Phosphorus-substituted carbothioamides

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A facile procedure was developed for the synthesis of phosphorus-substituted carbothioamides by the reaction of the corresponding nitriles with *O*,*O*-diisopropyl dithiophosphate in the presence of methanol. The structural features and hydrogen bonding in crystals of structurally different P-thioamides are discussed.

Key words: phosphorus-substituted acetonitriles, thionation, *O*,*O*-diisopropyl dithiophosphate, thioacetamides, thiobenzamides, X-ray diffraction analysis, intramolecular and intermolecular hydrogen bonds.

Various methods were developed for the synthesis of carbothioamides based on thionation of the corresponding nitriles with hydrogen sulfide and phosphorus monothio and dithio acids.[1] In the latter case, the synthesis of the target products requires either the use of an excess of dithio acid[2] or the involvement of the third component[3—6] (hydrogen chloride, alcohol, water, or organic acids) which can decompose intermediate imidoyl dithiophosphates.

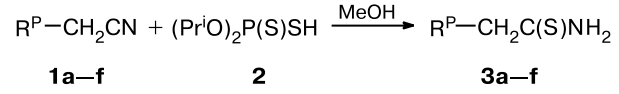
On the contrary, data concerning the procedures for the synthesis of primary thioamides of the corresponding phosphorus-substituted carboxylic acids are scarce. Only several examples of mercaptolysis of diethoxyphosphorylacetonitrile in a basic medium giving rise to diethoxyphosphorylthioacetamide were reported.[7—11] The formation of this compound in the reaction of diethoxyphosphorylacetonitrile with diphenyldithiophosphinic acid was mentioned,[12] but data on the yield of the target product were lacking in the publication. In addition, ring-opening of 1,3-dithietanes with carboxylic acid hydrazides resulted in phosphorylthioacetamides containing the 1,3,4-oxadiazole ring.[13]

In our opinion, phosphorus-containing carbothioamides are of obvious interest as chelating agents analogously to phosphorus-substituted thioureas[14] and also as building blocks for the preparation of various five- and six-membered heterocyclic compounds. Therefore, it is worth developing a general preparative procedure for the synthesis of such compounds.

Taking into account the advantages and drawbacks of methods developed earlier for the preparation of carbothioamides,[1—6] we chose thionation of nitriles with *O*,*O*-diisopropyl dithiophosphate in the presence of methanol (1 : 1 : 2 reagent ratio) for the synthesis of their phosphorus-substituted analogs as the most convenient laboratory procedure. This procedure has been proposed[4] for the synthesis of thiobenzamides $ArC(S)NH_2$ from the corresponding aromatic nitriles. It appeared that various phosphorus-substituted thioacetamides can easily be prepared in high yields, the procedure being preparatively much more convenient compared to the known approach to the synthesis of $(EtO)_2P(O)CH_2C(S)NH_2$ with the use of hydrogen sulfide.[7—11]

In spite of the fact that alkanenitriles behave ambiguously in this reaction,[4] the reactions of acetonitriles containing the electron-withdrawing phosphoryl fragment (**1a—d**) as well as the phosphonium (**1e**) or (thiophosphoryl)thio group (**1f**) with the above-mentioned thionating system based on *O*,*O*-diisopropyl dithiophosphate (**2**) proceeded smoothly to give the corresponding thioamides **3a—f** (~20 °C, 2 days) in satisfactory yields (Scheme 1).

Scheme 1



R^P = $(EtO)_2P(O)$ (**a**), $Me(Pr^iO)P(O)$ (**b**), $Ph(EtO)P(O)$ (**c**), $Ph_2P(O)$ (**d**), $Ph_3P^+Cl^-$ (**e**), $(EtO)_2PSS$ (**f**)

Although the introduction of an additional substituent into the methylene fragment of acetonitrile **1** has no effect on the final result of the process, it leads to deceleration of the reaction rate and a slight decrease in the yield of the target products. For example, 5—6 days are required for completion of the reactions of (benzyl)phosphorylacetonitrile (**4**) and 2,3,5,6-tetramethyl-1,4-

