J. Am. Chem. Soc. 1992, 114, 8147–8153 8147

# Aza- and Thiaarsolidinium Cations: Novel Structural Features for Carbene Analogues

**Neil Burford,*[†] Trenton M. Parks,[†] Bruce W. Royan,[†] Bozena Borecka,[†] T. Stanley Cameron,[†] John F. Richardson,[‡] Eric J. Gabe,[§] and Rosemary Hynes[§]**

*Contribution from the Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada, Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, and National Research Council, Ottawa, Ontario K1A 0R6, Canada.*

*Received May 18, 1992*

**Abstract:** The preparation, isolation, and structural characterization of salts containing the first arsolidinium cations are reported. Reactions between equimolar amounts of 2-chloro-1,3-dimethyl-1,3-diaza-2-arsolidine or 2-chloro-1,3-dithia-2-arsolidine with $AlCl_3$ or $GaCl_3$ result in quantitative chloride ion abstraction to give the corresponding cations $[\overline{\text{N(Me)CH}_2\text{CH}_2\text{N(Me)As}}]^+$ and $[\overline{\text{SCH}_2\text{CH}_2\text{SAs}}]^+$ as tetrachloroaluminate and gallate salts. X-ray crystallography reveals a centrosymmetric dimeric arrangement for three derivatives in which the cations are bound together by relatively weak As–N or As–S interactions. A complex between the respective chloroarsolidine and arsolidinium cation is formed in reaction mixtures which provide appropriate stoichiometry. The X-ray structure of the thia derivative, $[\overline{\text{SCH}_2\text{CH}_2\text{SAs}}\overline{\text{SAs(Cl)SCH}_2\text{CH}_2}][\text{GaCl}_4]$, shows a single, noticeably weaker interring connection, but otherwise the compound exhibits similar structural features. The aza derivative of the complex can be readily interconverted with the dicationic diazarsolidinium upon addition of a Lewis acid. Variable temperature $^1H$ NMR spectroscopy shows both the dication dimers and the complexes to be fluxional in solution, and a dissociative process is envisaged. Consequently, the cations are viewed as examples of stable arsenium (carbene analogue) units, unique in the absence of a steric shield or Hückel π-delocalization. The weakly associated structures represent alternatives to *alkenic* dimerization, typical of carbenes.

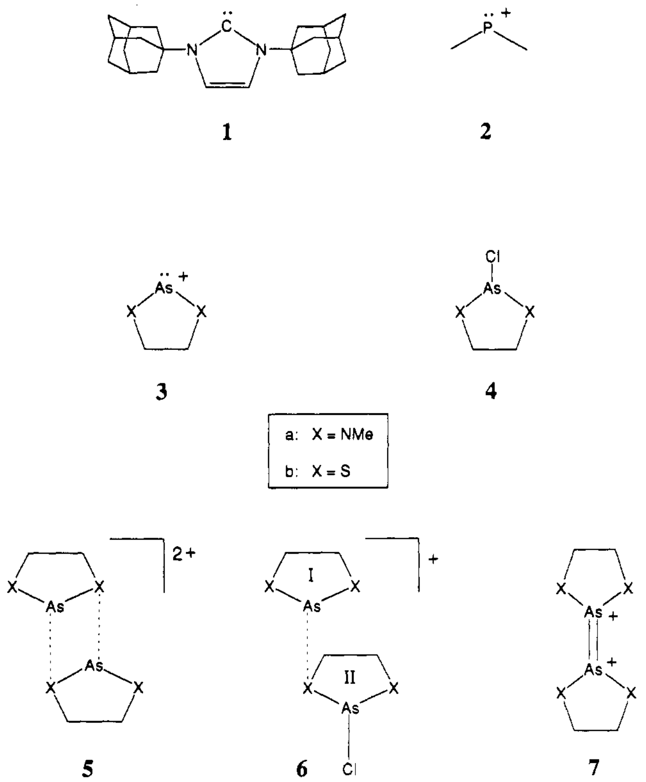
## Introduction

Electron deficient, coordinatively unsaturated atomic centers are a fascination for any chemist by virtue of their structural, electronic, and reactive novelty. Furthermore, systems of this type are recognized as important synthetic fragments in that they represent simple building blocks. Most familiar are the carbenes, which already have an extensive chemistry as reactive intermediates.[1] The recent isolation of stable carbene derivatives[2,3] and confirmation of the nonlinear dicoordinate carbon center in compound **1**[3] have revitalized interest.[4] Derivatives of germylenes[5,6] and stannylenes,[6–9] isovalent analogues of carbenes, are well-known as stable species, and most recently a convincing example of a dicoordinate tin center was reported in the first dialkylstannylene.[9]

As *carbenic* centers (carbene-like, dicoordinate, formally six valence electrons) possess a nonbonding electron pair (lone pair), they are perhaps more easily accessible for the electron rich elements. Consequently, a series of phosphenium cations (containing environment **2**) are now known,[10,11] in which the formal positive charge on the dicoordinate phosphorus center is delocalized by means of π-donation from the neighboring electron rich centers of the substituents [e.g., $(^i\text{Pr}_2\text{N})_2\text{P}^+$,[12] $\text{Me}_2\text{N(Cl)P}^+$,[13] $\text{C}_6\text{H}_4\text{S}_2\text{P}^+$[14]]. Low coordinate cationic arsenic centers have been observed in the novel structure of $\text{Cp*}_2\text{As}^+$,[15] which involves multihapto (bent sandwich π-complex) coordination, and the inorganometallic complex $[\text{Cp*(CO)}_2\text{Mn}]_2\text{As}^+$, which contains the first *allenic* arsonium center.[16] Nevertheless, reports of arsenium cations are very rare,[17] and isolation of the first structurally characterized example[18,19] was only made possible by incorporating the *carbenic* arsenic unit into a heteronaphthalenic (10π-electron) framework.[20]

Here we present a number of salts containing arsolidinium cations **3**, formal examples of stable arsenium units (carbene analogues) without the presence of steric protection or π-delocalization aided by Hückel stabilization. The *nakedness* of the arsenium center imposes novel structural features in the solid state and interesting behavior in solution.

