

Five-Membered Arsenic–Sulfur–Nitrogen Heterocycles, RAs(S₂N₂)

Vit Matuska, Alexandra M. Z. Slawin and J. Derek Woollins*

*Department of Chemistry University of St Andrews,
North Haugh, St Andrews, Fife, KY16 9ST, United Kingdom
jdw3@st-and.ac.uk*

Abstract

A series of 5-alkyl/aryl-1,3λ⁴δ²,2,4,5-dithiadiazarsoles RAs(S₂N₂) (R = Me, Et, ⁱPr, ^tBu, Ph, Mes) were prepared by a ligand exchange between [ⁿBu₂Sn(S₂N₂)]₂ and the corresponding organodihalogenoarsines RAsX₂ (X = Cl, I). All products were characterized by NMR, IR and Raman spectroscopies and mass spectrometry. The crystal structures of the aryldithiadiazarsoles (R = Ph, Mes) were determined.

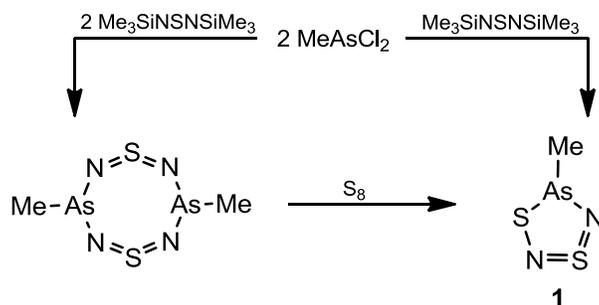
Key words: dithiadiazarsoles, sulfur–nitrogen rings, structure elucidation, spectroscopy

*Corresponding author. Fax +44.1334.463804, e-mail jdw3@st-andrews.ac.uk.

1. Introduction

The reaction between $\text{Me}_3\text{SiNSNSiMe}_3$ and MeAsCl_2 leads to the formation of eight- or five-membered arsenic–sulfur–nitrogen heterocycles. The outcome depends on stoichiometric ratio of the reactants.^{1,2} The eight-membered ring can be converted into the five-membered one by reaction with sulfur, though the yield is low (Scheme 1).^{1,2}

Scheme 1.



While the eight-membered rings were thoroughly investigated,^{3,4,5,6} $\text{MeAs(S}_2\text{N}_2)$ (**1**) has been the only known five-membered $\text{As(S}_2\text{N}_2)$ heterocycle for nearly 40 years. It was formed in a low yield as an orange, air-sensitive and volatile liquid and was characterized by ^1H NMR, IR, UV spectroscopies and mass spectrometry.

Nowadays, a methodical research in this area is hindered predominantly by complicated access to what used to be commercially available starting materials. Here we report the synthesis and characterization of a series of 1,3,2,4,5-dithiadiazarsoles $\text{RAs(S}_2\text{N}_2)$ ($\text{R} = \text{Me, Et}$ (**2**), ^iPr (**3**), ^tBu (**4**), Ph (**5**), Mes (**6**)). Single crystal X-ray structures of **5** and **6** were determined and reactivity of **5** was briefly studied.

2. Experimental

-
- (1) Scherer, O. J.; Wies, R. *Angew. Chem.-Int. Edit. Engl.* **1971**, *10*, 812–813.
(2) Scherer, O. J.; Wies, R. *Angew. Chem.-Int. Edit. Engl.* **1972**, *11*, 529.
(3) Alcock, N. W.; Holt, E. M.; Kuyper, J.; Mayerle, J. J.; Street, G. B. *Inorg. Chem.* **1979**, *18*, 2235–2239.
(4) (a) Gieren, A.; Betz, H.; Hübner, T.; Lamm, V.; Herberhold, M.; Guldner, K. *Z. Anorg. Allg. Chem.* **1984**, *513*, 160–174. (b) Gieren, A.; Hübner, T.; Herberhold, M.; Guldner, K.; Süß-Fink, G. *Z. Anorg. Allg. Chem.* **1987**, *544*, 137–148. (c) Herberhold, M.; Schamel, K.; Herrmann, G.; Gieren, A.; Ruiz-Pérez, C.; Hübner, T. *Z. Anorg. Allg. Chem.* **1988**, *562*, 49–61. (d) Herberhold, M.; Schamel, K. *J. Organomet. Chem.* **1988**, *346*, 13–22. (e) Herberhold, M.; Guldner, K.; Gieren, A.; Ruiz-Pérez, C.; Hübner, T. *Angew. Chem.* **1987**, *99*, 81–82.
(5) Chivers, T.; Dhathathreyan, K. S.; Lensink, C.; Richardson, J. F. *Inorg. Chem.* **1988**, *27*, 1570–1574.
(6) (a) Spang, C.; Edelmann, F. T.; Noltemeyer, M.; Roesky, H. W. *Chem. Ber.* **1989**, *122*, 1247–1254. (b) Edelmann, F.; Spang, C.; Noltemeyer, M.; Sheldrick, G. M.; Keweloh, N.; Roesky, H. W. *Z. Naturforsch. (B)* **1987**, *42*, 1107–1109.

Materials. All reactions were carried out in an oxygen-free nitrogen atmosphere using standard Schlenk and syringe techniques. Dry solvents were used from the Solvent purification system MB-SPS-800 (MBraun GmbH).

CH₃I and C₂H₅I were purchased from Fluka, diethyl ether solutions of ¹PrMgCl and ¹BuMgCl from Aldrich and 2-bromomesitylene from Alfa-Aesar. AsCl₃ was purchased from ABCR and once used up, it was prepared according to the published procedure.⁷ Phenylarsonic acid and As₂O₃ were obtained from the departmental store. CH₃AsI₂,⁸ EtAsI₂,^{8,9} ¹PrAsCl₂,¹⁰ ¹BuAsCl₂,¹¹ PhAsCl₂¹² and MesAsCl₂^{3,13} were prepared according to published procedures. MesAsCl₂ was used for further synthesis in a crude form, *i.e.* as a mixture of mesitylarsenic chloride and bromide.³ **Caution!** Organodihalogenoarsines (esp. PhAsCl₂) are vesicants. Heavy rubber gloves should be worn when working with these substances. Further details about the syntheses of RAsX₂ are presented in Supporting Information. [ⁿBu₂Sn(S₂N₂)],¹⁴ Pt(COD)Cl₂,¹⁵ Cp₂Ti(CO)₂¹⁶ and Cp*Co(CO)₂¹⁷ were prepared according to literature procedures.

