(3)	0.088(3)	1.9(7)
H(14.1)	-0.346(7)	0.011(5)	-0.040(5)	8(2)
H(14.2)	-0.232(4)	-0.049(3)	-0.045(3)	2.7(8)
H(14.3)	-0.367(5)	-0.098(4)	-0.077(4)	3(1)
H(15.1)	-0.288(3)	-0.010(3)	0.246(3)	1.8(7)
H(15.2)	-0.149(4)	0.060(3)	0.277(3)	1.9(7)
H(16.1)	-0.362(7)	0.105(5)	0.104(5)	7(2)
H(16.2)	-0.336(6)	0.161(4)	0.212(4)	5(1)
H(16.3)	-0.266(7)	0.177(6)	0.148(5)	7(2)

## Experimental

Crystals of 2 are monoclinic, m.p. 88 °C, at -150 °C,  $a = 10.288(3)$  Å,  $b = 13.269(2)$  Å,  $c = 13.840(3)$  Å,  $\beta = 108.24(2)^\circ$ ,  $V = 1794(1)$  Å<sup>3</sup>,  $d_{calc} = 1.35$  g cm<sup>-3</sup>,  $Z = 4$ , space group *Cc*, C<sub>17</sub>H<sub>20</sub>NPS<sub>3</sub>.

Cell parameters and intensities of 2298 independent reflections with  $I \geq 3\sigma$  were measured at -150 °C on an ENRAF-NONIUS CAD-4 automated four-circle diffracto-

**Table 2.** Bond lengths ( $d$ ), valence ( $\omega$ ), and torsion angles ( $\tau$ ) of the structure of **2**

Bond	$d/\text{\AA}$	Angle	$\omega/\text{deg}$	Angle	$\tau/\text{deg}$
S—P	1.937(1)	P—S(1)—C	106.39(9)	S—P—S(1)—C	63.1
S(1)—P	2.122(1)	S—P—S(1)	118.65(4)	C—S(1)—P—C(1)	−177.9
S(1)—C	1.790(3)	S—P—C(1)	113.25(9)	C—S(1)—P—C(7)	−70.9
S(2)—C	1.659(3)	S—P—C(7)	115.43(9)	P—S(1)—C—S(2)	8.7
S(2)...P	3.315(1)	S(1)—P—C(1)	93.54(8)	P—S(1)—C—N	−172.2
P—C(1)	1.822(2)	S(1)—P—C(7)	108.17(9)	S(1)—C—N—C(15)	−6.7
P—C(7)	1.805(2)	C(1)—P—C(7)	105.0(1)	S(2)—C—N—C(13)	−4.7
N—C	1.335(4)	C—N—C(13)	119.5(3)		
N—C(13)	1.480(3)	C—N—C(15)	124.2(2)		
N—C(15)	1.473(4)	C(13)—N—C(15)	116.3(2)		
		S(1)—C—S(2)	121.2(2)		
		S(1)—C—N	113.1(2)		
		S(2)—C—N	125.7(2)		

meter ( $\lambda(\text{Mo-K}\alpha)$ , graphite monochromator,  $\omega/(5/30)$ -scanning,  $\theta \leq 30^\circ$ ). The structure was resolved by the direct method according to the MULTAN program and first refined in the isotropic approximation and then in the anisotropic approximation. All hydrogen atoms were revealed from the difference series of electron density and refined isotropically in the final cycles of the full-matrix least-squares method. The final values of coefficients of divergence are  $R = 0.029$ ,  $R_w = 0.040$ .

Coordinates of atoms in the structure of **2** are presented in Table 1, and main geometric parameters are presented in Table 2.

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