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# Communication

# $N \rightarrow As$ intramolecularly coordinated organoarsenic(III) chalcogenides: Isolation of terminal As–S and As–Se bonds

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# 1. Introduction

Significant progress has been recently achieved in the field of preparation and structure description of heavier group 15 elements (especially Sb(III), Bi(III)) organometallic chalcogenides, which often show pronounced tendency to oligomerization [1]. Thus, instead of stabilization of terminal RM=E bonds (where M = Sb or Bi; E = S, Se, Te) dimers (RME)<sub>2</sub>, trimers (RME)<sub>3</sub> or even higher oligomers are formed with chalcogen atoms forming bridges between the pnictogen atoms [1]. These compounds may be stabilized either kinetically using bulky substituents or thermodynamically by the presence of multidentate ligands and intramolecular  $N \rightarrow M$  dative interaction. The bulky substituents were successfully used by Tokitoh [2] and Breunig [3] et al. for stabilization of series of both antimony and bismuth (poly)sulfides, selenides and rare examples of tellurides including unprecedented three-membered M<sub>2</sub>Te ring systems [4]. Nevertheless, compounds with terminal M=E bonds could not be prepared as stable species using this type of ligands. On the contrary, we and others have demonstrated that using of NC- or NCN-chelating ligand represents an interesting alternative for stabilization of these chalcogenides [5] and using of NCN pincer type ligands allowed isolation of the

#### ABSTRACT

Unprecedented NCN – intramolecularly chelated organoarsenic(III) sulfide and selenide LASE (where  $L = [2,6-(Me_2NCH_2)_2C_6H_3]^-$  and E = S (**2**) or Se (**3**)) were prepared by the reaction of the parent chloride LASCl<sub>2</sub> (**1**) with Li<sub>2</sub>E. Analogously, the reaction of NC chelated compound L'ASCl<sub>2</sub> (**4**) (where  $L' = [2-(2',6'-i-Pr_2C_6H_3)N=CH)C_6H_4]^-$ ) with Li<sub>2</sub>S gave the corresponding sulfide L'ASS (**5**). The molecular structures of **3** and **4** were established in the solid state using X-ray diffraction technique.

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first terminal Sb=E (E = S, Se, Te) bonds (Fig. 1A) [6]. In comparison to the rich chemistry of organoantimony(III) and organobismuth(III) chalcogenides corresponding organoarsenic(III) compounds have gained only limited interest, among published results the five-membered cycles  $RAs(E)(E_2)AsR$  (E = S, Se) [7] and the only arsenic telluride derived from the 9,10-epichalcogeno-9,10-dihydroarsathrene backbone (Fig. 1B) are noteworthy [8]. Organoarsenic(III) compounds with terminal As=E bonds are, to the best of our knowledge, unknown and compound with simple alkyl substituents tend to oligomerize [9]. As we were able to observe terminal Sb=E bonds in compounds using advantage of intramolecular interactions mediated by the NCN pincer type ligands, we were interested whether the same or related NC chelating ligand system will be good candidate for the stabilization of the terminal As=E bonds.

Herein, we report the syntheses and structures of organoarsenic(III) chalcogenides LASE (where  $L = [2,6-(Me_2NCH_2)_2C_6H_3]^$ and E = S (**2**) or Se (**3**)) and L'ASS (**5**) (where  $L' = [2-((2',6'-i-Pr_2C_6H_3)N=CH)C_6H_4]^-)$  containing terminal As=E bond (E = S or Se) both in the solid state and in solution.

# 2. Result and discussion

The intramolecularly coordinated organoarsenic(III) chloride LAsCl<sub>2</sub> (**1**) [10] reacts smoothly with *in situ* [11] prepared Li<sub>2</sub>S or



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Fig. 1. (A) Compounds with terminal Sb=E bonds. (B) Structures of selected organoarsenic(III) chalcogenides.