Instrumentation. All NMR spectra were recorded in CDCl₃ at 298 K. ¹H NMR spectra were recorded on Jeol GSX spectrometer at the frequency of 270 MHz (compound **6** also on Bruker Avance 500 at 500 MHz), with δ (ppm) referenced to external tetramethylsilane and calibrated to the peak of residual CHCl₃ (7.26 ppm).¹⁸ ¹³C NMR spectra were recorded on Jeol GSX spectrometer at 67.9 MHz with δ referenced to external tetramethylsilane. All ¹³C NMR spectra are proton-decoupled. ¹⁴N NMR spectra were recorded on Bruker Avance II 400 spectrometer at 28.9 MHz with δ referenced to external liquid ammonia. Simulations of NMR spectra were performed using WIN-DAISY module in Topspin 2.1 processing software (Bruker). IR spectra were recorded as liquid films between CsI discs or as thin pressed KBr discs on Perkin-Elmer 2000 FT/IR/Raman spectrometer, Raman spectra were recorded in glass capillaries in the range 3500–100 cm⁻¹ using the same spectrometer. Mass spectrometry was

(7) Pandey, S. K.; Steiner, A.; Roesky, H. W. *Inorg. Synth.*, **1997**, *31*, 148–150.

(8) Millar, I. T.; Heaney, H.; Heinekey, D. M.; Fernelius, W. C. *Inorg. Synth.* **1960**, *6*, 113–115.

(9) McKenzie, A.; Wood, J. K. *J. Chem. Soc.* **1920**, *117*, 406–415.

(10) Dicarolo Jr., R. L.; Shenai-Khatkhate, D. V.; Power, M. B.; Amamchyan, A. *Preparation of monoalkyl group 15 dihalides and dihydrides for use as chemical vapor deposition precursors*; Eur. Pat. Appl. No.EP1335416, 2003.

(11) Tzschach, A.; Deylig, W. *Z. Anorg. Allg. Chem.* **1965**, *336*, 36–41.

(12) Adams, E.; Jeter, D.; Cordes, A. W.; Kolis, J. W. *Inorg. Chem.* **1990**, *29*, 1500–1503.

(13) Vedejs, E.; Lee, N. *J. Am. Chem. Soc.* **1995**, *117*, 891–900.

(14) Aucott, S. M.; Slawin, A. M. Z.; Woollins, J. D. *Can. J. Chem.* **2002**, *80*, 1481–1487.

(15) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528.

(16) Sikora, D. J.; Moriarty, K. J.; Rausch, M. D. *Inorg. Synth.* **1990**, *28*, 248–256.

(17) Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 273–280.

(18) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515.

performed by the University of St Andrews Mass Spectrometry Service and elemental analyses were performed by the St Andrews University School of Chemistry Service.

Cyclic voltammetry was performed using an EcoChemie μ Autolab apparatus controlled by GPES 4.2 software. Three-electrode system consisted of a glass-embedded platinum disc working electrode (area = 0.008 cm²), platinum wire counter electrode and Ag/AgCl reference electrode. Typically, 5 mM solutions of the analyte in dry CH₃CN were placed in an electrochemical cell of 10 mL capacity and were provided with 1.0 mmol of supporting electrolyte ([ⁿBu₄N][PF₆]). A small amount (0.2 mg) of solid ferrocene was added as internal standard. The voltammograms were calibrated for the half-wave potential of the ferrocene/ferrocenium couple $E_{1/2} = 0V$.

Single crystal X-ray structure data were collected on Rigaku MM007 Saturn or Mercury CCD diffractometers using Mo-K α radiation (confocal optic, $\lambda = 0.71073 \text{ \AA}$), and corrected for absorption. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 values of all data. Refinements were performed using SHELXTL (Version 6.1, Bruker-AXS, Madison WI, USA, 2001).

Preparations. MeAs(S₂N₂) (1). MeAsI₂ (370 mg, 1.08 mmol) dissolved in CH₂Cl₂ (10 mL) was added dropwise at room temperature to a stirred solution of [ⁿBu₂Sn(S₂N₂)₂] (351 mg, 0.538 mmol) in CH₂Cl₂ (10 mL). The color of the mixture changed from yellow to orange, no heat evolution was observed. The mixture was gently refluxed for 3 hours and after cooling to room temperature was filtered through a sinter. The solvent was removed from the filtrate to leave a dark red oil, which was distilled under vacuum (B14 microdistillation apparatus insulated with glass wool; 0.3 Torr, oil bath temperature 90 °C). Pure **1** distilled as an orange/brown, air-sensitive, volatile oil and was collected to a flask immersed in a small acetone/dry ice cooling bath to avoid loss of the product to the vacuum line cold trap. The distillation residue consisted of ⁿBu₂SnI₂ (verified by ¹H NMR) contaminated by unspecified impurities, and was discarded. **1** did not crystallize upon cooling. Yield 54 mg (30 %). MS (EI⁺TOF): m/z 181.89 (18 %) [M]⁺, 166.87 (100 %) [AsS₂N₂]⁺, 135.92 (8 %) [MeAsSN]⁺, 120.90 (10 %) [AsSN]⁺, 106.89 (10 %) [AsS]⁺, 89.94 (5 %) [MeAs]⁺, 74.92 (2 %) [As]⁺. ¹H NMR: δ 1.17 (s, 3H, CH₃). ¹³C NMR: δ 24.5 (CH₃). ¹⁴N NMR: δ 274.2 (AsN), 301.4 (SNS). IR (cm⁻¹, neat liquid between CsI discs): 1054, 926, 677, 605, 503, 363 (As(S₂N₂) ring vibr.), 561 (ν As–C). Raman (cm⁻¹): 1057, 929, 679, 506, 562.