**Chart I**



---

[†] Dalhousie University.
[‡] University of Louisville.
[§] National Research Council.

(1) See, for example; Closs, G. L.; Gaspar, P. P.; Hammond, G. S.; Hartzler, H. D.; Mackay, C.; Seyferth, D.; Trozzolo, A. M.; Wasserman, E. *Carbenes*; Moss, R. A., Jones, M., Eds.; John Wiley & Sons: New York, 1975. Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press, Inc.: New York, 1971. Hine, J. *Divalent Carbon*; The Ronald Press Co.: New York, 1964.

0002-7863/92/1514-8147$03.00/0

## Experimental Section

**General Procedures.** Arsenic trichloride (AESAR) and triethylamine (BDH) were distilled under $N_2$ before use. Aluminium chloride and gallium chloride (Aldrich) were sublimed under vacuum before use. Methylene chloride and hexane were dried over $P_2O_5$ and $CaH_2$ and stored in evacuated bulbs. Deuterated solvents were dried over $P_2O_5$. All solids were manipulated in a Vacuum/Atmospheres nitrogen filled glovebox. Glass equipment was flame dried before use. Reactions were performed in an evacuated ($10^{-3}$ Torr) dual compartment vessel, unless otherwise indicated. Melting points were recorded on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany. IR spectra were recorded as Nujol mulls or neat liquids on CsI plates using a Perkin-Elmer 283B spectrophotometer. NMR spectra were recorded on Nicolet NT-360 and Bruker AC250 spectrometers in 5- or 10-mm flame sealed Pyrex tubes. Chemical shifts ($^1$H and $^{13}$C) are reported in ppm relative to TMS and are calibrated to the internal solvent signal. Variable temperature $^1$H NMR studies involved temperature changes of 10 °C and equilibration times of 15 min.

**Isolation Procedures and Characterization Data. $N(Me)CH_2CH_2N(Me)AsCl$ 4a.**[21] A solution of $AsCl_3$ (20.59 g, 113.6 mmol) in diethyl ether (50 mL) was slowly added dropwise to a stirred solution of $HN(Me)CH_2CH_2N(Me)H$ (20.00 g, 226.9 mmol) in diethyl ether (200 mL) over a period of 1 h. Immediate reaction produced copious white precipitate, and the mixture was stirred for 90 min. The solution was decanted from the solid, which was filtered and washed with fresh solvent. The solvent was removed by rotary evaporation, and the resulting liquid was distilled under vacuum to produce a colorless, thermally unstable liquid, characterized as 2-chloro-1,3-dimethyl-*cyclo*-1,3-diaza-2-arsapentane (referred to as 2-chloro-1,3-dimethyl-1,3-diaza-2-arsolidine in the text) (ca. 50%): bp 45 °C (vac, ~1 mm Hg), mp ≈ 18 °C; IR (neat liquid, yellow coloration on the plates) 2980 vs (sh), 2930 vs, 2865 vs, 2805 vs, 2720 m, 2680 m, 1460 s, 1440 s, 1420 s, 1365 m, 1335 m, 1250 s, 1195 vs, 1130 vs, 1025 vs, 1000 s, 915 vs, 840 s, 665 m, 580 vs, 570 vs, 405 s, 310 s, 295 s $cm^{-1}$; $^1$H NMR 3.29, 2.82 ppm.

**$[N(Me)CH_2CH_2N(Me)As]_2$ (5a) $[GaCl_4]_2$.** A solution of $N(Me)CH_2CH_2N(Me)AsCl$ (**4a**) (1.31 g, 6.65 mmol) in $CH_2Cl_2$ (11 mL) was added to a stirred solution of $GaCl_3$ (1.17 g, 6.65 mmol) in $CH_2Cl_2$ (11 mL) over a period of 30 min. The bright yellow reaction mixture was stirred for 20 min, during which time the color gradually darkened to a light orange. Slow removal of solvent (>75%) in vacuo promoted precipitation/crystallization of a buff-colored solid, which was isolated from the solution by decantation. The solid was then recrystallized from fresh warm (65 °C) $CH_2Cl_2$ (22 mL) by slow cooling to room temperature and very slow removal of solvent in vacuo. The resulting crystals were washed three times by back distillation, and the pale orange solid (crystallographic quality) was characterized as bis(1,3-dimethyl-1,3-diaza-2-arsolidinium tetrachlorogallate) (2.01 g, 2.70 mmol, 81.2%): mp 104–105 °C; IR 1265 m, 1225 m, 1205 w, 1170 m, 1130 m, 1115 m, 1080 m, 1040 s, 1010 m, 985 m, 890 s, 815 s, 595 w, 570 m, 515 vs, 445 s, 415 w, 385 vs, 370 vs, 355 vs, 320 m, 280 m $cm^{-1}$; $^1$H NMR 3.83, 3.20 ppm; $^{13}$C NMR 57.8, 37.6 ppm. Elemental Anal. Calcd: C, 12.90; H, 2.71; N, 7.52. Found: C, 13.02; H, 2.77; N, 7.58.

**$[N(Me)CH_2CH_2N(Me)As]_2$ (5a) $[AlCl_4]_2$.** A crystalline sample (31% yield) of this compound (suitable for X-ray crystallography) was obtained in a similar manner to that described above for the $GaCl_4$ salt. However, the material gave a broad melting point and poor chemical analysis and was difficult to obtain as a pure material in preparative quantities.

