Heteroatom Chemistry
Volume 11, Number 4, 2000

Synthesis, Molecular and Crystal Structure, and Properties of 10-Propylthio-5,10-dihydrophenarsazine

Il'yas S. Nizamov, Tat'yana P. Sorokina, Alexey V. Matseevskii, Dmitry B. Krivolapov, Aidar T. Gubaidullin, Igor A. Litvinov, Boris E. Abalonin, Elvira S. Batyeva, and Vladimir A. Alfonsov

A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Arbuzov Str. 8, 420088 Kazan, Russia

Received 27 December 1999; revised 22 February 2000

ABSTRACT: *10-Propylthio-5,10-dihydrophenarsazine* **2** *was obtained by the reaction of 10-chloro-5,10-dihydrophenarsazine* **1** *with propanethiol in the presence of triethylamine under mild conditions. The structure of* **2** *was established by X-ray single crystal diffraction. The reaction of* **2** *with 2,4-bis(ethylthio)-1,3,2,4-dithiadiphosphetane-2,4-disulfide* **3** *at room temperature affords a novel route to S-10(5,10-dihydrophenarsazine) S′-ethyl-S″-propyltetrathiophosphate* **4**. © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:287–291, 2000

INTRODUCTION

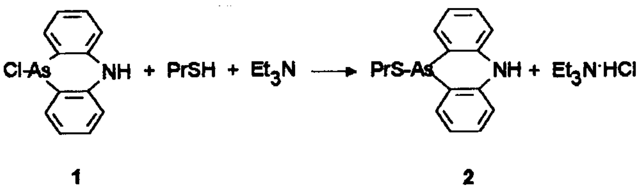
Organothiophosphorus derivatives of trivalent arsenic are used as pesticides [1], analytical reagents [2], and for regeneration of cracking catalysts [2]. Cyclic arsenic(III) dithiophosphates containing the P(S)S–As fragment have been obtained by the reactions of ammonium or sodium dithiophosphates with 1-chloro-2,5,1-dithiarsolane and 2-chloro-1,3,2-dioxarsolanes and -arsenanes [1,3,4]. Reactions of O,O′-dialkyldithiophosphoric acids or their potassium salts with 10-methoxy or 10-chloro derivatives of 5,10-dihydrophenarsazine result in S-10(5,10-dihydrophenarsazine) O,O′-dialkyldithiophosphates [1]. Organothiophosphorus derivatives of 5,10-dihydrophenarsazine containing tetrathiophosphato moieties are presently unknown. In this article, an alternative method is presented for the synthesis of S-10(5,10-dihydrophenarsazine) S′-ethyl-S″-propyl tetrathiophosphate **4** directly from the ethyl homologue of Davy's reagent **3**.

RESULTS AND DISCUSSION

For the synthesis of new cyclic arsenic(III) derivatives of phosphorus(V) thioacids, we have used 5,10-dihydrophenarsazine derivatives and their reactions with 1,3,2,4-dithiadiphosphetane-2,4-disulfides. 10-Alkylthio- or 10-arylthio-5,10-dihydrophenarsazines have been reported to be prepared by the reaction of 10-methoxy-5,10-dihydrophenarsazine with thiols or by the treatment of 10-chloro-5,10-dihydrophenarsazine with sodium mercaptides [5]. We have now developed a new method for synthesizing 10-propylthio-5,10-dihydrophenarsazine **2** by the reaction of 10-chloro-5,10-dihydrophenarsazine **1** with propanethiol in the presence of triethylamine in anhydrous benzene at 20°C (Reaction 1).