EtAs(S₂N₂) (2). Prepared from EtAsI₂ (0.627 g, 1.75 mmol) and [ⁿBu₂Sn(S₂N₂)₂] (0.572 g, 0.877 mmol) in the same way as **1** (vacuum distillation at 0.3 Torr, oil bath temperature 120 °C). **2** in the distillate was slightly contaminated with ⁿBu₂SnI₂ and was purified by silica column chromatography

(25×1.5 cm). The byproduct was removed by elution with hexane and pure **2** was eluted by toluene. Removal of the solvent left **2** as an orange oil which did not crystallize upon cooling. Yield 86 mg (25 %).¹⁹ MS (CI⁺TOF): *m/z* 196.92 (100 %) [MH]⁺, 166.87 (65 %) [AsS₂N₂]⁺, 149.94 (6 %) [EtAsSN]⁺, 136.92 (6 %) [EtAsSH]⁺, 117.96 (20 %) [EtAsN]⁺, 106.89 (13 %) [AsS]⁺, 104.97 (4 %) [EtAsH]⁺. ¹H NMR: ABX₃ spin system: δ 0.99 (dd, 3H, CH₃), 1.36 (m, 1H, H-A in CH₂), 1.52 (m, 1H, H-B in CH₂), *J*_{AB} = 13.42 Hz, *J*_{AX} = 7.59 Hz, *J*_{BX} = 7.78 Hz. ¹³C NMR: δ 6.5 (CH₃), 32.5 (CH₂). ¹⁴N NMR: δ 271.6 (AsN), 303.3 (SNS). IR (cm⁻¹, neat liquid between CsI discs): 1059, 931, 675, 611, 503, 370 (As(S₂N₂) ring vibr.); 1021 (ν C–C); 546, 522 (ν As–C). Raman (cm⁻¹): 1061, 932, 679, 612, 506, 367, 548, 523.

¹PrAs(S₂N₂) (3). ¹PrAsCl₂ (0.4 mL, 0.660 g, 3.50 mmol) dissolved in CH₂Cl₂ (25 mL) was added dropwise at room temperature to a stirred solution of [ⁿBu₂Sn(S₂N₂)]₂ (1.14 g, 1.75 mmol) in CH₂Cl₂ (25 mL). The mixture was stirred at room temperature overnight. The resulting cloudy orange reaction mixture was reduced to a quarter of its original volume and was filtered through a short glass pipette with a small celite plug directly onto a Bio-Beads S-X8 column (27×1.5 cm) soaked in reagent grade CH₂Cl₂.²⁰ Elution with CH₂Cl₂ (reagent grade) removed impure ⁿBu₂SnCl₂ as a yellowish band followed by a broad orange band of the product. The orange fraction was collected, reduced in volume (if necessary) and subjected twice more to Bio-Beads size-exclusion chromatography. **3** was isolated as an orange, volatile oil which did not crystallize upon cooling. Yield 169 mg (23 %). Anal. Calcd for C₃H₇AsS₂N₂: C, 17.1; H, 3.3; N, 13.3. Found: C, 16.8; H, 3.0; N, 13.3. MS (EI⁺TOF): *m/z* 209.93 (8 %) [M]⁺, 166.87 (100 %) [AsS₂N₂]⁺, 120.90 (1 %) [AsSN]⁺, 89.93 (3 %) [AsN]⁺. ¹H NMR: δ 0.942 (d, 3H, CH₃), 0.960 (d, 3H, CH₃), 1.62 (qqrt, 1H, CH), *J* = 7.16 Hz. ¹³C NMR: δ 15.1 (CH₃), 15.7 (CH₃), 38.2 (CH). ¹⁴N NMR: δ 272.3 (AsN), 303.4 (SNS). IR (cm⁻¹, KBr disc): 1059, 932, 678, 601, 505, 367 (As(S₂N₂) ring vibr.); 1156, 868 (ν C–C); 547 (ν As–C). Raman (cm⁻¹): 1060, 934, 680, 508, 367, 1158, 869, 549.

¹BuAs(S₂N₂) (4). Prepared from ¹BuAsCl₂ (400 mg, 1.97 mmol) and [ⁿBu₂Sn(S₂N₂)]₂ (643 mg, 0.986 mmol) in the same way as **3**. **4** was obtained as an orange, volatile oil with characteristic pungent onion-like odor. **4** did not crystallize at low temperatures. Yield 88 mg (20 %). Anal. Calcd for C₄H₉AsS₂N₂: C, 21.4; H, 4.0;. Found: C, 22.0; H, 4.2 MS (EI⁺TOF): *m/z* 223.94 (5 %) [M]⁺, 166.86 (100 %) [AsS₂N₂]⁺, 120.90 (5 %) [AsSN]⁺, 106.89 (3 %) [AsS]⁺, 91.95 (2 %) [S₂N₂]⁺, 57.07 (37 %)

(19) The microanalysis of **2** could not be performed because of technical issues with the apparatus (the viscosity of the oil). Integrated ¹H NMR spectra of **2** can be found in high resolution in Supporting Information.

(20) Bio-Beads tend to float, since their density is lower than that of CH₂Cl₂. During the preparation of the column, the Bio-Beads/CH₂Cl₂ slurry was stirred frequently to ensure good swelling of the beads. To prevent floating of the packed column, a glass wool plug was put on top.

$[\text{C}_4\text{H}_9]^+$. ^1H NMR: δ 0.91 (s, 9H, ^tBu). ^{13}C NMR: δ 23.3 (s, 3C, $3\times\text{CH}_3$), 41.4 (C–As). ^{14}N NMR: δ 272.6 (AsN), 303.7 (SNS). IR (cm^{-1} , KBr disc): 1060, 933, 679, 611, 507, 362 (As(S_2N_2) ring vibr.); 1203, 791 ($\nu\text{C}-\text{C}$). Raman (cm^{-1}): 1061, 935, 681, 616, 511, 366, 1204, 792, 518.