Li<sub>2</sub>Se to yield expected molecular chalcogenides LAsE (where E = S (2) or Se (3), Scheme 1). Both compounds were isolated after workup as colorless (2) or yellow (3) crystalline solids, which are indefinitely stable under inert conditions. The identity of both compounds was established by the help of elemental analysis and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

The molecular structure of **3** was unambiguously determined by the help of single crystal X-ray diffraction analysis [12] and is depicted with relevant structural parameters in Fig. 2. The results of the analysis proved an exclusively monomeric structure of 3 with isolated terminal As-Se bond, which is the first example of such a compound. The bond length As(1)-Se(1) 2.2736(5) Å is significantly shorter (6%) than the corresponding sum of the respective covalent radii for the As–Se single bond  $\Sigma_{cov}(As, Se) = 2.37 \text{ Å} [13].$ This value also approaches the theoretically determined value of 2.21 Å for the As=Se double bond by Pyykkö [13]. These facts indicate multiple character of this bond, but the shortening of the bond length may also be in part ascribed to the electrostatic interaction between bonding partners, because the terminal bond is most probably polarized  $(As(\delta+)-Se(\delta-))$  as recently proved by us in closely related NCN chelated systems containing Sb-E terminal bonds (E = S, Se, Te) [6]. The presence of partial positive charge on the central arsenic atom is also reflected in the presence of two strong intramolecular  $N \rightarrow As$  interactions, where the bond lengths As(1)-N(1) 2.312(3) and As(1)-N(2) 2.351(3) Å are fairly shorter than the sum of van der Waals radii  $\Sigma_{vdW}(As, N) = 3.75$  Å. The coordination polyhedron of the central arsenic atom may be described as a pseudo-trigonal bipyramid (so called see-saw structure) with the nitrogen atoms located in the axial positions (the bonding angle N(1)-As(1)-N(2) 153.42(10) $^{\circ}$ ) and the *ipso*carbon atom C(1), selenium atom Se(1) and the lone pair of electrons occupy the equatorial positions. The value of the bonding angle C(1)-As(1)-Se(1) 100.99 $(9)^{\circ}$  is more acute than ideal value 120° reflecting repulsion with the lone pair of arsenic.

The monomeric structure of **3** determined in the solid state is retained in solution ( $C_6D_6$ ) and, similarly, compound **2** is



E = S(2), Se(3)

Scheme 1. Synthesis of the intramolecularly coordinated organoarsenic(III) chalcogenides 2 and 3.

monomeric in solution as proved by the help of <sup>1</sup>H and <sup>13</sup>C NMR spectra. Thus, the <sup>1</sup>H NMR spectrum of both **2** and **3** revealed only one set of signals, where the signal for the diastereotopic CH<sub>2</sub>N protons are observed as an AX-type pattern at  $\delta_A$  2.87 and  $\delta_x$  3.77 for  $2(\delta_A 2.86 \text{ and } \delta_x 3.80 \text{ for } 3)$  and one singlet for N(CH<sub>3</sub>)<sub>2</sub> protons. This finding indicates both non-symmetric coordination environment of the arsenic atom and the presence of rigid intramolecular  $N \rightarrow As$ interactions, which render rotation around the C(ligand)-As bond and, thus, proving the same monomeric structure as determined for 3 in the solid state. Similarly, the monomeric antimony chalcogenides LSbE (E = Se, Te) showed an AX-type pattern for the diastereotopic CH<sub>2</sub>N protons, that was also ascribed to the rigid  $N \rightarrow Sb$ interactions and presence of terminal Sb–E bonds. The <sup>77</sup>Se NMR spectrum of **3** showed one signal at  $\delta$  0.0 and this value is shifted to the higher frequency in comparison with the analogous antimony selenide LSbSe ( $\delta$  –153.0) [6a]. Another proof for the presence of terminal As–S(Se) bonds stems from the Raman spectra, where only one strong band at 453  $\text{cm}^{-1}$  for As–S bond in **2** and at 310  $\text{cm}^{-1}$  for As-Se bond in 3 was observed. Both values are significantly shifted