**NMR Identification of $[N(Me)CH_2CH_2N(Me)AsN(Me)As(Cl)N(Me)CH_2CH_2]$ (6a) $[GaCl_4]$.** Two equivalents of $N(Me)CH_2CH_2N(Me)AsCl$ (**4a**) and 1 equiv of $[N(Me)CH_2CH_2N(Me)As]_2$ (**5a**) $[GaCl_4]_2$ were combined in $CD_2Cl_2$ solution: $^1$H NMR, 3.58, 3.03 ppm. The spectrum achieved two coalescence points on cooling to −90 °C as shown in Figure 5.

**NMR Studies of Mixtures of 5a$[GaCl_4]_2$ and 4a.** Five equivalents of **5a** and 1 equiv of **4a** were combined in $CD_2Cl_2$, and the $^1$H NMR spectrum showed only two peaks at 3.78 and 3.16 ppm, with an integration ratio of 3:2. Twenty equivalents of **4a** and 1 equiv of **5a** showed a similar spectrum, but with chemical shifts of 3.34 and 2.86 ppm.

**$SCH_2CH_2SAsCl$ (4b).**[22] A solution of ethanedithiol (14.48 g, 153.7 mmol) in $CCl_4$ (70 mL) was slowly added dropwise to a stirred solution of $AsCl_3$ (27.90 g, 153.9 mmol) in $CCl_4$ (55 mL) over a period of 1 h. The liberation of HCl gas (vented) was almost instantaneous and accompanied by self-cooling of the reaction mixture. The solution was sealed, stirred overnight, and then cooled over dry ice, producing copious white crystals. The cold supernatant was decanted, and the crystals were dried in vacuo and characterized as 2-chloro-*cyclo*-1,3-dithia-2-arsapentane (referred to as 2-chloro-1,3-dithia-2-arsolidine in the text) (27.00 g, 133.3 mmol, 86.72%) mp 38.5–39.0 °C: IR (yellow coloration on the plates) 1405 s, 1280 s (sh), 1275 s, 1230 s, 1145 m, 1105 m, 990 m, 930 s, 830 vs, 660 m, 645 s, 445 vs, 385 vs, 355 vs, 320 vs (sh), 310 vs, 280 s (sh) $cm^{-1}$; $^1$H NMR 3.74 ppm multiplet; $^{13}$C NMR 44.6 ppm.

**$[SCH_2CH_2SAs]_2$ (5b) $[GaCl_4]_2$.** A solution of $SCH_2CH_2SAsCl$ (**4b**) (0.981 g, 4.84 mmol) in $CH_2Cl_2$ (30 mL) was added to a stirred solution of $GaCl_3$ (0.856 g, 4.86 mmol) in $CH_2Cl_2$ (30 mL) over a period of 20 min. Immediate reaction gave a bright yellow solution. The reaction mixture was stirred overnight. Slow removal of the solvent (>75%) in vacuo left a bright yellow oil which crystallized when agitated. The remaining solution was decanted from the solid, which was recrystallized from fresh warm $CH_2Cl_2$ (60 °C, 10 mL) by slow cooling to room temperature. The pale yellow crystalline solid, suitable for crystallography, was characterized as bis(1,3-dithia-2-arsolidinium tetrachlorogallate) (1.56 g, 2.06 mmol, 85.0%): mp 94.0–95.5 °C; IR 1430 m, 1400 m, 1280 m, 1230 m, 1150 m, 1110 m, 990 w, 925 m, 830 s, 735 w, 650 m, 620 m, 450 m, 390 vs, 380 vs, 360 vs, 345 s, 320 s $cm^{-1}$; $^1$H NMR 4.06 ppm; $^{13}$C NMR 45.8 ppm. Elemental Anal. Calcd: C, 6.34; H, 1.06; S, 16.94. Found: C, 6.33; H, 1.16; S, 16.97.

**$[SCH_2CH_2SAsSAs(Cl)SCH_2CH_2]$ (6b) $[GaCl_4]$.** A solution of $GaCl_3$

---

(2) Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1429. Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621. Gillette, G. R.; Igau, A.; Grutzmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463. See, also: Dixon, D. A.; Dobbs, K. D.; Arduengo, A. J. III; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 8782.

(3) Arduengo, A. J. III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. See, also: Arduengo, A. J. III; Kline, M.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1991**, *113*, 9704. Arduengo, A. J. III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(4) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 674.

(5) See, for example: Meller, A.; Grabe, C.-P. *Chem. Ber.* **1985**, *118*, 2020. Satge, J. *J. Organomet. Chem.* **1990**, *400*, 121.

(6) Cetinkaya, B.; Gumrukcu, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2088. Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639. Hitchcock, P. B.; Lappert, M. F.; Samways, B. J.; Weinberg, E. L. *J. Chem. Soc., Chem. Commun.* **1983**, 1492. Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 939. Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

(7) Engelhardt, L. M.; Jolly, B. S.; Lappert, M. F.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 336. Bigwood, M. P.; Corvan, P. J.; Zuckermann, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7643.

(8) Grutzmacher, H.; Pritzkow, H.; Edelmann, F. T. *Organometallics* **1991**, *10*, 23.

(9) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7785, and references therein.

(10) *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990.

(11) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.

(12) Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784.

(13) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994. Kopp, R. W.; Bond, A. C.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3042.

(14) Burford, N.; Royan, B. W.; Linden, A.; Cameron, T. S. *Inorg. Chem.* **1989**, *28*, 144.

(15) Jutzi, P.; Wippermann, T.; Krüger, C.; Kraus, H. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 250.

(16) Strube, A.; Huttner, G.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1529.