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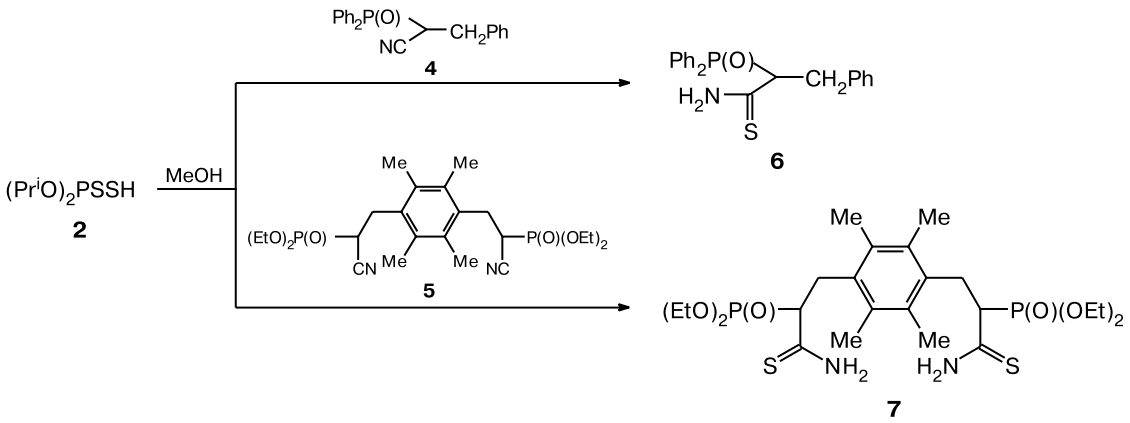
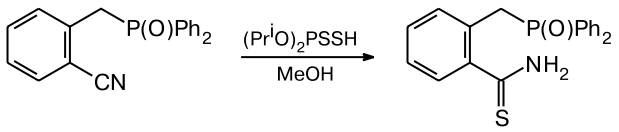
Scheme 2



bis[(2-phosphoryl-2-cyano)ethyl]benzene (**5**) with *O*,*O*-diisopropyl dithiophosphate (**2**) (Scheme 2). It should be noted that the reaction of compound **5** led to thionation of both nitrile groups of the molecule.

As mentioned above, these reaction conditions have earlier been used[4] for the preparation of thiobenzamides from benzonitrile and its *p*-bromo- and *p*-dimethylamino derivatives. Using 2-(diphenylphosphorylmethyl)benzonitrile (**8**) as an example, we demonstrated that this procedure makes it also possible to perform thionation of the nitrile group in *ortho*-substituted benzonitriles. After mixing of the reagents and storage of the reaction mixture at ~20 °C for 2 days, the corresponding thioamide **9** was isolated in ~80% yield (Scheme 3).

Scheme 3



8 **9**

All primary thioamides were prepared as crystalline compounds. Their compositions and structures were confirmed by data from elemental analysis and IR and NMR spectroscopy (Tables 1 and 2).

In the IR spectra of thioamides **3a—d**, **6**, **7**, and **9** (KBr) containing the phosphoryl fragment, absorption of

Table 1. Yields, melting points, and data from elemental analysis and IR spectroscopy for phosphorus-substituted thioamides

Compound	Yield (%)	M.p. /°C	Found / Calculated (%)			Molecular formula	IR spectrum, ν/cm^{-1}	
			C	H	N		ν(P=O)	ν(C=S) + δ(CH$_2$) + δ(NH) + ν(N—C=S)
3a	75	72—74[a]	—	—	—	—	1230	1315, 1435—1445 br
3b	68	152—154	36.82 / 36.92	7.37 / 7.23	7.11 / 7.17	$C_6H_{14}NO_2PS$	1205	1300, 1315, 1442, 1450
3c	78	146—148	49.68 / 49.37	6.19 / 5.80	5.56 / 5.76	$C_{10}H_{14}NO_2PS$	1220	1315, 1385, 1450 br
3d	75	250—251	61.04 / 61.08	5.07 / 5.13	5.07 / 5.09	$C_{14}H_{14}NOPS$	1195	1300, 1320, 1438, 1455
3e	70	255—257	—	—	—	$C_{20}H_{19}ClNPS$[b]	—	1440—1490 br
3f	35	30—32	—	—	—	$C_6H_{14}NO_2PS_2$[c]	658[d]	1380, 1450—1465
6	58	268—270	68.88 / 69.02	5.36 / 5.52	4.02 / 3.83	$C_{21}H_{20}NOPS$	1175	1300, 1430, 1457
7	63	262—263	49.68 / 49.64	4.75 / 4.82	7.29 / 7.29	$C_{24}H_{42}N_2O_6P_2S_2$	1235	1300, 1395, 1445, 1450
9	79	295—297	68.41 / 68.36	5.21 / 5.16	3.98 / 3.99	$C_{20}H_{18}NOPS$	1180—1190 br	1320, 1380, 1445, 1460

