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Reaction of Elemental Phosphorus (P_4) with Thiophenol in the Presence of Amines

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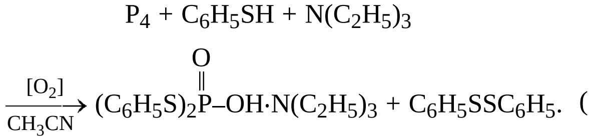
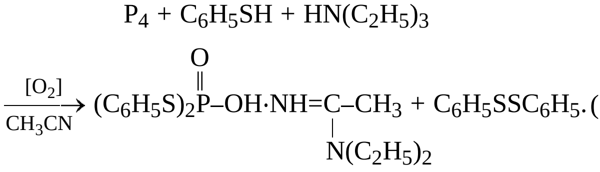
Abstract—Elemantal phosphorus (P_4) reacts with thiophenol and amines at elevated temperature in acetonitrile to give ammonium or acetimidamidium *S,S*-diphenyl phosphorodithioates, depending on the nature of the amine. Analogous salts were isolated in the reaction of triphenyl phosphorotrithioite with thiophenol and corresponding amines in acetonitrile. The molecular and crystal structures of the acetimidamidium salt was confirmed by X-ray diffraction. With two different types of intermolecular interactions taken into account, a 1*D* supramolecular structure formed by infinite cylinders, rather that 0*D* structures, dimers of anion–cation pairs formed by classical hydrogen bonds exclusively, was obtained. *S,S,S*-Triphenyl phosphorotrithioate is formed by the reactions of P_4 with thiophenol and a catalytic amount of an amine or in the presence of diphenyl disulfide.

We recently reported [1] on with new reaction of elemental phosphorus (P_4) with thiophenol and triethylamine, yielding triethylammonium *S,S*-diphenyl phosphorodithioate (**I**). The reaction was carried out in acetonitrile without special protection of the reaction medium from air oxygen.


(1)

$$P_4 + C_6H_5SH + N(C_2H_5)_3 \xrightarrow[CH_3CN]{[O_2]} (C_6H_5S)_2\overset{O}{\overset{\|}{P}}–OH\cdot N(C_2H_5)_3 + C_6H_5SSC_6H_5. \quad (1)$$

Proceeding with these studies, we focused on reactions of P_4 with thiophenol in the presence of a secondary amine (diethylamine) or in the presence of catalytic amounts of an amine (triethylamine, diethylamine, or dimethylaniline). It was found that the reaction of P_4 with thiophenol in the presence of diethylamine results in formation of a crystalline compound whose spectral characteristics differ from those of the expected diethylamonium *S,S*-diphenyl phosphorodithioate (the IR spectrum contained a band at 1640 cm^{-1}, characteristic of the C=C bond). Basing on this data, we assigned the product the structure of *N,N*-diethylacetimidamidium *S,S*-diphenyl phosphorodithioate (**II**).


(2)

$$P_4 + C_6H_5SH + HN(C_2H_5)_3 \xrightarrow[CH_3CN]{[O_2]} (C_6H_5S)_2\overset{O}{\overset{\|}{P}}–OH\cdot NH=\underset{N(C_2H_5)_2}{\underset{|}{C}}–CH_3 + C_6H_5SSC_6H_5. \quad (2)$$

The amidine structure of salt **II** was confirmed by X-ray diffraction analysis. Figure 1 depicts the molecular geometry of the isolated compound, and Table 1 lists selected geometric parameters of the molecule.

The diphenyl phosphorodithioate anion has an unsymmetrical structure. The benzene rings are turned by different angles about the C–S bonds: Along the S^1–C^1 bond, an almost orthogonal conformation is realized [$P^1S^1C^1C^2$ angle –77.8(1)°] and along S^2–C^7, a staggered conformation [$P^1S^2C^7C^1C^2$ angle 38.9(1)°]. This difference also reveals itself in the principal geometric parameters of the anion, specifically, the bond lengths and bond angle involving S^2 are significantly increased compared to the respective values for S^1 (Table 2).