(17) Payrastre, C.; Wolf, J. G.; Kim, T. C.; Sanchez, M. *Bull. Soc. Chim. Fr.* **1992**, *129*, 157. Payrastre, C.; Madaule, Y.; Wolf, J. G. *Tetrahedron Lett.* **1992**, *33*, 1273. Payrastre, C.; Madaule, Y.; Wolf, J. G. *Tetrahedron Lett.* **1990**, *31*, 1145. Veith, M.; Bertsch, B.; Huch, V. *Z. Anorg. Allg. Chem.* **1988**, *559*, 73. Baxter, S. G.; Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1981**, *103*, 5573. Gamon, N.; Reichardt, C.; Allmann, R.; Waskowška, A. *Chem. Ber.* **1981**, *114*, 3289. Markl, G.; Lieb, F. *Tetrahedron Lett.* **1967**, *36*, 3489.

(18) Burford, N.; Royan, B. W.; White, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 3746. Burford, N.; Royan, B. W. *J. Chem. Soc., Chem. Commun.* **1989**, 19.

(19) Burford, N.; Parks, T. M.; Royan, B. W.; Richardson, J. F.; White, P. S. *Can. J. Chem.* **1992**, *70*, 703.

(20) Burford, N.; Dipchand, A. I.; Royan, B. W.; White, P. S. *Inorg. Chem.* **1990**, *29*, 4938.

(21) Using the reaction mentioned: Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 702.

(22) A modification of the procedure mentioned: Rueggeberg, W. H. C.; Ginsburg, A.; Cook, W. A. *J. Am. Chem. Soc.* **1946**, *68*, 1860.

**Table I.** Crystallographic Data[a]

| | **5a** $[AlCl_4]_2$ | **5a** $[GaCl_4]_2$ | **5b** $[GaCl_4]_2$ | **6b** $[GaCl_4]$ | **4b** |
|---|---|---|---|---|---|
| formula | $C_8H_{20}Al_2As_2Cl_8N_4$ | $C_8H_{20}As_2Cl_8Ga_2N_4$ | $C_4H_8As_2Cl_8Ga_2S_4$ | $C_4H_8As_2Cl_5GaS_4$ | $C_2H_4AsClS_2$ |
| fw | 659.70 | 745.18 | 757.28 | 581.19 | 202.56 |
| space group | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ | $Pna2_1$ | $P2_1/c$ |
| *a*, Å | 9.3554 (7) | 9.324 (1) | 6.454 (2) | 14.830 (4) | 9.930 (2) |
| *b*, Å | 13.7425 (8) | 13.719 (2) | 14.360 (3) | 13.610 (3) | 7.141 (1) |
| *c*, Å | 9.7191 (4) | 9.692 (2) | 11.536 (2) | 8.581 (2) | 9.432 (2) |
| *b*, deg | 101.939 (4) | 101.62 (2) | 104.62 (2) | | 112.23 (1) |
| *V*, $Å^3$ | 1222.5 | 1214.4 | 1034.5 | 1731.9 | 619.1 |
| *Z* | 2 | 2 | 2 | 4 | 4 |
| $D_{calcd}$, g $cm^{-3}$ | 1.79 | 2.04 | 2.43 | 2.23 | 2.17 |
| $\mu$, $cm^{-1}$ | 36.8 | 58.0 | 71.9 | 65.9 | 64.2 |
| abs corr | N/A | 0.77–1.19 | 0.83–1.36 | 0.86–1.00 | 0.85–1.00 |
| abs method | N/A | DIFABS | DIFABS | PSI | PSI |
| *R* | 0.055 | 0.033 | 0.033 | 0.029 | 0.026 |
| $R_w$ | 0.030 | 0.035 | 0.037 | 0.028 | 0.025 |
| GOF | 3.30 | 1.12 | 1.01 | 1.00 | 1.09 |

[a] Temp 22 (1) °C; Mo K$\alpha$ ($\lambda$ = 0.70930 Å) with graphite monochromator.

(0.740 g, 4.20 mmol) in $CH_2Cl_2$ (20 mL) was added to a stirred solution of $\overline{SCH_2CH_2SAs}Cl$ (**4b**) (1.703 g, 8.407 mmol) in $CH_2Cl_2$ (40 mL) over a period of 25 min. The initially pale yellow reaction mixture darkened during the addition. The mixture was stirred at room temperature overnight, during which time a pale yellow, microcrystalline precipitate formed. The solution volume was halved in vacuo and the remainder was carefully decanted from the solid, which was washed by repeated back distillation and dried under vacuum. Recrystallization from fresh warm $CH_2Cl_2$ (60 °C, 10 mL) by slow cooling to room temperature gave 2-chloro-*cyclo*-1,3-dithia-2-arsapentane-1,3-dithia-2-arsolidinium tetrachlorogallate (2.13 g, 3.67 mmol, 87.3%): mp 116–117 °C; IR 1415 w (sh), 1410 m, 1290 m, 1270 w, 1235 s, 1150 m, 1145 m, 1105 m, 1000 m, 980 w, 935 m, 925 s, 825 vs, 660 m, 650 m, 635 s, 450 vs, 405 vs (sh), 395 vs (sh), 385 vs, 375 vs, 365 vs, 350 vs, 340 vs, 320 vs, 300 m, 280 m (sh), 270 s, 260 m (sh) $cm^{-1}$; $^1H$ NMR 3.90 ppm; $^{13}C$ NMR 45.0 ppm. Elemental Anal. Calcd: C, 8.27; H, 1.39; S, 22.07. Found: C, 8.36; H, 1.44; S, 21.79.