[a] *Cf.* lit. data[11,12]: m.p. 73—75 °C.
[b] Found (%): P, 8.53; S, 8.40. Calculated (%): P, 8.33; S, 8.62.
[c] Found (%): P, 12.30; S, 37.24. Calculated (%): P, 11.94; S, 37.09.
[d] ν(P=S).

Table 2. Selected parameters of the ^1H and ^{31}P NMR spectra of thioamides (in DMSO-d_6)

Compound	NMR (δ, *J*/Hz)	
	^{31}P	^1H
3a	22.35	1.29 (t, 6 H, $C\underline{H}_3CH_2$, $^3J_{H,H}$ = 6.8); 3.25 (d, 2 H, PCH_2, $^2J_{P,H}$ = 22.5); 4.11—4.03 (m, 4 H, OCH_2); 9.05, 9.45 (both s, 1 H + 1 H, NH_2)
3b[a]	47.26	1.31 (d, 3 H $(C\underline{H}_3)_2CH$, $^3J_{H,H}$ = 6.0); 1.33 (d, 3 H, $(C\underline{H}_3)_2CH$, $^3J_{H,H}$ = 6.4); 1.63 (d, 3 H, PMe, $^2J_{P,H}$ = 11.6); 3.34 (t, 1 H_A, CH_AH_B, $^2J_{H,H}$ = $^2J_{P,H}$ = 14.0); 3.43 (dd, 1 H_B, CH_AH_B, $^2J_{H,H}$ = 14.0, $^2J_{P,H}$ = 19.2); 4.64—4.72 (m, 1 H, OCH); 8.04, 8.77 (both s, 1 H + 1 H, NH_2)
3c[a]	37.80	1.31 (t, 3 H, Me, $^3J_{H,H}$ = 6.4); 3.51 (t, 1 H_A, CH_AH_B, $^2J_{H,H}$ = $^2J_{P,H}$ = 15.0); 3.61 (dd, 1 H_B, CH_AH_B, $^2J_{H,H}$ = 15.0, $^2J_{P,H}$ = 18.0); 3.94—4.18 (m, 2 H, OCH_2); 7.35—7.80 (m, 5 H, Ph); 7.83, 8.75 (both s, 1 H + 1 H, NH_2)
3c	37.01	1.21 (t, 3 H, Me, $^3J_{H,H}$ = 7.0); 3.55 (d, 2 H, PCH_2, $^2J_{P,H}$ = 19.3); 3.89—3.93, 4.00—4.05 (both m, 2 H, OCH_2); 7.52—7.55, 7.59—7.63, 7.74—7.79 (three m, 4 H + 2 H + 4 H, Ph—P); 9.11, 9.48 (both s, 1 H + 1 H, NH_2)
3d	27.96	3.91 (d, 2 H, PCH_2, $^2J_{P,H}$ = 13.4); 7.49—7.84 (m, 10 H, Ph); 9.01, 9.42 (both s, 1 H + 1 H, NH_2)
3e	23.67	5.49 (d, 2 H, PCH_2, $^2J_{P,H}$ = 16.0); 7.35—7.80 (m, 15 H, Ph); 9.85, 10.45 (both s, 1 H + 1 H, NH_2)
3f	92.26	1.35 (t, 6 H, $C\underline{H}_3CH_2$, $^3J_{H,H}$ = 7.2); 3.82 (d, 2 H, PCH_2, $^3J_{P,H}$ = 12.7); 4.10—4.30 (m, 4 H, OCH_2); 9.24, 9.63 (both s, 1 H + 1 H, NH_2)
6	29.62	2.86 (t, 1 H_A, CH_AH_BAr, $^2J_{H,H}$ = $^3J_{H,H}$ = 11.7); 3.49 (dt, 1 H_B, CH_AH_BAr, $^2J_{H,H}$ = $^3J_{H,H}$ = 11.7, $^3J_{P,H}$ = 5.52); 4.37 (br.t, 1 H, P(O)CH, $^2J_{P,H}$ = $^3J_{H,H}$ = 11.7); 7.12—7.20, 7.45—7.56, 7.91—8.02 (3 m, 5 H + 6 H + 4 H, $CH_2C_6\underline{H}_5$ + Ph_2P); 8.90, 9.20 (both s, 1 H + 1 H, NH_2)
7	24.76	1.18 (m, 12 H, $C\underline{H}_3CH_2$); 2.20 (s, 12 H, MeAr); 3.42—3.49 (m, 6 H, CH_2Ar + CH); 3.94—4.00 (m, 8 H, OCH_2); 9.10, 9.47 (both s, 2 H + 2 H, NH_2)
9[b]	33.13	4.05 (d, 2 H, PCH_2, $^2J_{P,H}$ = 13.0); 6.60 (d, 1 H, C_6H_4, $^3J_{H,H}$ = 7.6); 7.05 (t, 1 H, C_6H_4, $^3J_{H,H}$ = 7.6); 7.20 (t, 1 H, C_6H_4, $^3J_{H,H}$ = 7.6); 7.48 (d, 1 H, C_6H_4, $^3J_{H,H}$ = 7.6); 7.53—7.70 (m, 6 H *p-, m*-PhP); 7.84—7.89 (m, 4 H, *o*-PhP)