Probably, the unsymmetrical conformation of the anion in structure **II** is caused by intermolecular interactions (vide infra) and is stabilized by the intramolecular hydrogen bond C^{12}–$H^{12}\cdots S^1$. Note that the triphenyl phosphorotrithioite molecule of C^3 symmetry [2, 3] has an orthogonal conformation along the S–C bonds. The conformation of the PhS groups in triphenyl phosphorotrithioate [4] and tetrakis(phenylsulfanyl)phosphonium hexachloroniobate [5] is also close to orthogonal and the bond lengths and angles of the sulfur atoms in these structures are close to those we found in **II**.

The P–O bond lengths are equal to each other within experimental error.

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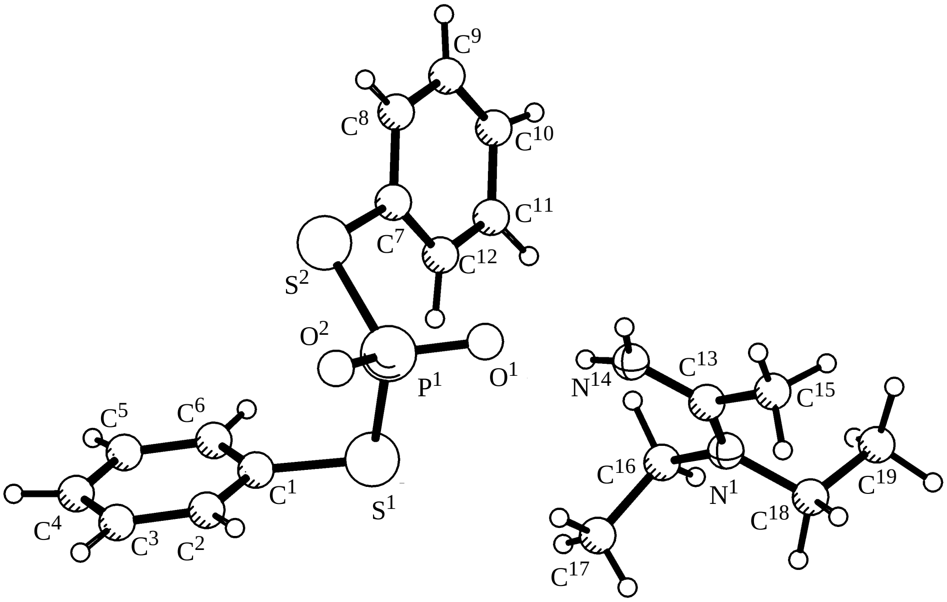


Fig. 1. Molecular geometry of compound **II** in crystal.

Table 1. Atomic coordinates in structure **II**, equivalent isotropic thermal parameters of non-hydrogen atoms and isotropic temperature parameters of hydrogen atoms $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j) B(i, j)$ (Å^2)