Correspondence to: Il'yas S. Nizamov

Contract Grant Sponsor: Russian Foundation for Basic Researches
Contract Grant Number: 95-03-09739a



(1)

The product **2** is a crystalline solid. Its structure has been confirmed by evaluation of IR, ^{1}H NMR, and mass spectra and by microanalyses. Bands of weak intensity present in the region ν 3365 cm^{-1} in the IR spectrum of **2** are due to the N–H valence vibrations of its phenarsazine fragment. Bands in the region ν 744 and 550 cm^{-1} are assigned to the C–S valence vibrations. The ^{1}H NMR spectrum of **2** shows the characteristic resonances due to the presence of a thiopropyl group attached to the arsenic(III) atom. The $\underline{CH_3}CH_2CH_2SAs$ protons appear as a triplet in the region of $\delta = 0.97$ with $^3J_{HH}$ 7.5 of **2**. A triplet observed in the region of $\delta = 2.85$ has been assigned to the methylene protons of $CH_2CH_2\underline{CH_2}SAs$ attached to the sulfur atom of **2**. The electron impact mass spectrum of **2** exhibits the mass peak *m/e* 317 that may be attributed to its molecular ion $[M]^{+\cdot}$.

It should be emphasized that X-ray analysis previously performed [6] for the reagent 10-chloro-5,10-dihydrophenarsazine **1** shows that its molecule is slightly folded about the As···N axis, the angle between the benzene rings being 169° 20′ and the chlorine atom being outside this angle; however, the central ring is planar. Each benzene ring of **1** is thus displaced by about 5° from a completely planar arrangement [6,7]. Evidence for the existence of several crystalline forms of **1** and the possibility of geometrical isomerism of **1** has also been provided by an X-ray investigation [6]. X-ray investigations of other 5,10-dihydrophenarsazine derivatives, such as 10-bromo-[8], 10-(*m*-tolyl)- [9], 5-(3-methoxyphenyl)- [10], 5-methyl- [11], and 5,10-diphenyl-5,10-dihydrophenarsazines [12], were also carried out.

The molecular and crystal structure of **2** was also established by X-ray single crystal diffraction (Figures 1, 2, and 3; Tables 1–4). This experiment reveals three crystallographically independent molecules of **2** in an asymmetrical part of its crystal cell. The molecular structure, hydrogen bonds, and supramolecular arrangement of the molecules of **2** in its crystal are displayed in Figures 1, 2, and 3, respectively, with atoms of elements marked by A, B, and C. The bond distances, bond angles, and torsion angles for the nonhydrogen atoms of **2** and hydrogen bond parameters between two molecules of **2** are listed in Tables 1, 2, 3, and 4, respectively. These three kinds of mol-

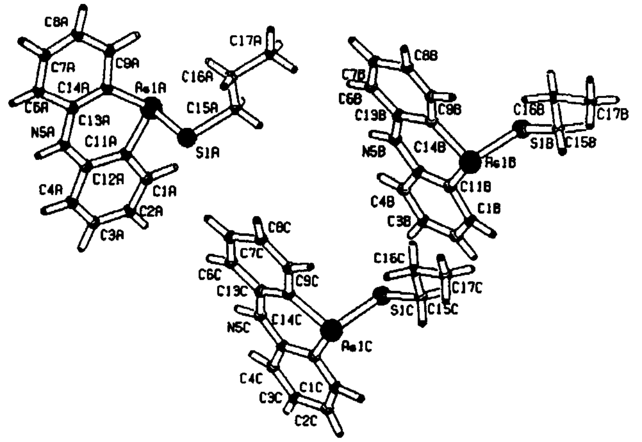


FIGURE 1 Molecular structures of the three independent molecules of **2**.

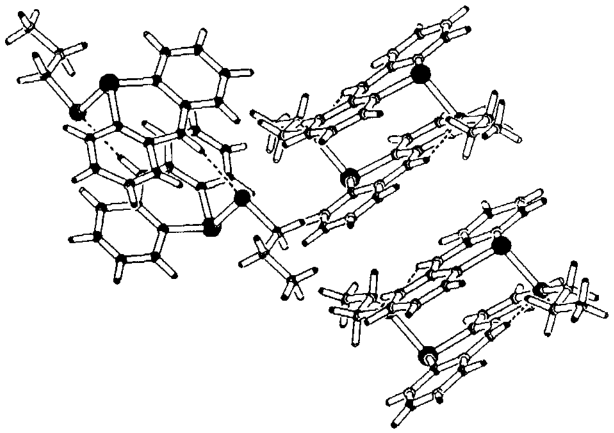


FIGURE 2 A drawing of dimeric pairs of molecules of **2**.