[a] The spectra were recorded in $CDCl_3$.

[b] ^{13}C NMR (DMSO-d_6), δ: 33.81 (d, CH_2, $^1J_{P,C}$ = 64.0 Hz); 125.47 (d, C(1), $^3J_{P,C}$ = 8.4 Hz); 126.59 (d, C(3), $^3J_{P,C}$ = 2.0 Hz); 128.48 (C(4)); 128.92 (d, *m*-PhP, $^3J_{P,C}$ = 11.9 Hz); 129.86 (C(5)); 130.88 (d, *o*-PhP, $^2J_{P,C}$ = 9.6 Hz); 132.01 (d, *ipso*-PhP, $^1J_{P,C}$ = 98.8 Hz); 135.32 and 132.50 (*p*-PhP); 144.52 (d, C(2), $^2J_{P,C}$ = 5.4 Hz); 201.92 (C=S).

the P=O group is observed at 1180—1230 cm^{-1}, the band being shifted as expected to a lower frequency as the number of P—C bonds in the molecule increases. The absorption band at 1315—1320 cm^{-1} was assigned to stretching vibrations of the C=S group by analogy with the published data.[12] Only weak bands at 1300 and 1340 cm^{-1} are observed for thioacetamide **3e** containing the phosphonium substituent. The band of the C=S group in the spectra of thioacetamide **3f** and bis-thioamide **7** is shifted to 1380 and 1395 cm^{-1}, respectively. Overlapping of the bending bands of the CH_2 and NH groups and the ν(N—C=S) band is responsible for the appearance of a broad medium-intensity absorption band at 1435—1455 cm^{-1}. In the spectra of all the thioamides synthesized, a broadened stretching band of the amido group is observed as a doublet in the region of 3100—3300 cm^{-1}, the band being shifted by ~100 cm^{-1} compared to NH_2 vibrations in the spectra of amides of the corresponding carboxylic acids. Broadening of this vibrational band, the appearance of a series of additional bands in this region, and the shift of the band are indicative of the presence of intra- and intermolecular associates formed through hydrogen bonds involving the amide protons.

The ^{31}P NMR spectra of compounds **3a—f**, **6**, and **9** show singlets in regions characteristic of this type of environment about the P atom. It should be noted that a singlet is observed also for bis-thioamide **7** in spite of the presence of two asymmetric centers in the molecule (correspondingly, **7** is formed as the *meso* and *d*,*l* forms).* In the ^1H NMR spectra of thioacetamides **3a,c—f** in DMSO-d_6, the signals for the protons of the $PCH_2C(S)$ group appear as doublets. In the spectra (in $CDCl_3$) of compounds **3b,c** containing the asymmetrical P atom, these signals are observed as ABX systems. The magnetic nonequivalence of the methylene protons in the spectra of compounds **3b,c** in $CDCl_3$ is apparently indicative of sterically hindered rotation about the P—C bond in this solvent due to specific solvation. The spin-spin coupling constant of the protons of the CH_2 group with the P atom and δ for this signal are close to the analogous parameters for the starting nitriles and decrease on going from phosphonates to phosphinates and then to phosphine oxides. The position of the signal for these protons depends

* The starting bis-nitriles **5** represented mixtures of *meso* and *d*,*l* isomers, which are characterized by individual signals in the ^{31}P NMR spectra (see Ref. 15).