**Fig. 2.** ORTEP view of **3**. The thermal ellipsoids are drawn with 50% probability. Benzene molecule is omitted for clarity. Selected bond distances (Å) and angles (°): As(1)-C(1) 1.945(3), As(1)-Se(1) 2.2736(5), As(1)-N(1) 2.312(3), As(1)-N(2) 2.351(3), N(1)-As(1)-N(2) 153.42(10), C(1)-As(1)-Se(1) 100.99(9), C(1)-As(1)-N(1) 79.08(10), C(1)-As(1)-N(2) 78.27(10).

in comparison with the values usually obtained for the bridging As– S(Se)–As bonds in oligo- or polymeric species [14].

To get some additional insight into the structures of compounds 2 and 3 and to describe the terminal As=E bonds in particular, DFT calculations on these structures were performed using the Gaussian 09 program [15]. Starting from the crystal structure of 3. a geometry optimization of this molecule was performed at the B3LYP [16]/cc-pVTZ [17] level of theory. The equilibrium geometry obtained was found to be in good agreement with the crystal structure of 3. In addition, the geometry of compound 2 was optimized at the same level of theory. In order to probe the features of the terminal As–S and As–Se bonds, an NBO analysis [18] was performed on the optimized structures; in addition, the Wiberg bond order [19] for these bonds were computed. From this analysis, it can be stated that, as was previously found for organoantimony(III) compounds containing antimony-selenium and tellurium terminal bonds [6a], the bond between As and S or Se is intermediate between a polarized single bond and a double bond. The NBO charge on As amounts to +0.830 and +0.740 in 2 and 3 respectively, the charge on S and Se being -0.726 and -0.645, respectively. For compound **2**, the Wiberg bond order for the As–S bond order is 1.481, whereas in the case of the As-Se bond it is 1.475. For comparison, the corresponding values in the compounds LSbSe and LSbTe are 1.409 and 1.426, respectively [6a].

The ligand L' has been investigated to test the possible stabilization of similar monomeric arsenic(III) chalcogenides by only one N-donor functionality (Scheme 2). The starting chloride L'AsCl<sub>2</sub> ( $\mathbf{4}$ ) was prepared by conversion of the lithium precursor with arsenic(III) chloride in diethylether. Compound **4**. stable under inert conditions, was isolated as yellowish crystals in high yield. The identity of 4 was established by the help of elemental analysis and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The molecular structure of **4** was proven by the help of single crystal X-ray diffraction analysis [12] and is depicted with relevant structural parameters in Fig. 3. The nitrogen donor atom of L' ligand is strongly coordinated to the central arsenic atom with the As(1)-N(1) bond length of 2.329(3) Å. This value is comparable with the N $\rightarrow$ As interaction (2.351(9) Å) observed in the related N,C chelated compound [8-(Me<sub>2</sub>N)C<sub>10</sub>H<sub>6</sub>]AsCl<sub>2</sub> [20]. The coordination polyhedron of the central atom may be described as a see-saw structure, similarly to 3, with the N(1) and Cl(1) atom occupying the axial position (the bonding angle N(1)As(1)-Cl(1) is  $171.94(8)^{\circ}$  and the equatorial plane is formed by the *ipso-C*(1) atom, the chlorine atom Cl(2) and the lone pair of the arsenic atom.