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
S^1	0.22528(5)	–0.35061(3)	0.10095(3)	3.395(7)	H^2	–0.107(3)	–0.417(2)	0.077(2)	6.9(5)
S^2	0.02084(5)	–0.15443(3)	0.29465(3)	3.361(8)	H^3	–0.329(3)	–0.337(2)	–0.020(2)	7.9(6)
P^1	0.09582(5)	–0.33564(3)	0.27401(3)	2.574(6)	H^4	–0.285(3)	–0.138(2)	–0.113(2)	9.7(7)
O^1	0.2447(1)	–0.38284(8)	0.32577(8)	3.49(2)	H^5	–0.045(2)	–0.051(1)	–0.122(1)	5.1(4)
O^2	–0.0887(1)	–0.38311(9)	0.30955(8)	3.68(2)	H^6	0.167(3)	–0.132(2)	–0.016(2)	6.2(5)
N^1	0.6259(2)	–0.6525(1)	0.36488(9)	2.98(2)	H^8	0.095(3)	0.013(2)	0.403(1)	5.9(4)
N^{14}	0.3351(2)	–0.5804(1)	0.46999(9)	3.02(2)	H^9	0.344(3)	0.116(2)	0.394(2)	8.1(6)
C^1	0.0528(2)	–0.2853(1)	0.0367(1)	2.94(3)	H^{10}	0.643(3)	0.046(2)	0.272(2)	7.7(6)
C^2	–0.0953(2)	–0.3447(2)	0.0378(1)	4.50(4)	H^{11}	0.676(3)	–0.089(2)	0.156(1)	6.8(5)
C^3	–0.2220(3)	–0.2951(2)	–0.0185(2)	5.58(4)	H^{12}	0.409(2)	–0.176(1)	0.156(1)	4.9(4)
C^4	–0.2017(3)	–0.1853(2)	–0.0752(1)	5.44(4)	H^{141}	0.313(2)	–0.520(1)	0.419(1)	4.6(4)
C^5	–0.0563(3)	–0.1249(2)	–0.0756(1)	4.96(4)	H^{142}	0.253(2)	–0.581(1)	0.535(1)	4.4(4)
C^6	0.0711(2)	–0.1739(1)	–0.0202(1)	3.85(3)	H^{151}	0.403(3)	–0.729(1)	0.619(1)	5.7(4)
C^7	0.2280(2)	–0.0892(1)	0.2838(1)	3.08(3)	H^{152}	0.606(2)	–0.725(1)	0.580(1)	3.7(3)
C^8	0.2121(3)	–0.0009(1)	0.3521(1)	4.45(4)	H^{153}	0.501(4)	–0.819(2)	0.532(2)	9.8(7)
C^9	0.3677(3)	0.0562(2)	0.3460(2)	5.66(4)	H^{161}	0.563(2)	–0.487(2)	0.298(1)	5.7(4)
C^{10}	0.5350(3)	0.0255(2)	0.2736(2)	5.37(4)	H^{162}	0.741(2)	–0.564(1)	0.229(1)	4.4(4)
C^{11}	0.5530(2)	–0.0607(2)	0.2047(2)	4.75(4)	H^{171}	0.571(3)	–0.687(2)	0.174(2)	6.4(5)
C^{12}	0.3999(2)	–0.1182(1)	0.2085(1)	3.85(3)	H^{172}	0.385(2)	–0.614(1)	0.238(1)	4.8(4)
C^{13}	0.4857(2)	–0.6539(1)	0.4584(1)	2.59(2)	H^{173}	0.535(3)	–0.558(2)	0.129(1)	6.6(5)
C^{15}	0.4943(2)	–0.7398(1)	0.5567(1)	3.62(3)	H^{181}	0.827(3)	–0.767(1)	0.274(1)	5.5(4)
C^{16}	0.6204(2)	–0.5685(1)	0.2672(1)	3.75(3)	H^{182}	0.764(2)	–0.820(1)	0.401(1)	5.1(4)
C^{17}	0.5195(3)	–0.6122(2)	0.1950(1)	4.90(4)	H^{191}	0.899(3)	–0.677(2)	0.471(1)	6.3(5)
C^{18}	0.7951(2)	–0.7348(1)	0.3507(1)	3.85(3)	H^{192}	1.068(3)	–0.743(2)	0.360(2)	9.0(6)
C^{19}	0.9501(2)	–0.6841(2)	0.3774(2)	4.85(4)	H^{193}	0.977(3)	–0.624(2)	0.330(1)	5.9(5)

Table 2. Bond lengths (*d*, Å) and bond (ω, deg) and torsion (τ, deg) angles in structure **II**