$[\overline{SCH_2CH_2SAs}\overline{SAs(Cl)SCH_2CH_2}]$ (**6b**) $[GaCl_4]$ was also obtained from the following reactions: (a) $[\overline{SCH_2CH_2SAs}]_2$ (**5b**) $[GaCl_4]_2$ (0.30 g, 0.39 mmol) and $\overline{SCH_2CH_2SAs}Cl$ (**4b**) (0.16 g, 0.79 mmol) in $CH_2Cl_2$ (20 mL), giving a yield of 0.39 g, 0.67 mmol, 85%: mp 113–114 °C. (b) $[\overline{SCH_2CH_2SAs}]_2$ (**5b**) $[GaCl_4]_2$ (0.05 g, 0.06 mmol) and $Ph_3PO$ (0.02 g, 0.06 mmol) in $CH_2Cl_2$ (10 mL) gave a $^{31}P$ NMR signal at 49 ppm, distinctive for $Ph_3POGaCl_3$,[23] and a small amount of the solid isolated gave a melting point of 110–113 °C.

**X-ray Crystallography.** Crystals suitable for crystallography were obtained as described in the text for each compound and were selected and mounted in Pyrex capillaries in the drybox. Unit cell parameters were obtained from the setting angles of a minimum of 25 accurately centered reflections having $\Theta > 12°$; the choice of space groups was based on systematically absent reflections and confirmed by the successful solution and refinement of the structures. All pertinent crystallographic data are summarized in Table I. Data were collected at room temperature on Enraf-Nonius CAD-4 diffractometers (Mo K$\alpha$, $\lambda$ = 0.7093 Å, graphite monochromator) using the $\omega/2\Theta$ scan technique. The stability of the crystals was monitored using three standard reflections; no significant decay was observed. Data were corrected for Lorentz and polarization effects, and, for four of the structures, the absorption corrections were applied based on a series of $\psi$ scans or the program DIFABS;[24] transmission coefficients are listed in Table I. Scattering factors[25] were corrected for anomalous dispersion.

Structures were solved by direct methods to find the heavy atoms with the remaining atoms located from difference Fourier syntheses.[26] Hydrogen atoms were included and the coordinates were refined for all structures with the exception of **6b**$[GaCl_4]$ (fixed coordinates). Isotropic thermal parameters of the hydrogen atoms were refined in each of the structures of **5a** but were set to $B_{iso} = 1.3 \times B$ of the bonded C atom for the others. Disorder was evident in the positions of C(3) and C(4) of **6b**$[GaCl_4]$ and was modelled using a ring flip motion. The model gave inconsistent occupancies for the two atoms involved but did not effect the gross structure of the cation and was not incorporated into the final cycle of refinement. The choice of enantiomer for **6b**$[GaCl_4]$ was based on a lower *R* factor in the final stages (0.031 vs 0.035). The models were refined using full-matrix least squares techniques based on *F*, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight is defined as $w = k/[\sigma(F)^2 + (pwtF)^2 + qwt]$ and $\sigma$ is derived from counting statistics (supplementary material).[27]

## Results and Discussion

**Arsolidinium Cations.** The halide ion abstraction reaction has proven to be an efficient and versatile synthetic procedure for new nonmetal cations.[11-16,28] Consistently, slow addition of $CH_2Cl_2$ solutions of 2-chloro-1,3-dimethyl-1,3-diaza-2-arsolidine (**4a**) or 2-chloro-1,3-dithia-2-arsolidine (**4b**) to suspensions of $AlCl_3$ or solutions of $GaCl_3$ proceed rapidly and quantitatively to give the first arsolidinium **3a** and **3b** salts. The ionic character of these compounds is confirmed in the IR spectra, which display characteristic absorptions at 485 $cm^{-1}$ (E = Al) and 390 $cm^{-1}$ (E = Ga), assigned to the $\nu_3$ vibration of the $ECl_4^-$ (E = Al, Ga) anions.[29] However, the new cations are shown by crystallographic examination (see below) to exist as dimeric dications **5a** and **5b**[30] in the solid state.

Reaction of **4** with $GaCl_3$ in a 2:1 molar ratio effects formation of the novel bicyclic monocationic salts of **6a** and **6b**, which can be viewed as Lewis complexes of the chloroarsolidine **4** and the arsolidinium cation **3**. The structure of **6b** is confirmed by X-ray crystallography, and the low temperature (−85 °C) $^1H$ solution NMR spectrum of **6a** is consistent with a similar structure (see below). Both derivatives of **5** react readily with 2 equiv of the corresponding chloroarsolidine **4** to produce the corresponding derivative of **6**. A similar result is observed upon reaction of **5** with 1 equiv of $Ph_3PO$. Acting as a strong base, $Ph_3PO$ preferentially coordinates to the $ECl_3$ of the complex anion $ECl_4^-$ releasing $Cl^-$, which subsequently coordinates to a cationic arsenic center forming a molecule of **4** and ultimately **6**. The reverse reaction is also possible for compound **6a**$[GaCl_4]$, which can be quantitatively transformed into the dication dimer **5a** by addition of an equivalent of $GaCl_3$ to **6a**. However, the corresponding reaction for **6b**$[GaCl_4]$ has not been observed, even with heating.

---

(23) Burford, N.; Royan, B. W.; Spence, R. E. v. H.; Linden, A.; Cameron, T. S.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1990**, 1511.

(24) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

(25) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(26) Computations were performed using the following packages. **5a**$(AlCl_4)_2$: NRCVAX; Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Cryst.* **1989**, *22*, 384. **5a**$(GaCl_4)_2$: SHELX76 Program for Crystal Structure Determination; Sheldrick, G. M. University of Cambridge, England, 1976. **5b**$(GaCl_4)_2$, **6b**$GaCl_4$ and **4b**: Enraf-Nonius VAX/SDP System of Crystallographic Programs; Frenz, B. A. *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., vanKoningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978.

(27) Killean, R. C. G.; Lawrence, J. L. *Acta Crystallogr.* **1969**, *B25*, 1750.