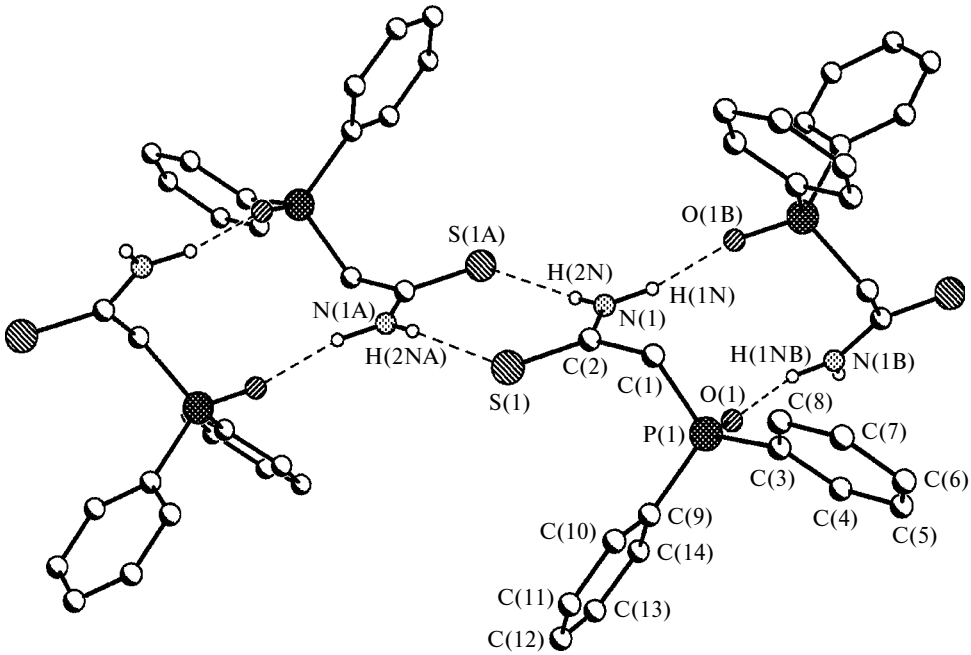


Fig. 1. Overall view of molecule **3d** and a fragment of a hydrogen-bonded chain in the crystal.

directly on the acidifying effect of the phosphorus-containing fragment, *i.e.*, the signal is shifted downfield as the CH-acidity increases.[16]

It should also be noted that the signals for the amide protons are magnetically nonequivalent and appear as two singlets in the spectra of all the thioamides synthesized regardless of the solvent in which the spectra were recorded, whereas the positions of the signals depend on the solvent. In DMSO, these signals are substantially shifted downfield compared to their chemical shifts in $CDCl_3$ (*cf.* the ^1H NMR spectra of **3c** in $CDCl_3$ and DMSO, see Table 2).

Since most of the compounds synthesized contain the carbothioamide and phosphoryl groups along with the methylene fragment characterized by rather high acidity of CH protons, it was of interest to study their molecular and, in particular, crystal structures* with special emphasis on specific interactions. For this purpose, we carried out single-crystal X-ray diffraction study of diphenylphosphorylthioacetamide (**3d**) and 2-(diphenylphosphorylmethyl)thiobenzamide (**9**). The overall views of molecules **3d** and **9** are shown in Figs. 1 and 2, respectively. Their selected geometric parameters are given in Table 3. In both molecules, the P atoms are characterized by a slightly distorted tetrahedral coordination. The C(3)—P(1)—C(9) bond angle decreases on going from **3d** to **9**. The mutual arrangement of the phosphoryl group and the substituent at the C(1) atom (the aryl fragment in **9** or the $C(S)NH_2$ group in **3d**) is nearly *syn*-periplanar; the corresponding torsion angles are 53.6 and 59.8°, respectively. Due to steric repulsion, the carbothioamide group in compound **9** is twisted with respect to the plane of the phenyl ring by 52.5°.