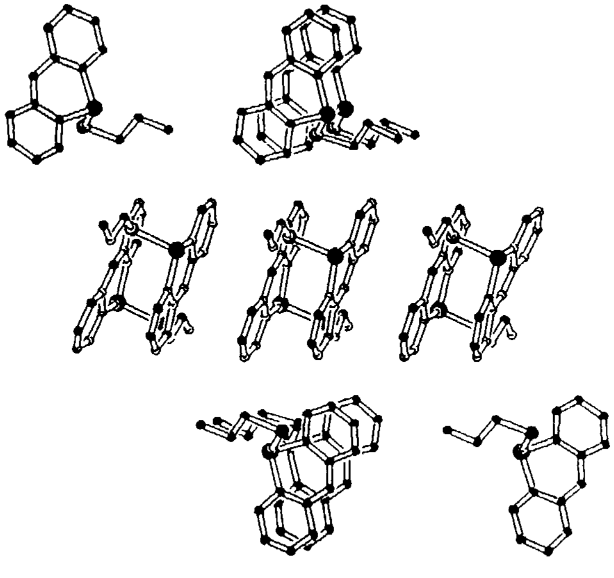


FIGURE 3 The packing of molecules of **2** in crystal lattice.

TABLE 1 Bond Distances (Å) in **2** with Estimated Standard Deviations in Parentheses

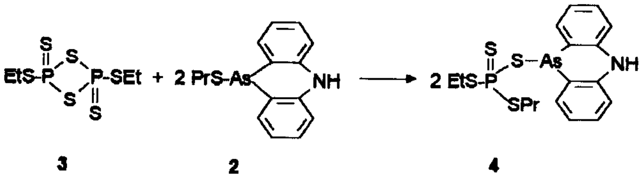
Bond	A	B	C
As1–S1	2.258(5)	2.259(5)	2.262(5)
As1–C11	1.90(1)	1.94(1)	1.90(1)
As1–C14	1.93(1)	1.91(1)	1.92(1)
S1–C15	1.91(2)	1.86(2)	1.84(2)
N5–C12	1.37(1)	1.41(1)	1.35(1)
N5–C13	1.40(1)	1.38(1)	1.39(1)
N5–H5	0.99(1)	0.98(1)	0.98(1)
C1–C2	1.34(2)	1.39(2)	1.31(2)
C4–C12	1.40(2)	1.42(2)	1.37(2)
C1–C11	1.43(2)	1.45(2)	1.38(2)
C2–C3	1.32(2)	1.37(2)	1.39(2)
C6–C7	1.37(2)	1.42(2)	1.37(2)
C3–C4	1.39(2)	1.37(2)	1.37(2)
C6–C13	1.44(2)	1.37(2)	1.40(2)
C7–C8	1.29(2)	1.41(2)	1.41(2)
C8–C9	1.35(2)	1.29(2)	1.38(2)
C16–C17	1.56(4)	1.61(3)	1.49(3)
C9–C14	1.41(2)	1.36(2)	1.38(2)
C11–C12	1.43(2)	1.32(2)	1.39(2)
C13–C14	1.35(2)	1.45(2)	1.37(2)
C15–C16	1.32(3)	1.40(2)	1.43(3)

TABLE 2 Bond Angles (°) in **2** with Estimated Standard Deviations in Parentheses