Bond	*d*	Bond	*d*
S^1-P^1	2.1073(4)	C^7-C^8	1.377(2)
S^1-C^1	1.777(2)	C^7-C^{12}	1.387(2)
S^2-P^1	2.1169(5)	C^8-C^9	1.396(3)
S^2-C^7	1.782(2)	C^9-C^{10}	1.351(2)
P^1-O^1	1.479(1)	$C^{10}-C^{11}$	1.359(3)
P^1-O^2	1.483(1)	$C^{11}-C^{12}$	1.389(3)
N^1-C^{13}	1.321(1)	$C^{13}-C^{15}$	1.491(2)
N^1-C^{16}	1.468(2)	$C^{16}-C^{17}$	1.507(3)
N^1-C^{18}	1.475(2)	C^3-C^4	1.371(3)
$N^{14}-C^{13}$	1.315(2)	C^4-C^5	1.370(3)
$N^{14}-H^{141}$	0.92(2)	C^5-C^6	1.379(3)
$N^{14}-H^{142}$	0.86(1)	$C^{18}-C^{19}$	1.509(3)
C^1-C^2	1.378(3)	C^2-C^3	1.384(3)
C^1-C^6	1.387(2)		
Angle	ω	Angle	ω
$P^1S^1C^1$	103.57(4)	$S^2C^7C^8$	116.9(1)
$P^1S^2C^7$	107.24(5)	$S^2C^7C^{12}$	124.4(1)
$S^1P^1S^2$	107.27(2)	$S^1C^1C^2$	121.6(1)
$S^1P^1O^1$	103.07(4)	$S^1C^1C^6$	119.5(1)
$S^1P^1O^2$	110.47(5)	$N^1C^{18}C^{19}$	112.8(1)
$S^2P^1O^1$	111.59(5)	$N^{14}C^{13}C^{15}$	117.2(1)
$S^2P^1O^2$	101.68(4)	$N^1C^{16}C^{17}$	111.8(1)
$O^1P^1O^2$	122.19(6)	$N^1C^{13}N^{14}$	122.4(1)
$C^{13}N^1C^{16}$	121.3(1)	$N^1C^{13}C^{15}$	120.4(1)
$C^{13}N^1C^{18}$	122.9(1)	$C^{13}N^{14}H^{141}$	127.2(9)
$C^{16}N^1C^{18}$	115.8(1)	$C^{13}N^{14}H^{142}$	118.0(1)
Angle	τ	Angle	τ
$C^1S^1P^1S^2$	–58.5(1)	$C^7S^2P^1O^1$	36.2(1)
$C^1S^1P^1O^1$	–176.3(1)	$C^7S^2P^1O^2$	167.9(1)
$C^1S^1P^1O^2$	51.6(1)	$P^1S^2C^7C^8$	–143.9(1)
$P^1S^1C^1C^2$	–77.8(1)	$P^1S^2C^7C^{12}$	38.9(1)
$P^1S^1C^1C^6$	105.0(1)	$C^{16}N^1C^{13}N^{14}$	–0.6(2)
$C^7S^2P^1S^1$	–76.0(1)	$C^{18}N^1C^{13}N^{14}$	–179.7(1)
$C^{16}N^1C^{13}C^{15}$	–179.9(1)	$C^{18}N^1C^{13}C^{15}$	0.9(2)
$C^{18}N^1C^{16}C^{17}$	95.2(2)	$C^{16}N^1C^{18}C^{19}$	85.8(1)
$C^{13}N^1C^{18}C^{19}$	–94.9(1)	$C^{13}N^1C^{16}C^{17}$	–84.0(2)

The acetimidamidium cation is almost planar, and the torsion $C^{16}N^1C^{13}N^{14}$ angle in it is –0.6(2), what is caused by conjugation of the lone electron pair of the N^1 atom with the $C^{13}=N^{14}$ bond. As a result, the N^1-C^{13} bond is noticeably shorter than the other bonds at N^1. It is firmly established that the protonation site is N^{14}, but, therewith, the $C^{13}=N^{14}$ bond is only slightly elongated.

Table 3. Parameters of hydrogen bonds in the crystal of compound **II**

D–H···A triad[a]	D–H, Å	H···A, Å	D···A, Å	∠(D–H···A), deg
$N^{14}-H^{141}\cdots O^1$	0.92(2)	1.96(2)	2.869(2)	173(1)
$N^{14}-H^{142}\cdots O^{2'}$	0.86(1)	1.99(2)	2.838(2)	168(1)
$C^{15}-H^{151}\cdots O^{2'}$	0.88(2)	2.52(2)	3.262(2)	142(2)
$C^{15}-H^{152}\cdots O^{1''}$	1.01(2)	2.39(2)	3.316(2)	152(1)
$C^{16}-H^{161}\cdots O^1$	1.05(2)	2.50(2)	3.290(2)	131(1)
$C^{19}-H^{191}\cdots O^{1''}$	1.13(2)	2.58(2)	3.695()	168(1)
$C^{12}-H^{12}\cdots S^1$	0.97(2)	2.83(2)	3.675(2)	146(1)

[a] Symmetry codes: ' – *x*, 1 – *y*, –*z*; '' – 1 – *x*, 1 – *y*, 1 – *z*.

Intermolecular interactions in the crystal in hand are diverse and include classical hydrogen bonds like N–H···O and weak intermolecular interactions like C–H···S, C–H.··O, and C–H···π. The parameters of the strongest interactions that correspond to the shortened contacts are listed in Table 3.