PhAs(S_2N_2) (5). PhAsCl₂ (0.900 g, 4.0 mmol) dissolved in CH₂Cl₂ (50 mL) was added at room temperature to a stirred solution of [$^n\text{Bu}_2\text{Sn}(\text{S}_2\text{N}_2)$]₂ (1.32 g, 2.0 mmol) in CH₂Cl₂ (50 mL). The mixture was refluxed for 6 hours. The solvent was evaporated and the residue was distilled under vacuum (0.3 Torr, oil bath temperature 110–113 °C, air condenser). The orange distillate solidified into colorless needles of $^n\text{Bu}_2\text{SnCl}_2$ (verified by ^1H NMR) contaminated with a small amount of an orange oil, and was put aside. The orange/brown distillation residue was dissolved in toluene and was added to a silica column (25×2 cm). Elution with toluene separated sufficiently the residual $^n\text{Bu}_2\text{SnCl}_2$ (at the front) from the product, which was eluted as a yellow band. Evaporation of the solvent left an orange oil, which solidified in a freezer overnight into a non-glassy bulk. Repeated recrystallization from the melt led to formation of well shaped yellow crystals of **5**. The distillate provided up to 10 mg of **5**. Yield 0.568 g (51 %). M.p. 45–47 °C. Anal. Calcd for C₆H₅AsS₂N₂: C, 29.5; H, 2.1; N, 11.5. Found: C, 29.6; H, 2.2; N, 10.9. MS (EI⁺TOF): m/z 243.90 (75 %) [M]⁺, 197.93 (100 %) [PhAsSN]⁺, 166.87 (40 %) [AsS_2N_2]⁺, 165.96 (62 %) [PhAsN]⁺, 106.90 (10 %) [AsS]⁺, 77.04 (5 %) [C_6H_5]⁺. ^1H NMR: δ 7.27–7.41 (m, 5H, C₆H₅). ^{13}C NMR: δ 129.2 (s, C3,C5), 129.5 (s, C2,C6), 131.0 (C4), 146.4 (C1). ^{14}N NMR: δ 269.2 (AsN), 304.8 (SNS). IR (cm^{-1} , KBr disc): 1052, 932, 678, 602, 499, 361 (As(S_2N_2) ring vibr.); 995 (phenyl trigonal “breathing”). Raman (cm^{-1}): 1055, 931, 684, 505, 368, 999.

MesAs(S_2N_2) (6). Prepared from the mixture of mesitylarsenic chloride and bromide (1.97 g) and excess [$^n\text{Bu}_2\text{Sn}(\text{S}_2\text{N}_2)$]₂ (2.81 g, 4.32 mmol) in the same way as **5**. The red/brown tarry distillation residue was partially dissolved in a sufficiently small amount of the mixture toluene : petroleum ether (1:4) and was added to a silica column (27×2.5 cm). The same solvent system was used as eluant. The early yellow and orange bands were discarded and the broad red band was collected. The solvents were evaporated to leave **6** as dark red oil, which was evacuated for 1 hour, then was stored under nitrogen and crystallized spontaneously when allowed to stand at room temperature for 2 days. Yield 1.07 g (50 %). M.p. 46–48 °C. Anal. Calcd for C₉H₁₁AsS₂N₂: C, 37.8; H, 3.9; N, 9.8. Found: C, 37.3; H, 4.1; N, 9.4. MS (EI⁺TOF): m/z 285.96 (65 %) [M]⁺, 239.98 (90 %) [MesAsSN]⁺, 208.01 (60 %) [MesAsN]⁺, 166.87 (35 %) [AsS_2N_2]⁺, 151.06 (85 %) [MesS]⁺, 119.08 (100 %) [C_9H_{11}]⁺. ^1H NMR (500 MHz): δ 2.25 (s, 3H, $p\text{-CH}_3$), 2.45 (s, 6H, $2\times o\text{-CH}_3$), 6.82 (s, 2H, $2\times m\text{-H}$). ^{13}C NMR: δ 21.3 ($p\text{-CH}_3$), 21.7 (s, $2\times o\text{-CH}_3$), 130.5 (s, C3,C5), 140.8 (C1), 141.0 (C4), 141.9 (s, C2,C6). ^{14}N NMR: δ 265.9 (AsN), 309.8

(SNS). IR (cm^{-1} , KBr disc): 1057, 932, 681, 602, 494, 363 ($\text{As}(\text{S}_2\text{N}_2)$ ring vibr.); 558 (Mes-ring “breathing”). Raman (cm^{-1}): 1060, 932, 684, 607, 503, 369, 561.

Table 1. Crystallographic data for compounds **5** and **6**

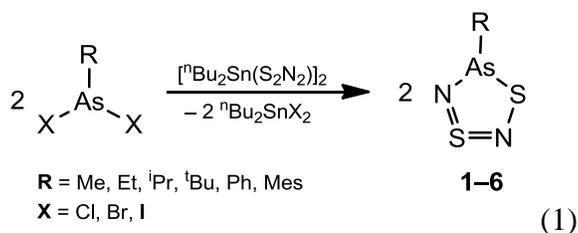
	5	6
Empirical formula	$\text{C}_6\text{H}_5\text{AsN}_2\text{S}_2$	$\text{C}_9\text{H}_{11}\text{AsN}_2\text{S}_2$
Formula weight	244.16	286.24
Temperature	93(2) K	93(2) K
Crystal color, habit	yellow prism	red prism
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$P2(1)/c$
a (Å)	5.046(2)	14.367(6)
b (Å)	8.330(4)	11.372(5)
c (Å)	10.155(6)	13.911(5)
α (deg)	103.427(13)	90
β (deg)	91.802(15)	91.685(10)
γ (deg)	93.833(13)	90
V (Å ³)	413.8(4)	2271.8(16)
Z	2	8
$d_{\text{calc.}}$ (Mg m^{-3})	1.960	1.674
μ (mm^{-1})	4.541	3.322
$F(000)$	240	1152
Measured reflections	2456	14163
Observed indt reflections (R_{int})	1367 (0.0313)	4133 (0.1453)
Final R_1 , wR_2 ($I > 2\sigma(I)$)	0.0477, 0.1047	0.0901, 0.2210
Largest diff. peak hole (e Å^{-3})	0.883 and -1.042	0.854 and -0.750

3. Results and Discussion

The ligand exchange between $[\text{Bu}_2\text{Sn}(\text{S}_2\text{N}_2)]_2$ and alkyl- or aryldihalogenoarsines offers a simple synthetic route to dithiadiazarsoles **1–6**. $[\text{Bu}_2\text{Sn}(\text{S}_2\text{N}_2)]_2$ ²¹ is a versatile reagent,^{14,22} which - unlike $\text{Me}_3\text{SiNSNSiMe}_3$ - is a stoichiometric source of the $[\text{S}_2\text{N}_2]^{2-}$ ligand (eq 1).

(21) $[\text{Bu}_2\text{Sn}(\text{S}_2\text{N}_2)]_2$ is an analogue of $[\text{Me}_2\text{Sn}(\text{S}_2\text{N}_2)]_2$ prepared by Roesky and Wiezer (see ref. 23). Both compounds form dimers in condensed phases.