Angle	A	B	C
S1–As1–C11	97.8(5)	97.2(5)	98.1(4)
S1–As1–C14	100.8(4)	101.4(4)	102.6(4)
C11a–As1–C14	96.4(6)	96.9(6)	95.1(5)
As1–S1a–C15a	101.2(7)	101.3(6)	104.1(7)
C12–N5–C13	128.(1)	129.(1)	132.(1)
C12–N5–H5	121.(1)	112.7(9)	117.(1)
C13–N5–H5	111.0(9)	118.3(9)	111.2(9)
C2–C1–C11	121.(2)	117.(1)	125.(2)
C3–C4–C12	119.(1)	118.(1)	118.(1)
C7–C6–C13	114.(1)	120.(1)	123.(1)
C8–C9–C14	120.(1)	128.(2)	119.(1)
N5–C13–C6	112.(1)	119.(1)	119.(1)
N5–C13–C14	125.(1)	120.(1)	123.(1)
C6–C13–C14	123.(1)	121.(1)	118.(1)
C1–C11–C12	118.(1)	118.(1)	115.(1)
As1–C11–C1	118.(1)	118.(1)	117.(1)
As1–C11–C12	124.0(8)	123.3(9)	127.8(8)
As1–C14–C9	120.(1)	120.(1)	115.(1)
As1–C14–C13	123.8(8)	124.7(8)	123.5(8)
C9–C14–C13	116.(1)	115.(1)	121.(1)
C4–C12–C11	118.(1)	124.(1)	123.(1)
N5–C12–C4	119.(1)	111.(1)	119.(1)
N5–C12–C11	122.(1)	126.(1)	119.(1)
S1–C15–C16	107.(2)	112.(1)	114.(2)
C15–C16–C17	108.(2)	104.(2)	112.(2)

ecules of **2** seem to be geometrical rotamers. Inspection of Tables 1–4 proves that each of these rotamers **A**, **B**, and **C** has its own values of bond lengths, valence, and torsion angles. The molecules of **2** are reproduced in the form of triplets of isomers in the crystal cell. The torsion angles of **2**, listed in Table 3, show that the central ring is planar, similar to **1**. Each benzene ring of **2** is displaced by 9°, 5°, and 2° from a completely planar arrangement for **A**, **B**, and **C** rotamers, respectively. From Figure 2, it is obvious that two neighboring molecules (**AA′**, **BB′**, and **CC′**) are oriented in such a way that hydrogen bonding takes place through the N–H···S–As fragment in the crystal cell.

We have recently developed facile methods for the synthesis of S-organoarsenic(III) derivatives of dithiophosphonic and trithiophosphonic acids by the action of 1,3,2,4-dithiadiphosphetane-2,4-disulfides [13,14]. We have now found that phenarsazine **2**, containing a rather reactive As-S bond, reacts with 2,4-bis(ethylthio)-1,3,2,4-dithiadiphosphetane-2,4-disulfide **3** to yield S-10(5,10-dihydrophenarsazine) S′-ethyl S″-propyltetrathiophosphate **4** (Reaction 2).



(2)

Reaction 2 proceeds in anhydrous benzene at room temperature during 8 hours. Compound **4** is an oily liquid, and it was purified by a falling-film distillation. There are bands in the region ν 693 and 675 cm^{-1} (P=S) and ν 525 cm^{-1} (P–S, C–S) in the IR spectrum of the tetrathiophosphate **4**. The ^{31}P NMR spectrum of 4 reveals a signal at δ = 88.1 (C_6H_6). Reaction 2 is of interest from the point of view of organophosphorus chemistry as it leads to a new arsenic(III) derivative of phosphorus(V) thioacids containing the $HN(C_6H_4)_2AsSP(S)S_3$ structural fragment.

EXPERIMENTAL

General Data

The ^{31}P NMR spectra were recorded with a Bruker MSL 400 (162 MHz) instrument in C_6H_6. The ^{1}H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in $CDCl_3$ or C_6D_6 with $(Me_3Si)_2O$ as an internal reference. The IR spectra were obtained as a KBr pellet with an UR-20 infrared spectrophotom-

TABLE 3 Torsion Angles (°) in **2** with Estimated Standard Deviations in Parentheses