Depending on the type of the interaction, different types of supramolecular structures can form in the crystal. For example, if only classical $N^{14}-H^{141}\cdots O^1$ and $N^{14}-H^{142}\cdots O^{2'}$ hydrogen bonds are considered, a structure comprising centrosymmetric hydrogen-bonded anion–cation dimers results (Fig. 2).

In this structure, the conformation of the anionic fragment is stabilized by intramolecular hydrogen bonds like C–H···S, and the O^2 atom is involved in a bifurcate hydrogen bond with the methylene H^{161} atom. However, these interactions are observed within dimers and do not affect the type of the supramolecular structure (0*D*). The methyl H^{152} and H^{191} atoms of the cation are involved into a C–H···O bifurcate hydrogen bond with the phosphoryl $O^{1''}$ atom of another molecule (1 – *x*, 1 – *y*, 1 – *z*), thus binding the dimers in infinite stacks along the 0*x* crystallographic axis (Fig. 3), where each dimer takes part in two such contacts, both as donor and as acceptor. Certain C–H···π interactions are also realized.

Hence, accounting for two different types of intermolecular contacts leads to a 1*D* supramolecular structure, viz. supramolecular ansembles in the form of infinite cylinders, rather than to 0*D* structures, viz. molecular dimers formed by means of classical hydrogen bonds. Therewith, a fairly high packing coefficient is attained (66.7%). Noteworthy is also localization of hydrophilic hydrophilic and hydrophobic molecular fragments. Within the frames of this notion, the three-dimensional steric structure of crystals of salt **II** can be considered to comprise cylindrical substructures packed along the 0*x* crystal-

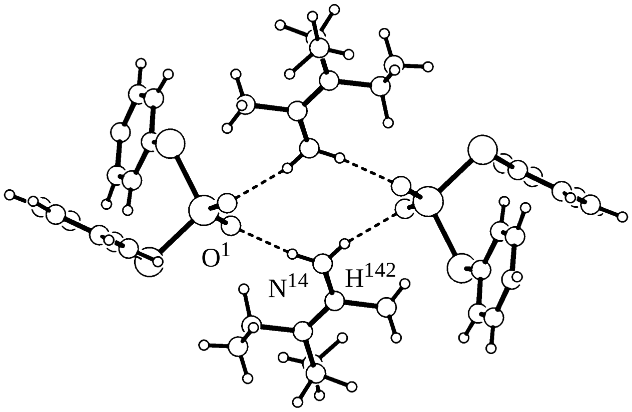


Fig. 2. Centrosymmetric hydrogen-bonded dimers in the crystal of compound **II** (hydrogen bonds are shown by dashed lines).

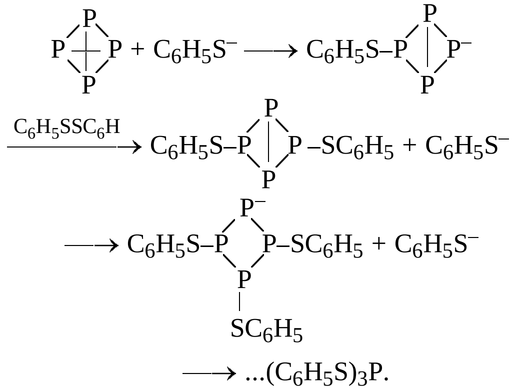
lographic axis as shown in Fig. 4. As seen, the inner part of the cylinder includes hydrogen bonds and is a hydrophilic field, while the outer hydrophobic shell consists of methyl and phenyl substituents.

Acetonitrile we use as solvent evidently reacts with thiophenol to form an intermediate thioaminoester that further reacts with the amine to give *N*,*N*-diethylacetamidine. The formation of thioiminoesters by reactions of thiols with nitriles [6] and their use in amidine synthesis [7, 8] have been reported.

The second isolated product is diphenyl disulfide whose formation provides evidence to show that thiophenol is oxidized in the presence of the basic reagent [9].

$$4C_6H_5SH + O_2 \longrightarrow 2C_6H_5SSC_6H_5 + 2H_2O.$$

The opening of the elemental phosphorus tetrahedron in the reactions of P_4 with thiophenol in the presence of both triethylamine and diethylamine occurs by a common scheme. Consecutive cleavage of the P_4 tetrahedron should give triphenyl phosphotrithioite (**III**).