(22) Matuska, V.; Tersago, K.; Kilian, P.; Van Alsenoy, C.; Blockhuys, F.; Slawin, A. M. Z.; Woollins, J. D. *Eur. J. Inorg. Chem.* **2009**, 4483–4490.



A facile cleavage of an Sn–N bond is well documented^{23,24} and the reaction between Me₃SnNSNSnMe₃ and MeSiCl₃, which results in Si–N bond formation, indicates an easier cleavage of an Sn–N bond. An additional driving force is the propensity of tin to form bonds with halogens.

In this work the tin reagent was allowed to react with chloro-, bromo- and iodoarsines with good results. The reactions were not exothermic, proceeded smoothly under mild conditions and were accompanied by a color change. The work-up procedures were chosen on the basis of known properties of the byproducts and **1**. The relatively high boiling points of ⁿBu₂SnX₂ (X = Cl, Br, I) (Table S1) together with reported volatility and thermal stability of **1**² encouraged us to use vacuum distillation as means of products separation. Compounds **1** and **2** distilled prior to ⁿBu₂SnI₂. **1** was obtained in good purity, **2** had to be purified by silica column chromatography. On the contrary, **5** and **6** were isolated from the distillation residue after ⁿBu₂SnCl₂ had distilled off. Since compound **4** decomposed during vacuum distillation, we decided to make use of the steric demand of the ⁱPr and ^tBu groups and separated both **3** and **4** by size-exclusion chromatography using Bio-Beads. The dithiadiazarsoles **1–4** are volatile oils with a characteristic onion-like odor. The odor of **4** is particularly pungent. **5** and **6** were obtained as dense oils with less intense odor. **5** solidified in a freezer overnight into a non-glassy solid which was recrystallized from the melt. **6** crystallized at room temperature in the course of two days, however, the quality of the crystals was average. Attempted recrystallization from the melt as well as gas phase diffusion of hexane into a CH₂Cl₂ solution of **6** did not yield well grown single crystals. We can confirm the reported air-sensitivity of **1**, however, we experienced only moderate air-sensitivity of compounds **2–6**. This was exploited also in the preparative procedures, when these compounds were purified by chromatographic methods using not dry solvents. Nevertheless, all the title compounds should be stored under an inert atmosphere.

The ¹H NMR chemical shifts of RAs(S₂N₂) are shielded with respect to the corresponding RAsX₂ (Table S2). Thus, the course of the reactions could be easily monitored. The identification of **2** and **3** was more difficult, since their signals overlapped with the much more intense ones of ⁿBu₂SnCl₂.

(23) Roesky, H.; Wiezer, H. *Angew. Chem.-Int. Edit. Engl.* **1973**, *12*, 674.

(24) Roesky, H. W.; Wiezer, H. *Angew. Chem.* **1974**, *86*, 130–131.

A molecule of RAsX_2 has a plane of symmetry and therefore the alkyl- and aryldihaloarsines give simple spectra (Table S2). The introduction of the $(\text{S}_2\text{N}_2)^{2-}$ moiety brings chirality to the molecules of $\text{RAs}(\text{S}_2\text{N}_2)$, which could be observed in the NMR spectra. The ^1H NMR spectrum of **2** showed an ABX_3 spin system consisting of a doublet of doublet (CH_3 group) and a more deshielded complex multiplet (the two inequivalent protons in the CH_2 group) (Figure 1). The chemical shifts and coupling constants are given in the experimental section.

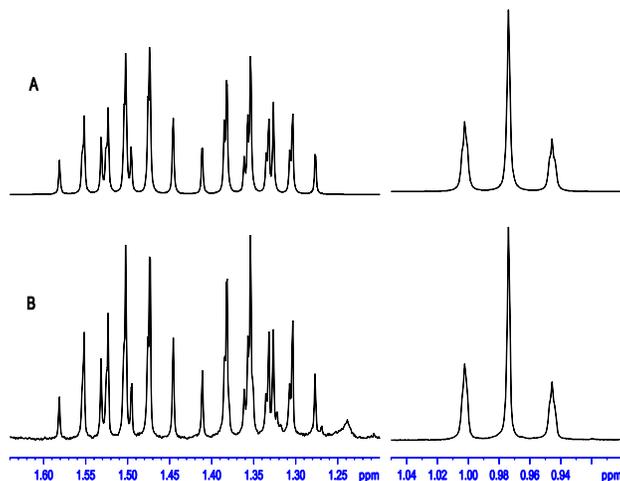


Figure 1. Simulated (A) and recorded (B) ^1H NMR spectrum of $\text{EtAs}(\text{S}_2\text{N}_2)$ (**2**).

3 gave a ^1H NMR spectrum containing two overlapping doublets (two inequivalent CH_3 groups) and a quartet of quartet formed by coupling of the CH signal by the two CH_3 groups. The ^{13}C NMR spectrum of **3** contained three signals, which is expected for an ^iPr group with inequivalent CH_3 groups. In the ^1H NMR spectrum of **6**, the presence of a chiral center did not result in anisochronicity of the diastereotopic *ortho*-Me groups of the mesityl moiety. The spectrum was recorded at both 270 and 500 MHz but all the proton signals appeared as isochronic. Similarly, no anisochronicity was observed in the ^{13}C NMR of **6**.

All dithiadiazarsoles gave ^{14}N NMR spectra with two well defined peaks. The chemical shift differences ($\Delta\delta$) between these two peaks show an increasing trend from **1** to **6**, *i.e.* with growing size of the organic group on arsenic. The $\Delta\delta$ increase in the spectra of **6** with respect to **5** is particularly noteworthy and can be explained by significant structural differences of the two compounds as determined by X-ray analysis. Since arsenic is a main group element and since the ^{14}N NMR chemical

shifts are similar to those measured for Roesky's ketone and sulfoxide,^{25,26} we assigned the lower chemical shift to the arsenic-bound nitrogen and the higher chemical shift to the SNS nitrogen.