(28) Grutzmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 709.

(29) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Interscience: Toronto, 1986.

(30) Preliminary communication: Burford, N.; Royan, B. W.; Whalen, J. M.; Richardson, J. F.; Rogers, R. D. *J. Chem. Soc., Chem. Commun.* **1990**, 1273.

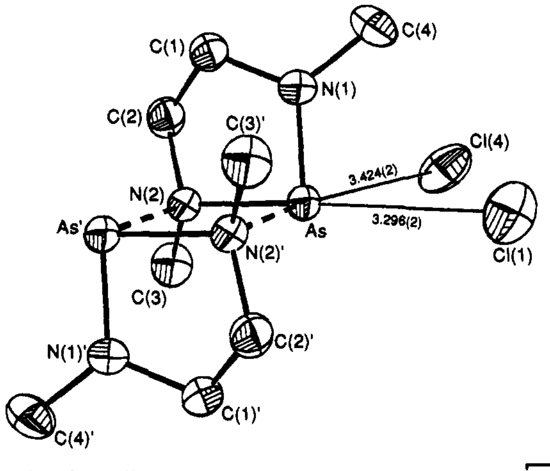


**Figure 1.** Crystallographic view of the cationic unit of $[\overline{N(Me)CH_2CH_2N(Me)As}]_2$ (**5a**) $[GaCl_4]_2$, showing anion–cation contacts.

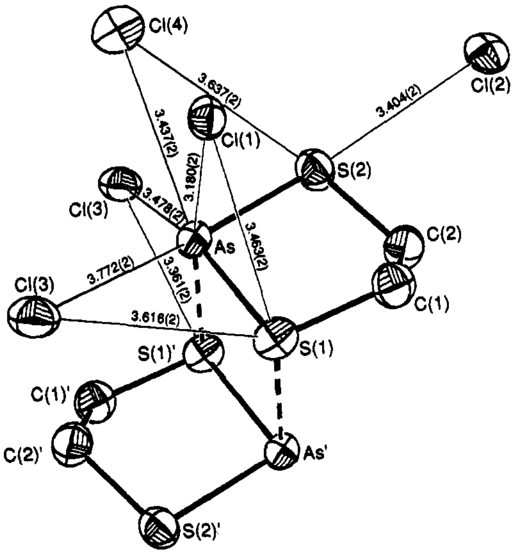


**Figure 2.** Crystallographic view of the cationic unit of $[\overline{SCH_2CH_2SAs}]_2$ (**5b**) $[GaCl_4]_2$, showing anion–cation contacts.

We believe this to be a function of the extremely low solubility of **6b**$[GaCl_4]$.

**Solid-State Structural Features.** Spectroscopic and analytical data for derivatives of **3** are of little value in the structural characterization of the arsolidinium salts. Consequently, we have determined the crystal structures of the ionic compounds **5a**$[AlCl_4]_2$, **5a**$[GaCl_4]_2$, **5b**$[GaCl_4]_2$, and **6b**$[GaCl_4]$ as well as that of the covalent 2-chloro-1,3-dithia-2-arsolidine **4b**, and the structural features are compared in Table II. Representative views[31] of the structures are shown in Figures 1–4. As may be expected, **5a**$[AlCl_4]_2$ and **5a**$[GaCl_4]_2$ are isostructural.

The cationic units in each of the ionic compounds contain the arsolidinium moiety **3** in an associated structural arrangement. The novel dicationic species **5** (**5a**, Figure 1, X = NMe; **5b**, Figure 2, X = S) can be viewed as dimers of **3** bound by a four-membered $As_2X_2$ ring, the center of which represents a crystallographic center of symmetry. They adopt a step-like conformation with long As–X bonds between the monomers (dotted lines), shorter As–X bonds for the adjacent sides of the $As_2X_2$ ring, and the shortest As–X bonds exocyclic to the $As_2X_2$ ring. Structural data for arsenic systems are limited; nevertheless, direct comparison with the chloroarsolidine **4b**, data for related thioarsine systems[32] and the compilation of As–S bond lengths provided by Gillespie,[33] allows for recognition of weak interactions between the five-membered rings (in the $As_2S_2$ four-membered tether) and typical or slightly shortened As–S bonds within the dithiarsolidinium ring. In view of the conformation observed for the dications **5**, it is interesting to note an incipient dimer interaction in the solid-state structure of the neutral chlorodithiarsolidine **4b**, with weak interring contacts [3.430 (1) Å], as illustrated in Figure 4.

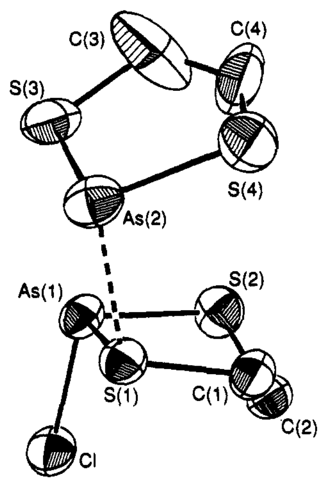


**Figure 3.** Crystallographic view of the cationic unit of $[\overline{SCH_2CH_2S}\overline{AsSAs(Cl)SCH_2CH_2}]$ (**6b**) $[GaCl_4]$.