III

Actually, the ^{31}P NMR spectra of the reaction mixtures contain the corresponding signal at δ_P 130 ppm. Then triphenyl phosphotrithioite reacts with thiophenol and an amine to give the final products, ammonium and acetimidamidium *S*,*S*-diphenyl phosphorodithiophosphates.

The involvement of product **III** in further transformations was proved with the help of model reactions. Hence, the reactions of triphenyl phosphorotrithioite, with thiophenol in the presence of diethyl-

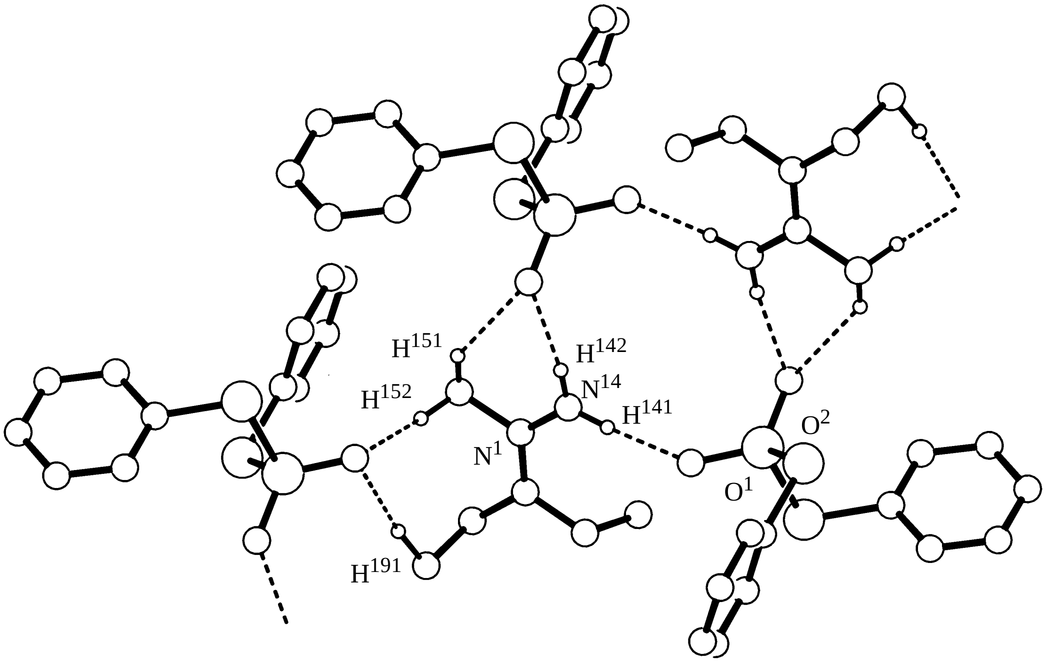
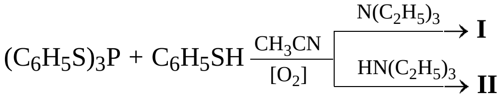


Fig. 3. Chains of C–H···O-bonded dimers in the crystal of compound **II** (hydrogen bonds are shown by dashed lines).

or triethylamine in acetonitrile in a 1 : 1–1.5 : 1.5–2 molar ratio gave salts **I** and **II** whose physicochemical and spectral characteristics were completely coincident with those of the compounds obtained by reactions (1) and (2).



$$(C_6H_5S)_3P + C_6H_5SH \xrightarrow[{[O_2]}]{CH_3CN} \begin{cases} \xrightarrow{N(C_2H_5)_3} \mathbf{I} \\ \xrightarrow{HN(C_2H_5)_3} \mathbf{II} \end{cases}$$

One of the possible pathways of the formation of these products is presented below.