Comparison of the main geometric parameters of molecules **3d** and **9** shows that the presence of the electron-withdrawing thioamide substituent at the C(1) atom in **3d** leads to a substantial shortening of the P(1)—O(1) bond (to 1.482(2) Å) compared to the analogous bond in **9** (1.497(1) Å). In spite of the fact that this effect of the electron-withdrawing substituent on the P=O bond length has been noted in our earlier study,[17] it is also not inconceivable that the observed differences in the bond lengths in molecules **3d** and **9** are associated with hydrogen bonding.

Analysis of the crystal packing demonstrated that the $C(S)NH_2$ group in both compounds is involved in N—H...O and N—H...S hydrogen bonds (see Table 3). In spite of rather high acidity of the methylene protons, they are not involved in C—H...O contacts in the crystals.

In both structures, the N—H...S hydrogen bonds give rise to centrosymmetrical dimers with a planar eight-membered H-bonded ring. The geometric parameters of these hydrogen bonds in two compounds are approximately the same.

In contrast, the type of N—H...O bonds in **3d** differs substantially from that in **9**. In the crystal of thioacet-

* It should be noted that the NH_2 group in the only known crystal structure of phosphorylated carbothioamides, *viz.*, diethyl [5-(*p*-tolyl)-1,3,4-oxadiazol-2-yl]thiocarbamoylmethylphosphonate,[13] forms hydrogen bonds (intra- and intermolecular) only of the N—H...O type, whereas the C=S bond is not involved in specific interactions.

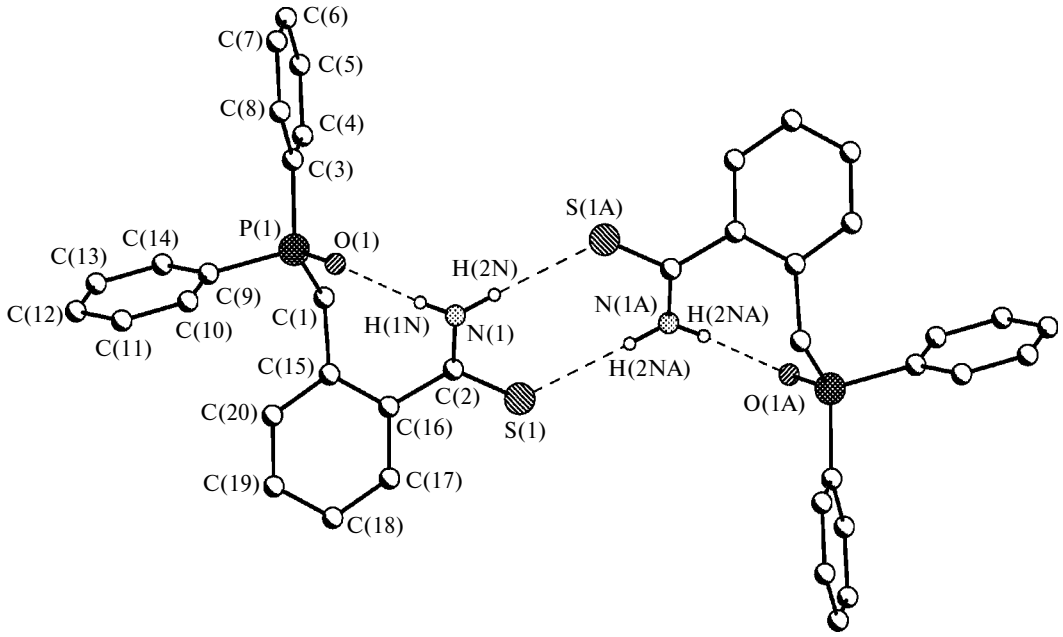


Fig. 2. Overall view of molecule **9** and centrosymmetrical N—H...S dimers in the crystal.