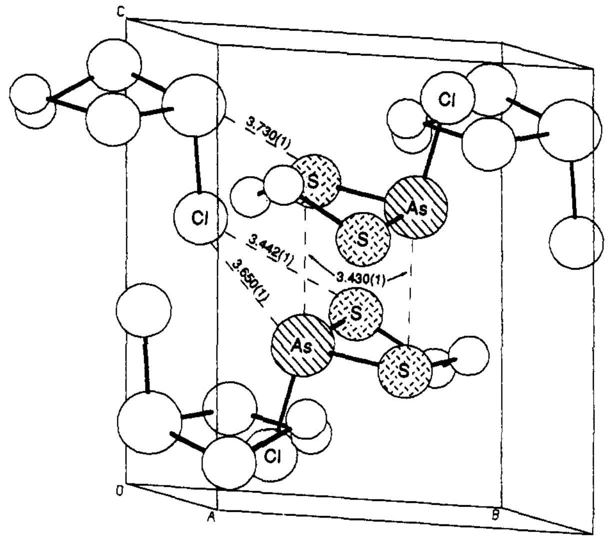


**Figure 4.** Crystallographic view of the unit cell of $\overline{SCH_2CH_2SAsCl}$ (**4b**).

Cation **6b** (Figure 3) is a bicyclic system involving two five-membered rings bound by a single interring As–S connection. In contrast to the step-like conformation observed for derivatives of **5**, the two rings are almost eclipsed with respect to the interring contact. The sulfur bound ring II contains an exocyclic As–Cl bond and is structurally similar to but not identical with the free chloroarsolidine **4b**. The anomalous bond lengths and angles about C(3) and C(4) are a result of slight disorder of these atoms (aspherical ellipsoids in Figure 3).

Interestingly, the interring tether in **6b** is substantially longer than the dimer interactions observed in **5b**. Otherwise, the heterocyclic As–S bond lengths are consistent within the two structures (**5b** and **6b**). As–S bonds between tricoordinate arsenic and dicoordinate sulfur centers are crystallographically identical in length and are slightly shorter than the average of the bonds in the neutral chloroarsolidine **4b** [2.210 (1) Å]. The As–S bond adjacent to the tricoordinate sulfur center is significantly longer than those in **4b**.

---

[31] Johnson, C. K. Report ORNL-3794, Oak Ridge National Laboratory, TN, 1965.

[32] Adams, E.; Jeter, D.; Cordes, A. W.; Kolis, J. W. *Inorg. Chem.* **1990**, *29*, 1500. DiMaio, A.-J.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 798.

[33] Christian, B. H.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1981**, *20*, 3410.

**Table II.** Selected Bond Lengths (Å) and Angles (deg)

Bond Lengths

| | **5a**[AlCl$_4$]$_2$ | **5a**[GaCl$_4$]$_2$ | **5b**[GaCl$_4$]$_2$ | | **6b**[GaCl$_4$] | | **4b** |
|---|---|---|---|---|---|---|---|
| | | | | | As–Cl | 2.226 (2) | 2.2525 (8) |
| | | | | | As(1)–S(1) | 2.318 (2) | 2.1942 (9) |
| | | | | | As(1)–S(2) | 2.195 (3) | 2.225 (1) |
| As–N(2) | 1.955 (7) | 1.949 (4) | As–S(1) | 2.326 (2) | As(2)–S(3) | 2.189 (3) | |
| As–N(1) | 1.763 (8) | 1.752 (5) | As–S(2) | 2.181 (1) | As(2)–S(4) | 2.175 (3) | |
| As–N(2)′ | 2.103 (8) | 2.103 (4) | As–S(1)′ | 2.422 (6) | As(2)–S(1) | 2.523 (2) | |
| C(2)–N(2) | 1.507 (14) | 1.462 (8) | C(1)–S(1) | 1.826 (6) | C(3)–S(3) | 1.77 (1) | |
| C(1)–N(1) | 1.470 (14) | 1.487 (8) | C(2)–S(2) | 1.826 (7) | C(4)–S(4) | 1.80 (1) | |
| C(1)–C(2) | 1.542 (16) | 1.500 (9) | C(1)–C(2) | 1.493 (9) | C(3)–C(4) | 1.36 (2) | |
| | | | | | C(1)–S(1) | 1.810 (9) | 1.819 (4) |
| | | | | | C(2)–S(2) | 1.833 (9) | 1.822 (4) |
| | | | | | C(1)–C(2) | 1.51 (1) | 1.501 (5) |

Bond Angles

| | **5a**[AlCl$_4$]$_2$ | **5a**[GaCl$_4$]$_2$ | **5b**[GaCl$_4$]$_2$ | | **6b**[GaCl$_4$] | | **4b** |
|---|---|---|---|---|---|---|---|
| | | | | | Cl–As(1)–S(1) | 91.29 (9) | 99.51 (3) |
| | | | | | Cl–As(1)–S(2) | 101.1 (2) | 98.21 (3) |
| | | | | | S(1)–As(1)–S(2) | 91.08 (9) | 93.50 (3) |
| | | | | | As(1)–S(1)–C(1) | 97.1 (1) | 106.4 (3) |
| | | | | | As(1)–S(2)–C(2) | 97.5 (3) | 100.8 (1) |
| | | | | | S(1)–C(1)–C(2) | 110.7 (6) | 110.2 (3) |
| | | | | | S(2)–C(2)–C(1) | 109.9 (6) | 111.2 (2) |
| As–N(2)–As′ | 99.3 (3) | 99.5 (2) | As–S(1)–As′ | 93.13 (6) | As(1)–S(2)–As(2) | 101.16 (8) | |
| N(1)–As–N(2)′ | 102.0 (3) | 100.9 (2) | S(1)–As–S(2)′ | 96.96 (6) | S(1)–As(2)–S(3) | 99.04 (9) | |
| N(2)–As–N(2)′ | 80.7 (3) | 80.5 (2) | S(1)–As–S(1)′ | 86.87 (6) | S(1)–As(2)–S(4) | 102.1 (2) | |
| N(1)–As–N(2) | 86.7 (4) | 87.2 (2) | S(1)–As–S(2) | 93.14 (6) | S(3)–As(2)–S(4) | 94.7 (1) | |
| As–N(2)–C(2) | 109.1 (6) | 107.6 (3) | As–S(1)–C(1) | 98.7 (2) | As(2)–S(3)–C(3) | 99.8 (4) | |
| As–N(1)–C(1) | 117.4 (7) | 116.2 (4) | As–S(2)–C(2) | 100.6 (2) | As(2)–S(4)–C(4) | 100.0 (5) | |
| N(2)–C(2)–C(1) | 106.1 (9) | 107.2 (5) | S(1)–C(1)–C(2) | 112.7 (5) | S(3)–C(3)–C(4) | 119 (2) | |
| N(1)–C(1)–C(2) | 105.7 (8) | 106.0 (5) | S(2)–C(2)–C(1) | 111.7 (4) | S(4)–C(4)–C(3) | 117 (1) | |