$$(C_6H_5S)_3P + C_6H_5SH \longrightarrow \begin{bmatrix} (C_6H_5S)_3\overset{+}{P}H \\ {}^{-}SC_6H_5 \end{bmatrix}$$

$$\xrightarrow{[O_2]} \begin{bmatrix} (C_6H_5S)_3\overset{+}{P}OH \\ {}^{-}SC_6H_5 \end{bmatrix}$$

$$\xrightarrow[-C_6H_5SSC_6H_5]{NR_2R'} (C_6H_5S)_2P\text{–}OH\cdot NR_2R'$$

$$\xrightarrow{[O_2]} \mathbf{I}, \mathbf{II},$$

$$R = R' = Et\ (\mathbf{I});\ R = Et,\ R' = \underset{\underset{NH}{\|}}{C}\text{–}CH_3\ (\mathbf{II}).$$

Continuing research into thje reaction of white phosphorus with thiophenol, we performed this reaction in the presence of catalytic amounts of amines [1 : 3.1 : (0.15–0.4) P_4 : thiophenol : amine molar ratio]. With such amines as triethylamine, diethylamine, and dimethylaniline, *S,S,S*-triphenyl phosphorotrithioate (**IV**) was isolated as the major reaction product.

$$P_4 + C_6H_5SH \xrightarrow[{[O_2]}]{R_3N} \underset{\mathbf{IV}}{(C_6H_5S)_3P{=}O}.$$

It is known that diphenyl disulfide has a weak S–S bond. Thiols can cleave this bond [10]. Suggesting that the phosphorus tetrahedron is cleaved under the action of the PhS^- anion, we took diphenyl disulfide as catalyst for the reaction at a 1 : 3 : 0.2 P_4–C_6H_5SH–$C_6H_5SSC_6H_5$ molar ratio. It was established that the thiophenol–diphenyl disulfide system opens the P_4 tetrahedron to form phosphate **IV**.

$$P_4 + C_6H_5SH \xrightarrow[{[O_2]}]{C_6H_5SSC_6H_5} \mathbf{IV}.$$

The ^{31}P NMR spectra of the reaction mixtures with both amine and diphenyl disulfide catalysts displayed the signal of triphenyl phophorotrithioite that was transformed to triphenyl phosphorotrithioate by known procedures [10].

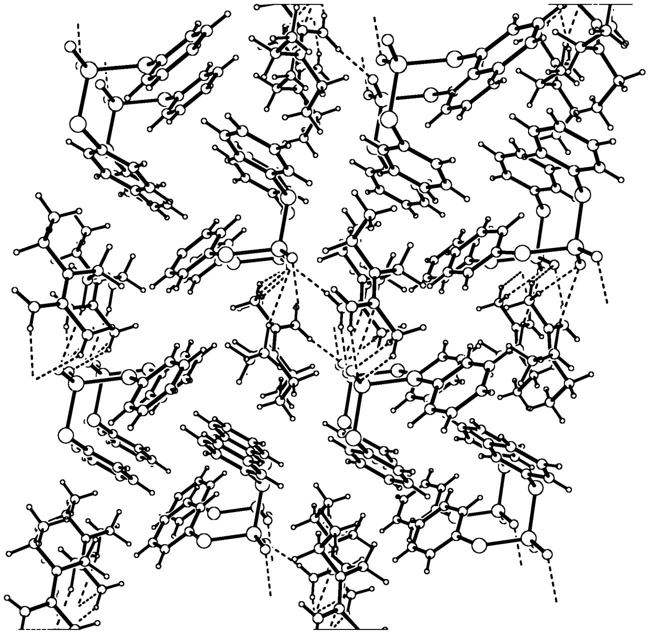


Fig. 4. Crystal packing of compound **II** as viewed along the 0*x* axis.

EXPERIMENTAL

The IR spectra were obtained on a Specord IR-75 spectrometer for suspensions in mineral oil between KBr plates. The ^1H and ^{31}P NMR spectra were recorded on a Bruker CXP-100 spectrometer (36.47 MHz) against 85% phosphoric acid.

X-ray diffraction analysis of compound II was performed on an Enraf–Nonius CAD-4 automated four-circle diffractometer. Crystals of compound **II**, $C_{18}H_{25}N_2O_2PS_2$, triclinic. At 20°C, a 7.572(3), b 11.493(2), c 12.501(2) Å, α 82.93(2)°, β 72.43(5)°, γ 82.97(2)°, V 1025(1) Å^3, Z 2, d_{calc} 1.28 g cm^{-3}, space group P-1.