Table 3. Selected bond lengths (*d*) and bond angles (ω) in the crystals of **3d** and **9**

Parameter	**3d**	**9**
Bond	*d*/Å	
P(1)—O(1)	1.482(2)	1.497(1)
P(1)—C(1)	1.816(3)	1.821(2)
P(1)—C(3)	1.805(3)	1.801(2)
P(1)—C(9)	1.798(3)	1.797(2)
S(1)—C(2)	1.663(3)	1.684(2)
C(2)—N(1)	1.304(3)	1.314(2)
C(1)—C(2)	1.500(3)	—
C(1)—C(15)	—	1.491(2)
Angle	ω/deg	
O(1)—P(1)—C(1)	113.0(1)	112.16(7)
O(1)—P(1)—C(3)	113.0(1)	113.13(7)
O(1)—P(1)—C(9)	111.3(1)	112.27(8)
C(3)—P(1)—C(9)	107.7(1)	105.35(8)
S(1)—C(2)—N(1)	124.4(2)	123.50(1)
N(1)—H(2N)...S(1A) bond[a]		
Bond	*d*/Å	
N(1)...S(1A)	3.416(2)	3.432(2)
Angle	ω/deg	
N(1)—H(1)—S(1A)	176	168
N(1)—H(1N)...O(1A) bond[b]		
Bond	*d*/Å	
N(1)...O(1A)	2.817(2)	2.813(2)
Angle	ω/deg	
N(1)—H(1)—O(1A)	163.5	169.0

[a] The atom was generated from the basis atom by the symmetry transformations ($-x + 1$, $-y + 2$, $-z$) and ($-x + 1$, $-y$, $-z + 1$) in **3d** and **9**.

[b] The atom was generated from the basis atom by the symmetry transformation ($-x + 1$, y, $-z + 1/2$) in **3d**.

amide **3d**, the molecules are linked in infinite chains through intermolecular N—H...O bonds (see Fig. 1). In thiobenzamide **9**, the N—H...O bond is, on the contrary, intramolecular and is involved in the formation of the second eight-membered H-bonded ring (see Fig. 2). It should be noted that the N...O distances generally used as estimates of the strength of hydrogen bonds are equal in **3d** and **9**. Consequently, the observed differences in the geometry of the molecules are determined primarily by inductive effects of the substituents rather than are associated with the difference in the crystal packing.

Thus, phosphorus-substituted nitriles can easily and efficiently be transformed into the corresponding thioamides with the use of *O*,*O*-diisopropyl dithiophosphate as the thionating agent.

Experimental

The NMR spectra were recorded on Bruker WP-200SY and Bruker AMX-400 instruments in $CDCl_3$ and DMSO-d_6 using residual signals for the protons of the deuterated solvents as the internal standards (^1H and ^{13}C) and 85% H_3PO_4 as the external standard (^{31}P). The ^{13}C NMR spectra were recorded in the JMODECHO mode; the signals for the C atoms bearing odd and even numbers of protons have opposite polarities. The IR spectra were recorded on a Magna-IR 750 (Nicolet) Fourier-transform spectrometer; the spectral resolution was 2 cm^{-1}; 128 scans (KBr pellets).

X-ray diffraction data sets for thioamides **3d** and **9** were collected on an automated three-circle SMART CCD-1000 diffractometer (Mo-Kα radiation, graphite monochromator, ω scanning technique). Single crystals were prepared by slow crystallization of compounds **3d** and **9** from dilute solutions in a 1 : 1 MeCN—EtOH mixture. The structures were solved by di-

Table 4. Principal crystallographic data and details of structure refinement for **3d** and **9**

Parameter	**3d**	**9**
Formula	$C_{14}H_{14}NOPS$	$C_{20}H_{18}NOPS$
T/K	298	120
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a/Å	9.320(2)	9.448(1)
b/Å	17.052(3)	9.592(1)
c/Å	17.383(4)	11.535(1)
α/deg	—	77.833(2)
β/deg	98.018(4)	78.494(2))
γ/deg	—	63.592(2)
V/Å^3	2735.7(9)	908.5(2)
Z (Z')	8 (1)	2 (1)
M	275.29	351.38
μ/cm^{-1}	3.40	2.72
F(000)	1152	368
d_{calc}/g cm^{-3}	1.337	1.285
$2\theta_{max}$/deg	57.00	58.00
Number of measured reflections (R_{int})	6505 (0.0302)	7978 (0.0260)
Number of independent reflections	3330	4519
Number of observed reflections with $I > 2\sigma(I)$	2110	3895
Number of parameters	296	289
R_1	0.0563	0.0448
wR_2	0.1392	0.1153
GOOF	1.088	1.065
$(\rho_{max}/e \cdot Å^{-3})/\rho_{min}/e \cdot Å^{-3})$	0.524/–0.262	0.588/–0.352