Angle	**A**	**B**	**C**
C11–As1–S1–C15	−142.97(0.72)	148.79(0.67)	142.14(0.74)
C14–As1–S1–C15	118.92(0.72)	−112.64(0.69)	−120.71(0.78)
C14–As1–C11–C1	−172.87(1.16)	−77.87(1.18)	175.67(1.17)
S1–As1–C11–C12	−98.07(1.14)	101.58(1.26)	98.99(1.23)
S1–As1–C11–C1	85.27(1.13)	179.61(1.20)	−80.77(1.14)
C11–As1–C14–C9	172.74(1.17)	−176.07(1.22)	−178.57(1.15)
S1–As1–C14–C13	94.24(1.19)	−100.44(1.13)	−95.14(1.16)
S1–As1–C14–C9	−88.07(1.15)	85.09(1.19)	81.91(1.11)
C14–As1–C11–C12	3.79(1.26)	−0.94(1.38)	−4.57(1.34)
C11–As1–C14–C13	−4.94(1.30)	−1.60(1.26)	4.38(1.26)
C13–N5–C12–C11	−9.61(2.07)	1.64(2.26)	3.79(2.10)
As1–S1–C15–C16	−87.18(1.67)	88.04(1.40)	77.47(1.63)
C13–N5–C12–C4	176.90(1.27)	−177.92(1.27)	−174.41(1.31)
C12–N5–C13–C14	8.47(2.18)	−4.36(2.04)	−3.82(2.19)
C12–N5–C13–C6	−168.44(1.24)	176.87(1.27)	175.27(1.32)
C11–C1–C2–C3	2.23(2.52)	1.25(2.35)	−0.62(2.56)
C2–C1–C11–As1	178.62(1.27)	178.33(1.14)	−179.04(1.35)
C2–C1–C11–C12	1.76(2.23)	−1.15(2.19)	1.16(2.29)
C2–C3–C4–C12	−5.87(2.32)	−0.86(2.24)	1.01(2.19)
C3–C4–C12–N5	−176.69(1.27)	−179.49(1.30)	177.69(1.27)
C3–C4–C12–C11	9.53(1.99)	0.93(2.23)	−0.43(2.09)
C13–C6–C7–C8	−4.40(2.28)	−1.64(2.07)	−0.92(2.22)
C7–C6–C13–N5	178.78(1.24)	179.47(1.24)	178.32(1.32)
C7–C6–C13–C14	1.82(2.08)	0.71(2.00)	−2.54(2.10)
C6–C7–C8–C9	6.23(2.62)	4.49(2.17)	4.49(2.22)
C7–C8–C9–C14	−5.12(2.48)	−7.04(2.47)	−4.51(2.27)
C8–C9–C14–As1	−175.33(1.20)	−179.11(1.31)	−176.22(1.14)
C8–C9–C14–C13	2.52(2.17)	5.90(2.32)	0.89(2.23)
As1–C11–C12–N5	2.22(1.90)	1.13(2.11)	1.50(1.89)
As1–C11–C12–C4	175.79(1.03)	−179.36(1.10)	179.63(1.08)
C1–C11–C12–C4	−7.55(1.96)	0.09(2.19)	−0.61(2.01)
C1–C11–C12–N5	178.87(1.29)	−179.41(1.32)	−178.73(1.24)
C6–C13–C14–As1	176.71(1.06)	−177.16(1.03)	179.42(1.02)
N5–C13–C14–As1	0.14(2.05)	4.09(1.83)	−1.47(1.88)
N5–C13–C14–C9	−177.62(1.29)	178.84(1.26)	−178.33(1.31)
C6–C13–C14–C9	−1.05(2.08)	−2.41(1.94)	2.56(2.05)
S1–C15–C16–C17	−178.29(1.57)	175.64(1.24)	−175.95(1.50)

TABLE 4 Hydrogen bond Parameters in the crystal of **2**

Donor—H. . .Acceptor	*d*(*D-H*) (*Å*)	*d*(*H. . .A*) (*Å*)	*d*(*D. . .A*) (*Å*)	<*D-H. . .A* (°)
N(5A)–H(5A) .. S(1B) [1/2 − x, −1/2 + y, 1/2 − z]	0.9928	2.4156	3.400(12)	171.20
N(5B)–H(5B) .. S(1A) [1/2 − x, 1/2 + y, 1/2 − z]	0.9846	2.5258	3.396(12)	147.28
N(5C)–H(5C) .. S(1C) [1 − x, 1 − y, 1 − z]	0.9850	2.5446	3.458(12)	154.26

eter. Mass spectra (EI, 70 eV; CI, 100 eV) were determined on a M 80 B Hitachi chromatomass spectrometer.