The reactions of **4** with lithium chalcogenides Li<sub>2</sub>E (E = S, Se) were studied. In the case of the selenide, only a complicated mixture of non-separable products was observed, however the reaction of **4** with Li<sub>2</sub>S gave smoothly the expected sulfide L'AsS (Scheme 2) as a bright yellow air sensitive solid. The identity of **5** was established by the help of elemental analysis and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Unfortunately, all numerous attempts to obtain



**Fig. 3.** ORTEP view of **4**. The thermal ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): As(1)–C(1) 1.959(4), As(1)–Cl(1) 2.3299(10), As(1)–Cl(2) 2.2043(9), As(1)–N(1) 2.329(3), N(1)As(1)–Cl(1) 171.94(8), C(1)–As(1)–Cl(1) 95.46(9), C(1)–As(1)–Cl(2) 97.48(9), C(1)–As(1)–N(1) 77.94(12).

suitable single crystals for X-ray diffraction analysis failed and, thus, we are not able to speculate about the structure in the solid state. Nevertheless, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5** revealed only one set of signals for the ligand L' (see Experimental). Furthermore, upon cooling the sample of **5** in  $C_7D_8$  to 200 K the signals of the *i*-Pr groups on the flanking aromatic rings became non-equivalent suggesting the non-symmetric environment around the central arsenic atom. The Raman spectrum of **5** revealed four medium to strong bands at 331, 339, 364 and 375 cm<sup>-1</sup>, which are significantly shifted in comparison with value found for the terminal As–S bond in **2** (453 cm<sup>-1</sup>). More importantly, these values fall within the interval typical for bridging As–S–As groups [14]. These facts indicate oligomeric structure of **5** formed via As–S–As bridges.

#### 3. Conclusion

In conclusion, we have demonstrated that NCN chelating ligand L is a good candidate for preparation of molecular organoarsenic(III) sulfide and selenide. The application of the ligand L allowed



Scheme 2. Synthesis of the intramolecularly coordinated organoarsenic(III) compounds 4 and 5.

successful isolation of unprecedented compounds with preserved terminal As–S(Se) bonds both in the solid state and in solution. It is worth mentioning that development and utilization of more robust chelating ligands will be necessary for preparation of corresponding tellurides. Only the organoarsenic(III) sulfide could be prepared using the ligand L' proving significantly lower potential for stabilization of arsenic chalcogenides in the case of L', furthermore this ligand is not able to stabilize terminal As–S bond.

# 4. Experimental

## 4.1. General methods

The starting compounds [2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]AsCl<sub>2</sub> [10], and 2-((2',6'-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CH)C<sub>6</sub>H<sub>4</sub>Br [21] were prepared according to the literature procedures. The THF solutions of Li<sub>2</sub>S and Li<sub>2</sub>Se were prepared from sulfur (selenium) and Li[B(Et)<sub>3</sub>H] according to the literature procedure and used in situ [11]. All solvents were dried by standard procedures. The <sup>1</sup>H, <sup>13</sup>C, <sup>77</sup>Se NMR spectra were recorded on a Bruker Avance500 at 300 K in C<sub>6</sub>D<sub>6</sub> at 500.13, 125.77 and 95.38 MHz, respectively. The <sup>1</sup>H, <sup>13</sup>C, NMR chemical shifts  $\delta$  are given in ppm and referenced to the residual signals of the solvent  $(C_6D_6: \delta(^1H) = 7.16 \text{ ppm}, \delta(^{13}C) = 128.39 \text{ ppm})$ . The <sup>77</sup>Se chemical shifts were determined using  $\Xi = 19.071513$  MHz corresponding to proton frequency 100.00 MHz (i.e.,  $\delta(^{77}\text{Se}) = 0.0$  at 95.382358 MHz for proton frequency 500.13 MHz). Elemental analyses were performed on an LECO-CHNS-932 analyzer. Raman spectra of samples sealed in quarts capillaries were recorded on a Bruker IFS 55 with FRA 106 extension in region  $50-3500 \text{ cm}^{-1}$ .