Electron impact MS provided high quality spectra, in which molecular peaks could be identified and fragmentation paths followed. The m/z values and their assignments are listed in the experimental section. The mass spectra suggest relatively high stability of the $\text{As}(\text{S}_2\text{N}_2)$ ring, which gave base peaks in the spectra of all the alkylthiadiazarsoles.²⁷ The spectra of the arylthiadiazarsoles **5** and **6** demonstrated the stabilizing effect of the aromatic hydrocarbon on the molecules of **5** and **6**: the abundance of the molecular peaks was more than 60% while the abundance of the $\text{As}(\text{S}_2\text{N}_2)$ moiety did not exceed 40%.

Irrespective of the organic residue, the vibrational spectra of the dithiadiazarsoles **1–6** contained peaks at ca 1050, 932, 680, 602, 500 and 365 cm^{-1} . These peaks were observed in none of the spectra of the starting materials and are most likely due to the $\text{As}(\text{S}_2\text{N}_2)$ ring vibrational modes (Tables S3–S8).²⁸ The strong IR bands are those at 1050, 680, 602 and 365 cm^{-1} , the remaining peaks appear as strong Raman lines. According to Scherer and Wies, the bands at 1050 and 932 cm^{-1} are due to the NSN system.² Further assignment can be suggested by literature data: the stretching frequencies of a cyclic S–N single bond are found between 780 and 670 cm^{-1} .^{25,26,29} The As–N stretch gives IR bands around 585 cm^{-1} and the As–S stretches in cyclic molecules and cages range from 390 to 329 cm^{-1} .^{30,31} The deformation vibrations of all the above mentioned bonds are scattered over the remaining low-

(25) Tersago, K.; Van Droogenbroeck, J.; Van Alsenoy, C.; Herrebout, W. A.; van der Veken, B. J.; Aucott, S. M.; Woollins, J. D.; Blockhuys, F. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5140–5144.

(26) Tersago, K.; Matuska, V.; Van Alsenoy, C.; Slawin, A. M. Z.; Woollins, J. D.; Blockhuys, F. *Dalton Trans.* **2007**, 4529–4535.

(27) For technical reasons chemical ionization was used for **2**. The spectra were of comparable quality with the EI spectra of the other compounds. Thanks to the milder ionization method, **2** gave a spectrum with a $[\text{MH}]^+$ base peak and with the $\text{As}(\text{S}_2\text{N}_2)$ fragment being the second most abundant (65 %).

(28) (a) Durig, J. R.; Jumper, C. F.; Willis Jr., J. N. *Appl. Spectrosc.* **1971**, *25*, 218–225. (b) Ellermann, J.; Schössner, H.; Haag, A.; Schödel, H. *J. Organomet. Chem.* **1974**, *65*, 33–49. (c) Revitt, D. M.; Sowerby, D. B. *J. Chem. Soc. A* **1970**, 1218–1222. (d) Durig, J. R.; Cheng, M.-S.; Harris, M. E.; Hizer, T. J. *J. Mol. Struct.* **1989**, *192*, 47–62. (e) Klaboe, P. *Spectroc. Acta Pt. A-Molec. Spectr.* **1970**, *26*, 87–108. (f) Holmes, R. R.; Fild, M. *Spectroc. Acta Pt. A-Molec. Spectr.* **1971**, *27*, 1537–1547. (g) Evans, J. C.; Lo, G. Y.-S. *J. Am. Chem. Soc.* **1966**, *88*, 2118–2122. (h) Bertie, J. E.; Sunder, S. *Can. J. Chem.* **1973**, *51*, 3344–3353. (i) Revitt, D. M.; Sowerby, D. B. *Spectroc. Acta Pt. A-Molec. Spectr.* **1970**, *26*, 1581–1593. (j) Schindlbauer, H.; Stenzenberger, H. *Spectroc. Acta Pt. A-Molec. Spectr.* **1970**, *26*, 1707–1712. (k) Herzberg, G. *Molecular Spectra and Molecular Structure. Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*; D. Van Nostrand Company, Inc.: Princeton, New Jersey, USA, 1945. (l) Whiffen, D. H. *J. Chem. Soc.* **1956**, 1350–1356. (m) Kainz, B.; Schmidt, A. *Spectroc. Acta Pt. A-Molec. Spectr.* **1990**, *46*, 1361–1370.

(29) (a) Nevitt, I.; Rzepa, H. S.; Woollins, J. D. *Spectroc. Acta Pt. A-Molec. Spectr.* **1989**, *45*, 367–369. (b) Turowski, A.; Appel, R.; Sawodny W.; Molt, K. *J. Mol. Struct.* **1978**, *48*, 313–323.

(30) Davidson, G.; Phillips, S. *Spectroc. Acta Pt. A-Molec. Spectr.* **1979**, *35*, 141–146.

(31) (a) Bues, W.; Somer, M.; Brockner, W. *Z. Anorg. Allg. Chem.* **1983**, *499*, 7–14. (b) Muniz-Miranda, M.; Sbrana, G.; Bonazzi, P.; Menchetti, S.; Pratesi, G. *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.* **1996**, *52*, 1391–1401. (c) Davidson, G.; Ewer, K. P. *Spectroc. Acta Pt. A-Molec. Spectr.* **1983**, *39*, 419–428.

frequency region. However, it should be noted that the entire ring will most probably have its own vibrational motions, similarly to *e.g.* the phenyl ring.^{28k,l}

The X-ray structure of **5** is displayed on Figure 2. The central motif of the molecule is the five-membered As(S₂N₂) ring, which is slightly puckered. The (S₂N₂) and S(2)–As(1)–N(1) planes are inclined by 9.6°. Arsenic is situated approx. 0.246 Å above the least squares plane of the (S₂N₂) moiety and forms the vertex of a trigonal pyramid. The phenyl group is attached to the As atom by an As–C single bond, which is nearly perpendicular to the least squares plane of the As(S₂N₂) ring (the angle is 99.4°). The orientation of the phenyl group is interesting in that it is in a periplanar arrangement with the As(1)–S(2) bond, the dihedral angle between the phenyl ring and the S(2)–As(1)–C(1) plane is only 11.8°.