X-Ray Crystallography

Crystal cell data of **2** were measured at room temperature on an Enraf-Nonius CAD-4 four circle diffractometer fitted with graphite monochromatized Mo K_α radiation, $\lambda = 0.710$ Å, employing the $\omega/2\Theta$ technique to $\Theta \leq 27°$. From 6058 reflections measured, 1370 were assumed as observed applying the conditions $1 \geq 3\sigma(I)$. The empiric calculations of absorptions were performed (μMo = 24.67 cm^{-1}). Crystal data for **2:** $C_{15}H_{16}NAsS$, monoclinic, space group $P2_1/n$, at 20°C a = 18.663(3), b = 12.723(3), c = 18.723(5) Å, $\beta = 107.23(2)°$, $V = 4332(2)$ Å^3, $d_{Calc.} = 1.46$ g/cm^3, $Z = 12$. The structure was solved by the direct method, using the SIR program [15]. The arsenic, sulfur, and nitrogen atoms were refined with anisotropic temperature factors. The carbon atoms were refined isotropically. The hydrogen atoms were located by the difference Fourier method and are included in the model at fixed positions. The hydrogen atoms contributions in structural amplitudes were included in fixed positions and isotropic temperature parameters. The final disagreement indices are $R = 0.052$, $R_w = 0.054$ for 1613 independent reflections. All calculations were carried out on an Alpha Station 200 computer, using MolEN programs [16]. Drawings were plotted, using a PLATON program [17].

10-Propylthio-5,10-dihydrophenarsazine **2.** Compound **1** (3.4 g, 12.3 mmol) was added portionwise with stirring at 20°C to the solution of 4.6 g (60.4 mmol) of propanethiol and 3.6 g (35.6 mmol) of triethylamine in 20 mL of anhydrous benzene, and stirring was continued for 2 hours at 20°C. The mixture was centrifugated. The liquid layer was evaporated at reduced pressure (0.08 mm Hg) at 40°C for 2 hours and gave 2.5 g (64%) of crude oily **2** that was crystallized after 1 week. The yield of crystalline **2** was 1.0 g (26%). m.p. 83–85°C. ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.97 (t, 3H, $\underline{CH_3}CH_2CH_2S$, $^3J_{HH}$ 7.5), 1.20–1.88 (m, 2H, $CH_3\underline{CH_2}CH_2S$), 2.60 (t, 2H, $CH_3CH_2\underline{CH_2}S$, $^3J_{HH}$ 7.5), 6.70–7.57 (m, 8H, Ar$\underline{H}$). IR (vaseline oil): ν_{max} 3365 (N–H), 3050, 3015 (=C-H, Ar), 1590, 1570, 1515 (C=C, Ar), 744, 550 (C-S). MS (EI) *m/e* (I_{rel}) 317 $[M]^{+\cdot}$ (50), 273 $[M\text{–}Pr\text{–}H]^{+\cdot}$ (10), 241 $[M\text{–}S\text{–}Pr\text{–}H]^{+\cdot}$ (100). Anal. found: C, 56.61; H, 5.15; As, 23.14. $C_{15}H_{16}NAsS$ requires C, 56.77; H, 5.10; As, 23.63.