#### 4.2. Synthesis of compound 2

A solution of Li<sub>2</sub>S (2.61 mmol, prepared from 84 mg of sulfur, and 5.2 mL of 1 M THF solution of Li[B(Et)<sub>3</sub>H]) in THF (20 mL) was added to a solution of LAsCl<sub>2</sub> (761 mg, 2.27 mmol) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. Upon addition, the brown–orange material precipitated and the resulting mixture was stirred for additional 1 h at r.t. The reaction mixture was evaporated to dryness, and extracted with toluene (30 mL). The yellow extract was evaporated and the resulting material was washed with hexane (2 × 10 mL) to give yellowish solid characterized as **2**. Yield: 420 mg (62%). Mp. 102–104 °C. Anal. calcd for C<sub>12</sub>H<sub>19</sub>AsN<sub>2</sub>S (298.28 g mol<sup>-1</sup>): C, 48.3; H, 6.4. Found: C, 48.5; H, 6.5. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  2.21 (s (br), 12H, (CH<sub>3</sub>)<sub>2</sub>N), 2.87 and 3.77 (AX system, 4H, CH<sub>2</sub>N), 6.76 (d, 2H, Ar–H3,5), 7.04 (t, 1H, Ar–H4). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125.77 MHz):  $\delta$  44.9 ((CH<sub>3</sub>)<sub>2</sub>N), 62.1 (CH<sub>2</sub>N), 124.9 (Ar–C3,5), 128.7 (Ar–C4), 141.4 (Ar–C2,6), 153.4 (Ar–C1). Raman (cm<sup>-1</sup>): 453 (s) As–S.

# 4.3. Synthesis of compound 3

A solution of Li<sub>2</sub>Se (3.63 mmol, prepared from 287 mg of selenium powder, and 7.3 mL of 1 M THF solution of Li[B(Et)<sub>3</sub>H]) in THF (30 mL) was added to a solution of LAsCl<sub>2</sub> (1.09 g, 3.16 mmol) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. Upon addition, the brown–red material precipitated and the resulting mixture was stirred for additional 1 h at r.t. The reaction mixture was evaporated to dryness, and extracted with toluene (50 mL). The bright yellow extract was evaporated to *ca*. 10 mL and storage of this solution at 5 °C for overnight gave yellow single crystals of **3**, which were separated by decantation and washed with hexane (10 mL). Yield: 501 mg (46%). Mp. 140 °C. Anal. calcd for C<sub>12</sub>H<sub>19</sub>AsN<sub>2</sub>Se (345.17 g mol<sup>-1</sup>): C, 41.8; H, 5.6. Found: C, 42.1; H, 5.8. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz):  $\delta$  2.13 (s (br), 12H, (CH<sub>3</sub>)<sub>2</sub>N), 2.86 and 3.80 (AX system, 4H, CH<sub>2</sub>N), 6.78 (d, 2H, Ar–H3,5), 7.04 (t, 1H, Ar–H4). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125.77 MHz):  $\delta$  45.2

((CH<sub>3</sub>)<sub>2</sub>N), 62.0 (CH<sub>2</sub>N), 124.8 (Ar–C3,5), 128.4 (Ar–C4), 141.0 (Ar– C2,6), 152.7 (Ar–C1). Raman (cm<sup>-1</sup>): 310 (vs) As–Se.

#### 4.4. Synthesis of compound 4

A solution of n-BuLi (2.2 mL, 3.43 mmol, 1.6 M solution in hexane) was added to a solution of  $2-((2'.6'-i-Pr_2C_6H_3)N=CH)$  $C_6H_4Br$  (1.18 g. 3.43 mmol) in diethylether (50 mL) at -70 °C and stirred for 1 h at this temperature. The resulting yellow-orange suspension of the lithium compound was added to a solution of AsCl<sub>3</sub> (0.29 mL, 3.43 mmol) in diethylether (30 mL) pre-cooled to -78 °C. The resulting mixture was allowed to reach room temperature and stirred for additional 90 min. The yellowish precipitate was filtered and washed with additional hexane (10 mL). The precipitate was extracted with benzene (50 mL) and the obtained yellow extract was evaporated to dryness and washed with hexane (10 mL) to give 4 as yellowish powder. The single crystals were obtained by recrystallization from benzene/hexane mixture. Yield: 1.19 g (85%). Mp. 169-171 °C. Anal. calcd for C<sub>19</sub>H<sub>22</sub>AsCl<sub>2</sub>N (410.21 g mol<sup>-1</sup>): C, 55.6; H, 5.4. Found: C, 55.8; H, 5.7. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 1.02 (d (br), 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.86 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.86 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 6.94 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 7.10 (m, 4H, 2',6'-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>), 7.45 (s, 1H, CH=N), 8.97 (dd, 1H,  $C_6H_4$ ). <sup>13</sup>C NMR ( $C_6D_6$ , 125.77 MHz):  $\delta$  24.2 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 25.2 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 29.1 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 124.5, 127.5, 131.8, 132.0, 133.4, 134.4, 137.5, 140.5, 143.4, 148.4 (s, Ar-C), 165.4 (s, CH=N).