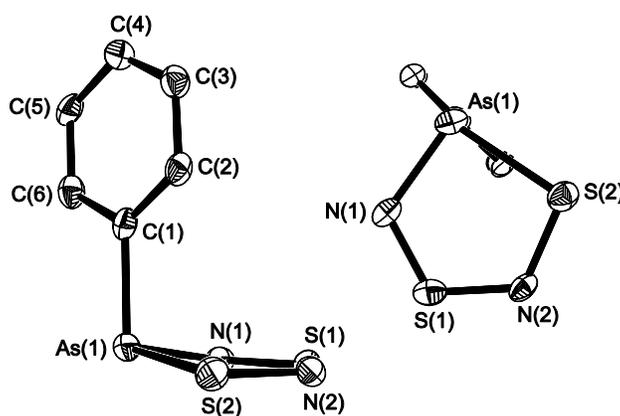


Figure 2. ORTEP³² drawing of the X-ray structure of **5** (50 % ellipsoids). Hydrogen atoms are omitted for clarity.

Selected bond lengths and angles are listed in Table 2. The As(1)–S(2) bond is elongated (2.303(19) Å) with respect to the As–S single bond in As₄S₄ (2.243 Å mean value).³³ The elongation is, however, not too dramatic. Examples of longer As–S single bonds were reported.³⁴ Elongation of the bond between the terminal sulfur of the (S₂N₂) moiety and the fifth element bound to this moiety has been observed in other five-membered main group sulfur–nitrogen heterocycles such as Roesky's ketone or Roesky's sulfoxide.^{26,35}

(32) Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.

(33) Porter, E. J.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1972**, 1347–1349.

(34) Burford, N.; Royan, B. W.; Whalen, J. M.; Richardson, J. F.; Rogers, R. D. *J. Chem. Soc., Chem. Commun.* **1990**, 1273–1275.

(35) Van Droogenbroeck, J.; Tersago, K.; Van Alsenoy, C.; Aucott, S. M.; Milton, H. L.; Woollins, J. D.; Blockhuys, F. *Eur. J. Inorg. Chem.* **2004**, 3798–3805.

Table 2. Selected bond lengths (Å) and angles (°) of **5** and **6**

	5	6^a	
As(1)–N(1)	1.899(5)	1.927(7)	(1.886(7))
N(1)–S(1)	1.540(5)	1.543(8)	(1.537(7))
S(1)–N(2)	1.573(5)	1.563(7)	(1.556(8))
N(2)–S(2)	1.671(5)	1.665(7)	(1.663(9))
S(2)–As(1)	2.3028(19)	2.315(3)	(2.339(3))
As(1)–C(1)	1.965(6)	1.969(9)	(1.973(9))
As(1)–N(1)–S(1)	116.6(3)	114.7(4)	(118.5(4))
N(1)–S(1)–N(2)	115.1(3)	117.3(4)	(114.7(4))
S(1)–N(2)–S(2)	116.9(3)	116.9(5)	(117.8(5))
N(2)–S(2)–As(1)	100.23(18)	100.4(3)	(100.0(3))
S(2)–As(1)–N(1)	90.01(15)	90.6(2)	(88.9(2))
S(2)–As(1)–C(1)	101.07(17)	105.2(3)	(106.9(2))
N(1)–As(1)–C(1)	96.5(2)	103.3(3)	(103.4(3))

^a Values for two independent molecules in the asymmetric unit.

The As(1)–N(1) bond length (1.899(5) Å) is in a good agreement with As–N single bonds found in eight-membered As–N and As–S–N ring compounds.^{3,4,6,36} The length of the As(1)–C(1) bond is 1.965(6) Å which is nearly identical to the mean As–C bond length in arsenobenzene.³⁷

The alternating sulfur and nitrogen atoms are connected by two shorter (1.540(5) and 1.573(5) Å) and one longer (1.671(5) Å) bonds. A comparison with Pauling's values of S=N double bonds³⁸ justifies the formal description of **5** by a Lewis formula with two double bonds coming from S(1). However, the S=N bonds in **5** are longer than those in dithiatetrazadiarsocines and acyclic sulfur diimides,^{3,4,6} whereas the N(2)–S(2) single bond is shortened. This slight bond length equalization suggests some degree of π -electrons delocalization in **5**. The delocalization of π -electrons and possible aromaticity of RAs(S₂N₂) are subjects of an ongoing computational study.

The distribution of the bond angles in **5** is comparable to other known five-membered sulfur–nitrogen rings. The most open angles are found at the N atoms. Their mean value together with that of the N(1)–S(1)–N(2) angle (116.7° and 115.1(3)°, respectively) is close to the optimum 120° expected

(36) (a) Avtomonov, E. V.; Megges, K.; Li, X.; Lorberth, J.; Wocadlo, S.; Massa, W.; Harms, K.; Churakov, A. V.; Howard, J. A. K. *J. Organomet. Chem.* **1997**, *544*, 79–89. (b) Weiss, J.; Eisenhuth, W. *Z. Anorg. Allg. Chem.* **1967**, *350*, 9–17.

(37) (a) Kraft, M. Y.; Borodina, G. M.; Strel'tsova, I. N.; Struchkov, Y. T. *Dokl. Akad. Nauk SSSR* **1960**, *131*, 1074–1076. (b) Hedberg, K.; Hughes, E. W.; Waser, J. *Acta Crystallogr.* **1961**, *14*, 369–374.

(38) (a) Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*; Cornell University Press: Ithaca, N.Y., USA, 3rd edn., 1960. (b) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37–40.

for a trigonal planar coordination, which supports the formal Lewis formula of **5**. The S(2)–As(1)–N(1) right angle corresponds well with the trend of inverse proportionality between van der Waals' radius of an atom and a bond angle value at this atom in five-membered sulfur–nitrogen rings.^{14,22,26,35,39}

The unit cell contains in total two molecules of **5**, of which only one forms the asymmetric unit. The surprising orientation of the phenyl ring seems to be fixed by a system of intra- and intermolecular contacts within the crystal. Figure 3 shows stacking arrangement of the molecules with the S(1B)–S(2) and S(1)–S(2A) distances (3.614(5) Å) being just on the edge of the sum of van der Waals' radii.