S-10(5,10-Dihydrophenarsazine) S′-ethyl S″-propyltetrathiophosphate **4.** Compound **3** [1.3 g (4.2 mmol)] was added portionwise with stirring at 20°C to 2.6 g (8.2 mmol) of **2** in 10 mL of anhydrous benzene under a dry atmosphere, and stirring was continued for 8 hours at 20°C. The mixture was filtered. The filtrate was evaporated at reduced pressure (0.1 and 0.02 mmHg) at 40°C and gave 2.6 g (67%) of crude **4.** Product **4** (0.5 g, 13%) was isolated from the residue by means of a falling-film distillation at 180°C (0.02 mmHg). ^{31}P NMR (C_6H_6, 162 MHz): δ 88.1, ^{1}H NMR (C_6D_6, 60 MHz) δ 0.73 (t, 3H, $\underline{CH_3}CH_2SP$, $^3J_{HH}$ 7.5), 0.78 (t, 3H, $\underline{CH_3}CH_2CH_2SP$, $^3J_{HH}$ 7.5), 1.08–1.85 (m, 2H, $CH_3\underline{CH_2}CH_2SP$), 2.27–3.20 (m, 2H, $CH_3CH_2\underline{CH_2}SP$ + 2H, $CH_3\underline{CH_2}SP$), 6.48–7.17 (m, 8H, Ar$\underline{H}$), 7.75–7.87 (m, 1H, N$\underline{H}$). IR (neat): ν_{max} 3385 (N–H), 3050, 3020 (=C-H, Ar), 2965, 2930, 2870 $\nu_{as,s}$ (CH_3, CH_2), 1590, 1490 (C=C, Ar), 750, 693, 675 (P=S), ν_{as} (PS_2), 525 (P-S, C-S), ν_s (PS_2). MS (EI) *m/e* 428 $[M - Pr - H]^{+\cdot}$ (10), 274 $[M - EtSP(S)SPr]^{+\cdot}$ (10). Anal. found: As, 17.43; P, 6.10. $C_{17}H_{21}AsNPS_4$ requires As, 17.89; P, 6.55.

REFERENCES

[1] Chadaeva, N. A.; Kamai, G. Kh., Mamakov, K. A. Zh Obshch Khim 1966, 36, 1994–1999 and references therein.

[2] Chauhan, H. P. S.; Srivastava, G.; Mehrotra, R. C. Polyhedron 1984, 3, 1337–1345 and references therein.

[3] Chaturvedi, A.; Nagar, P. N.; Srivastava, G. Phosphorus Sulfur Silicon 1993, 80, 141–146.

[4] Chauhan, H. P. S.; Srivastava, G.; Mehrotra, R. C. Synth React Inorg Met Org Chem 1981, 11, 565–575.

[5] Chadaeva, N. A.; Kamai, G. Kh., Mamakov, K. A. Zh Obshch Khim 1966, 36, 916–920.

[6] Camerman, A.; Trotter, J. J Chem Soc 1965, 730–738.

[7] Doak, G. O.; Freedman, L. D. Organometallic Compounds of Arsenic, Antimony, and Bismuth, John Wiley and Sons: New York, 1970.

[8] Fukuyo, M.; Nakatsu, K.; Shimada, A. Bull Chem Soc Jpn 1926, 39, 1614–1615.

[9] de Meester, P.; Chu, S. S. C.; Chu, T. L. Acta Crystallogr C (Cr Str Comm) 1986, 42, 753–755.

[10] de Meester, P.; Chu, S. S. C.; Jovanovic, M. V.; Biehl, E. R. J Heterocycl Chem 1985, 22, 1237–1241.

[11] de Meester, P.; Chu, S. S. C.; Jovanovic, M. V.; Biehl, E. R. J Heterocycl Chem 1986, 23, 1131–1133.

[12] Siriwardane, U.; Razzuk, A.; Khanapure, S. P.; Biehl, E. R.; Chu, S. S. C. J Heterocycl Chem 1988, 25, 1555–1559.

[13] Nizamov, I. S.; Matseevskii, A. V.; Batyeva, E. S.; Abalonin, B. E.; Vandyukova, I. I.; Shagidullin, R. R. Heteroatom Chem 1997, 8, 329–331.

[14] Nizamov, I. S.; Matseevskii, A. V.; Batyeva, E. S.; Vandyukova, I. I.; Abalonin, B. E.; Shagidullin, R. R. Phosphorus Sulfur Silicon 1997, 126, 137–143.

[15] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Viterbo, D. Acta Crystallogr A 1991, 47, 744–748.

[16] Straver, L. H.; Schierbeek, A. J. MolEN Structure Determination System. Nonius B. V.. 1994, 1; 2.

[17] Spek, A. L. Acta Crystallogr A 1990, 46, 34–40.