#### 4.5. Synthesis of compound 5

A solution of Li<sub>2</sub>S (0.89 mmol, prepared from 29 mg of sulfur, and 1.8 mL of 1 M THF solution of Li[B(Et)<sub>3</sub>H]) in THF (20 mL) was added to a solution of L'AsCl<sub>2</sub> (318 mg, 0.78 mmol) in 30 mL of THF. Upon addition, the white material precipitated and the resulting mixture was stirred for additional 1 h at r.t. The reaction mixture was evaporated to dryness, and extracted with toluene (30 mL). The vellow extract was evaporated to ca. 10 mL and hexane (15 mL) was added resulting to precipitation of yellowish material (from the mother liquor second crop was obtained by next addition of hexane and storage at 5 °C), which was filtered and washed with hexane  $(2 \times 5 \text{ mL})$  to give yellowish solid characterized as **5**. The product was may be recrystallized from toluene. Yield: 244 mg (85%). Mp. 215–217 °C. Anal. calcd for C<sub>19</sub>H<sub>22</sub>AsNS (371.37 g mol<sup>-1</sup>): C, 61.5; H, 6.0. Found: C, 61.3; H, 5.8. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz): δ 1.13 (d (br), 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.26 (sept, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 7.00 (m, 6H, 2',6'-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>), 8.03 (s, 1H, CH=N), 8.32 (dd, 1H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 125.77 MHz): δ 24.2 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 25.2 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 28.9 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 124.1, 126.0, 129.9, 131.3, 133.6, 135.7, 137.5, 139.5, 144.9, 147.4 (s, Ar–*C*), 164.7 (s, CH=N). <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, 500 MHz, 200 K): δ 0.96, 1.04, 1.11 and 1.27 (four doublets, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.24 (sept (br), 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.77 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 6.93 (d, 1H, C<sub>6</sub>H<sub>4</sub>), 7.05 (m, 4H, 2',6'-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>), 7.80 (s, 1H, CH=N), 8.36 (d, 1H, C<sub>6</sub>H<sub>4</sub>). Raman (cm<sup>-1</sup>): 331(s), 339(s), 364(m), 375(s) S–As–S.

#### 4.6. X-ray structure determination

The suitable single crystal of **3** and **4** were mounted on glass fiber with an oil and measured on four-circle diffractometer KappaCCD with CCD area detector by monochromatized MoK<sub>α</sub> radiation ( $\lambda = 0.71073$  Å) at 150(1) K. The numerical [22] absorption corrections from crystal shape were applied for all crystals. The structures were solved by the direct method (SIR92) [23] and refined by a full matrix least squares procedure based on  $F^2$ (SHELXL97) [24]. Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors  $H_{\rm iso}$ (H) = 1.2 U<sub>eq</sub> (pivot atom) or of 1.5 U<sub>eq</sub> for the methyl moiety with C-H = 0.96, 0.97, and 0.93 Å for methyl, methylene, and hydrogen atoms in aromatic ring, respectively.

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# Appendix A. Supplementary material

CCDC 835515 and 835513 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data\_request/cif.

# Appendix B. Supplementary material

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jorganchem.2012.10.029.

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