rect methods and refined anisotropically by the full-matrix least-squares method against F^2_{hkl}. The H atoms were revealed from difference Fourier syntheses and refined isotropically. All calculations were carried out using the SHELXTL PLUS program package. The principal crystallographic data are given in Table 4. The atomic coordinates were deposited with the Cambridge Structural Database.

The starting phosphorylacetonitriles **1a—d** were prepared by the reactions of the corresponding esters of trivalent phosphorus acids with chloroacetonitrile involving the Arbuzov rearrangement according to a known procedure.[18] Phosphorus-substituted acetonitriles **1e** [19] and **1f** [20] were synthesized according to the published procedures. Nitriles **4** and **5** were prepared by alkylation of phosphorylacetonitriles with benzyl bromide and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene, respectively, according to a procedure described earlier.[15]

2-[(Diphenylphosphoryl)methyl]benzonitrile (8) was prepared upon the Arbuzov rearrangement starting from methyl diphenylphosphinite and 2-(bromomethyl)benzonitrile.[21] *O*-Methyl diphenylphosphinite (2.4 g, 11.1 mmol) was added dropwise to a boiling solution of 2-(bromomethyl)benzonitrile (1.96 g, 0.01 mol) in xylene (20 mL) under a weak stream of argon for 15 min. The reaction mixture was refluxed for 2 h. A white precipitate that formed after cooling was filtered off and recrystallized from a benzene—ethanol system. The yield of product **8** was 1.8 g (56.8%), m.p. 168—169 °C (benzene—ethanol). Found (%): C, 75.90; H, 4.92; N, 4.55; P, 9.68. $C_{20}H_{16}NOP$. Calculated (%): C, 75.70; H, 5.08; N, 4.41; P, 9.76. IR, ν/cm^{-1}: 2230 (ν(CN)); 1195 (ν(P=O)). $^{31}P—\{^1H\}$ NMR ($CDCl_3$), δ: 29.15. ^1H NMR ($CDCl_3$), δ: 3.89 (d, 2 H, CH_2P, $^2J_{P,H}$ = 13.6 Hz); 7.44—7.47 (m, 4 H, Ph); 7.51—7.53 (m, 4 H, C_6H_4); 7.66—7.75 (m, 6 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 36.05 (d, CH_2, $^1J_{P,C}$ = 63.8 Hz); 113.04 (d, C(1), $^3J_{P,C}$ = 6.0 Hz); 117.62 (CN); 127.32 (C(3)); 128.61 (d, *m*-PhP, $^3J_{P,C}$ = 12.1 Hz); 129.84 (d, *ipso*-PhP, $^1J_{P,C}$ = 99.0 Hz); 131.03 (d, *o*-PhP, $^2J_{P,C}$ = 9.6 Hz); 131.31 (C(4)); 132.27 (*p*-PhP); 132.38 (C(5)); 132.71 (C(6)); 135.23 (C(2)).

Diethyl thiocarbamoylmethylphosphonate (3a). A mixture of equimolar amounts of diethoxyphosphorylacetonitrile (**1a**) and diisopropyldithiophosphoric acid **2** and 2 mol. equiv. of MeOH was kept at ~20 °C for 2 days. Then Et_2O was added to the reaction mixture. The oil that formed was separated and washed additionally with diethyl ether, after which the residue crystallized to give the target product in 75% yield (see Tables 1 and 2).

Thioacetamides **3**, **6**, **7**, and **9** were prepared analogously.

In the case of compound **3f**, the oil that was precipitated with diethyl ether was additionally purified by column chromatography on silica gel using benzene as the eluent.

Thioamides **3b—e**, **6**, **7**, and **9** crystallized from the reaction mixtures in the course of reactions. These compounds were separated by filtration, washed on a filter with diethyl ether, and recrystallized from EtOH (see Tables 1 and 2).

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