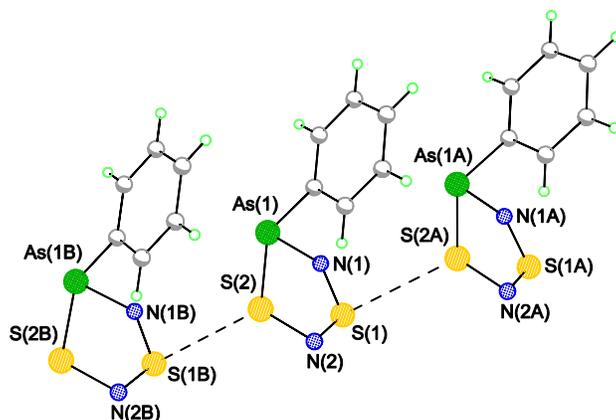
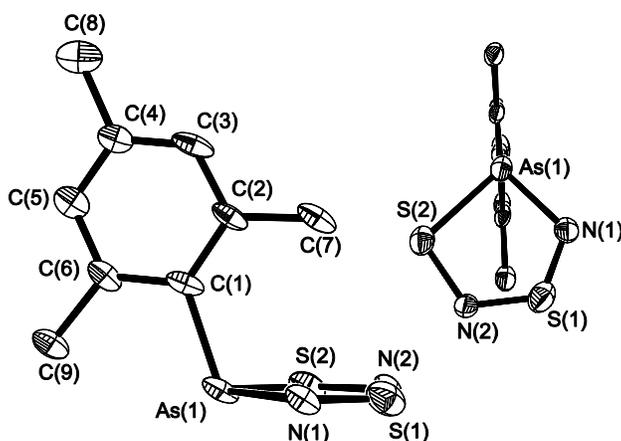


Figure 3. Stacking of molecules of **5** in the crystal.

The molecular structure of **6** differs to that of **5**. The As(S₂N₂) ring in **6** is essentially planar and the orientation of the mesityl group also changes - its plane bisects the As(S₂N₂) ring. The two planes are nearly perpendicular. One of the *ortho* methyl groups is situated directly above the five-membered ring (Figure 4).



(39) (a) Weiss, J. *Z. Anorg. Allg. Chem.* **1966**, *343*, 315–322. (b) Martan, H.; Weiss, J. *Z. Anorg. Allg. Chem.* **1984**, *514*, 107–114.

Figure 4. ORTEP³² drawing of the X-ray structure of **6** (20 % ellipsoids). Hydrogen atoms are omitted for clarity.

Due to greater steric demand of the mesityl compared to phenyl group, the molecule of **6** is more “open” than that of **5**: the mesityl group is bound to arsenic with a wider angle with respect to the least squares plane of the As(S₂N₂) ring (approx. 110° and 111° for the two independent molecules).

Selected bond lengths and angles are listed in Table 2. The bonding within the molecule can be formally described by a Lewis formula with two double bonds coming from the NSN sulfur atoms. The As–S, As–N and As–C bonds are single and are slightly longer than those in **5**, which can be explained as a consequence of the steric effect of the mesityl group and its better electron-donating ability. The S–N bond lengths can be regarded as intermediate between a single and a double S–N bonds and π -electrons delocalization can be expected.

The unit cell contains eight molecules of **6**, with two crystallographically independent molecules in the asymmetric unit. The five-membered rings in the asymmetric unit are approx. coplanar but slipped so that the S(1)–N(1) bond lies over the S(12)–N(12) bond of the second independent molecule (Figure S2). The S(1)–S(12) and N(1)–N(12) distances are 3.713(7) Å and 3.952(8) Å respectively, which is beyond the sum of van der Waals’ radii and thus there are no contacts between the two independent molecules. The molecules do not take up a stacking arrangement, presumably since the bulky mesityl group precludes an arrangement in closely packed layers. Similarly to **5**, the orientation of the mesityl group seems strongly determined by a number of intra- and intermolecular interactions.

Eight-membered AsSN rings are known to act as ligands coordinated to a metal center *via* the lone pair of electrons on arsenic.^{4,5,6} The reactions of **5** with Pt(COD)Cl₂, Mo(CO)₄(pip)₂ and Cp₂Ti(CO)₂ resulted in formation of tarry materials or powders, which could not be worked up towards crystallization. **5** reacted with Cp*Co(CO)₂ to yield a small amount of Cp*Co(S₂N₂) (proved by ¹H and ¹³C NMR and MS; see Supporting Information for details).²² [Oxidation and reduction of **5** was investigated by means of cyclic voltammetry, which](#) showed irreversible oxidation ($E_{pa} = 1.08$ V) and reduction ($E_{pc} = -1.71$ V) at both slower and faster scan rates (Figure S3, Table S9).

4. Summary

The 5-alkyl/aryl-1,3 $\lambda^4\delta^2$,2,4,5-dithiadiazarsoles **1–6** were prepared by an exchange reaction between RAsX₂ and the universal tin reagent [ⁿBu₂Sn(S₂N₂)]₂. The compounds are stable and with the

exception of **1** only moderately air-sensitive. The crystal structures of **5** and **6** revealed that the As(S₂N₂) ring is relatively flexible with **5** containing a puckered and **6** a planar As(S₂N₂) ring. A network of intra- and intermolecular interactions fixes the molecular geometries of **5** and **6**. Especially the geometry of **5** is interesting with a periplanar arrangement on the As–C bond. ¹H and ¹³C NMR spectra of **2** and **3** confirmed the presence of a chiral arsenic center. The constitution of the title compounds was further supported by ¹⁴N NMR, IR and Raman spectroscopies.

The reactivity of compound **5** was investigated. Oxidation and reduction of **5** leads to formation of unstable species and the tendency of **5** to serve as a donor of its lone pair of electrons appears low.

Acknowledgements

We wish to thank Dr Tomas Lebl for help with NMR spectra simulations and Dr Joe Crayston for advice during voltammetric measurements. This work was carried out with the financial support of Engineering and Physical Sciences Research Council (EPSRC), UK.

Supporting Information Available: CIF files for compounds **5** and **6**, comments on synthetic procedures for the RAsX₂ starting materials and for the reaction of **5** and Cp*Co(CO)₂, ¹H NMR spectra of **2**, melting and boiling points of Me₃SiX and ⁿBu₂SnX₂ (X = F, Cl, Br, I), ¹H and ¹³C NMR data of RAsX₂, selected IR and Raman wavenumbers of RAsX₂ and **1–6**, a view of the asymmetric unit of **6**, cyclic voltammogram of **5**, experimental values of *E*_p and *I*_p. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

Table of contents synopsis:

Five-membered AsSN heterocycles are stable compounds and can be isolated in good yields. An insight into their interesting structural features is provided especially by X-ray structure analysis, which has not been previously reported for these compounds.