The unit cell parameters and the intensities of 4485 reflections, 3952 of which had $I > 3\sigma$, were measured at 20°C (λMoK_α radiation, graphite monochromator, $\omega/2\theta$ scanning, $\theta \leq 26.29°$). No intensity decay of the three control reflections was observed during measurements. Empirical absorption correction was used (μMo 3.39 cm^{-1}). The structure was solved by the using the SIR program [12] and refined first isotropically and then anisotropically. Hydrogen atoms were revealed by difference synthesis and refined isotropically in final cycles of least-squares refinement. Final divergence factors: R 0.035 and R_W 0.053, on 3962 unique reflections with $F^2 \geq 3\sigma$. All calculations were carried out using the MolEN program package [12] on an AlphaStation 200 computer.

The coordinates of atoms and their thermal parameters are listed in Table 1, and the geometric parameters of the structure, in Table 2. The drawings were performed and the intermolecular interactions were calculated by the PLATON program [13].

Reaction of white phosphorus with thiophenol and diethylamine. To a mixture of 0.5 g of P_4, 4.5 g of thiophenol, and 4 ml of acetonitrile, 1.6 g of diethylamine was added dropwise. The reaction mixture was heated for 18 h at 80–90°C and then for 6 h at 95– 100°C. The solvent was removed in a vacuum to give a viscous yellow liquid that crystallized on cooling. It was thrice crystallized from acetone to obtain 2.8 g (43.8%) of salt **II**, mp 149–150°C. IR spectrum, ν, cm^{-1}: 1640 (C=N), 1580 (C_6H_5), 1250 (P=O). ^{31}P NMR spectrum: δ_P 25 ppm. Found, %: C 55.0; H 6.2; N 6.71; P 7.95; S 16.5. $C_{18}H_{25}N_2O_2PS_2$. Calculated, %: C 54.5; H 6.3; N 7.07; P 7.83; S 16.16.

Reaction of triphenyl phosphorotrithioite with thiophenol and diethylamine. To a mixture of 2.5 g of triphenyl phosphorotrithioite, 1.14 g of thiophenol, and 2 ml of acetonitrile, 0.76 g of diethylamine was added dropwise. The reaction mixture was heated for 6 h at 70-80°C and then for 10 h at 95°C. After cooling, 1.1 g (42%) of salt **II** was obtained. Their constants and physicochemical characteristics agree with those of the sample obtained by scheme (2).

Synthesis of *S,S,S*-triphenyl phosphotrithioate (IV). *a. Reaction of white phosphorus with thiophenol in the presence of triethylamine*. To a mixture of 1 g of P_4, 11 g of thiophenol, and 5 ml of acetonitrile, 0.5 g of triethylamine was added dropwise. The resulting mixture was heated for 15 h at 70–90°C. The solvent was removed, and the reaction mixture was cooled to isolate 6.7 g (56%) of compound **IV**, mp 116–117°C. IR spectrum, ν, cm^{-1}: 1220 (P=O). ^1H NMR spectrum, δ, ppm: 7.3 s (C_6H_5S). ^{31}P NMR spectrum, δ_P 54.7 ppm. Found, %: C 57.61; H 4.02; P 8.04; S 26.0. $C_{18}H_{15}OPS_3$. Calculated, %: C 57.7; H 4.01; P 8.29; S 25.6.

In a similar way, from 0.5 g of P_4, 5.5 g of thiophenol, and 6 ml of acetonitrile in the presence of 0.78 g of dimethylaniline we obtained 2.1 g (35%) of compound **IV**.

b. Reaction of white phosphorus with thiophenol in the presence of diphenyl disulfide. To a mixture of 0.26 g of P_4, 2.76 g of thiophenol, and 5 ml of acetonitrile, 0.36 g of diphenyl disulfide prepared by the procedure in[14] were added. The reaction mixture was heated for 8 h at 60–80°C. ^{31}P NMR spectrum of the reaction mixture, δ_P, ppm (%): 131.9 (3.2); 56.4 (66.5); 46.5 (16); 23.3 (5.3); 7.4 (9). The solvent was removed, and the reaction mixture crystallized. Phosphate **IV**, 1.7 g (55%), was isolated. The melting point and spectral characteristics of this sample were similar to those of the sample prepared by procedure *a*.

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