The five-membered rings are distorted from planarity, as expected for cyclopentane derivatives, and the series of thia derivatives illustrate interesting trends. All rings can be viewed in terms of a single carbon atom C(2) displacement from the S(2)–As–S(1)–C(1) plane (**5b**[GaCl$_4$]$_2$, 0.661 Å; **6b**[GaCl$_4$] ring I, 0.366 Å; ring II, 0.787 Å; **4b**, 0.511 Å), although the deviation of these four atoms from planarity varies considerably (maximum deviation from the best planes: **5b**[GaCl$_4$]$_2$, S(1) 0.047 Å; **6b**[GaCl$_4$] ring I, S(3) 0.060 Å; ring II, S(1) 0.049 Å; **4b**, S(1) 0.248 Å). In all derivatives of **5** the carbon atom is displaced toward the side of the dimer interaction (endo). The greatest distortions from planarity of the four atom unit are observed for the neutral system **4b**, although the displacement of C(4) in ring II of **6b** from the best plane is the more pronounced. Ring I of **6b** is the closest to planarity for all five atoms. The differences in planarity are not manifest in the endocyclic angles observed at arsenic and sulfur.

Anion–cation contacts (interatomic distances less than the sum of the van der Waals radii of the two atoms involved; lengths indicated in the figures) between the chlorine atoms of the anions and the arsenic or sulfur centers of the cations (contacts to nitrogen are not observed in salts of **5a**) are observed in all of the salt structures. However, in general they are of similar length or longer than the intermolecular As–Cl interactions evident in the structure of the neutral chloroarsolidine **4b** (Figure 4). Such interactions are very common in nonmetal salts[14,19,20,34] and are viewed as donations from the anion to the cation.[35] Our recent experimental experience shows that they play no role in the gross structural features of either anion or cation[36] and at most effect minor distortion of the tetrahedral geometry of a ECl$_4^-$ anion (E = Al or Ga). Similar conclusions can be drawn from the structural results presented here, recognizing the essentially identical structural arrangement of cations **5a** and **5b** despite the presence of more numerous and substantially shorter anion–cation contacts in the latter (see Figures 1 and 2).

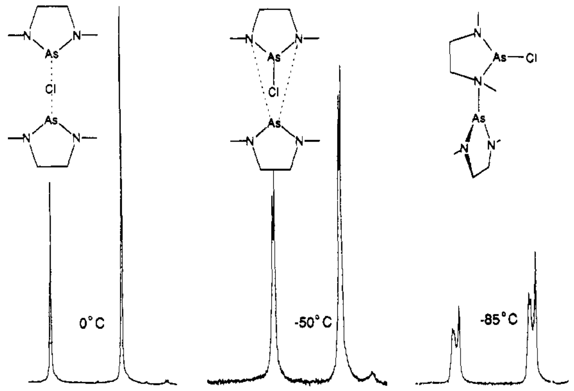


**Figure 5.** $^1$H NMR spectra at 0, −50, and −85 °C for [N(Me)CH$_2$CH$_2$N(Me)AsN(Me)As(Cl)N(Me)CH$_2$CH$_2$] (**6a**) [GaCl$_4$], with topological models for the cation to rationalize each spectrum.

**Solution NMR Features.** Solution $^1$H and $^{13}$C NMR spectroscopy at room temperature show a single line for salts of **5b** and **6b** and two lines (3:2 integration ratio) for salts of **5a** and **6a**, each with distinct chemical shifts. In the case of **6a**, line broadening and coalescence is observed on cooling. Each of the two room temperature signals is split into two below −30 °C, and ultimately each of the downfield signals is split into two below −60 °C. The VT experiment is illustrated in Figure 5. The coalescence points are concentration dependent; however, the solvent peak (residual CH$_2$Cl$_2$) exhibits broadening and coalescence at the same temperatures, implying that the concentration dependence may be the result of interaction between the cation and the solvent. The onset of coalescence is apparent at −90 °C for **5a**, the point at which the solvent begins to freeze. Low solubility of the thia derivatives **5b** and **6b** prevented VT studies.

---

(34) See, for example: Klapötke, T.; Passmore, J. *Acc. Chem. Res.* **1989**, *22*, 234, and references therein. Cardinal, G.; Gillespie, R. J.; Sawyer, J. F.; Verkis, J. E. *J. Chem. Soc., Dalton Trans.* **1982**, 765. McMullan, R. K.; Prince, D. J.; Corbett, J. D. *Inorg. Chem.* **1971**, *10*, 1749. Couch, T. W.; Lokken, D. A.; Corbett, J. D. *Inorg. Chem.* **1971**, *10*, 2319.

(35) Bader, R. F. W.; Gillespie, R. J.; MacDougall, P. J. From Atoms to Polymers. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1989; Vol. 11, p 1.

(36) Burford, N.; Mason, S.; Spence, R. E. v. H.; Whalen, J. M.; Richardson, J. F.; Rogers, R. D. *Organometallics* **1992**, *11*, 2241.

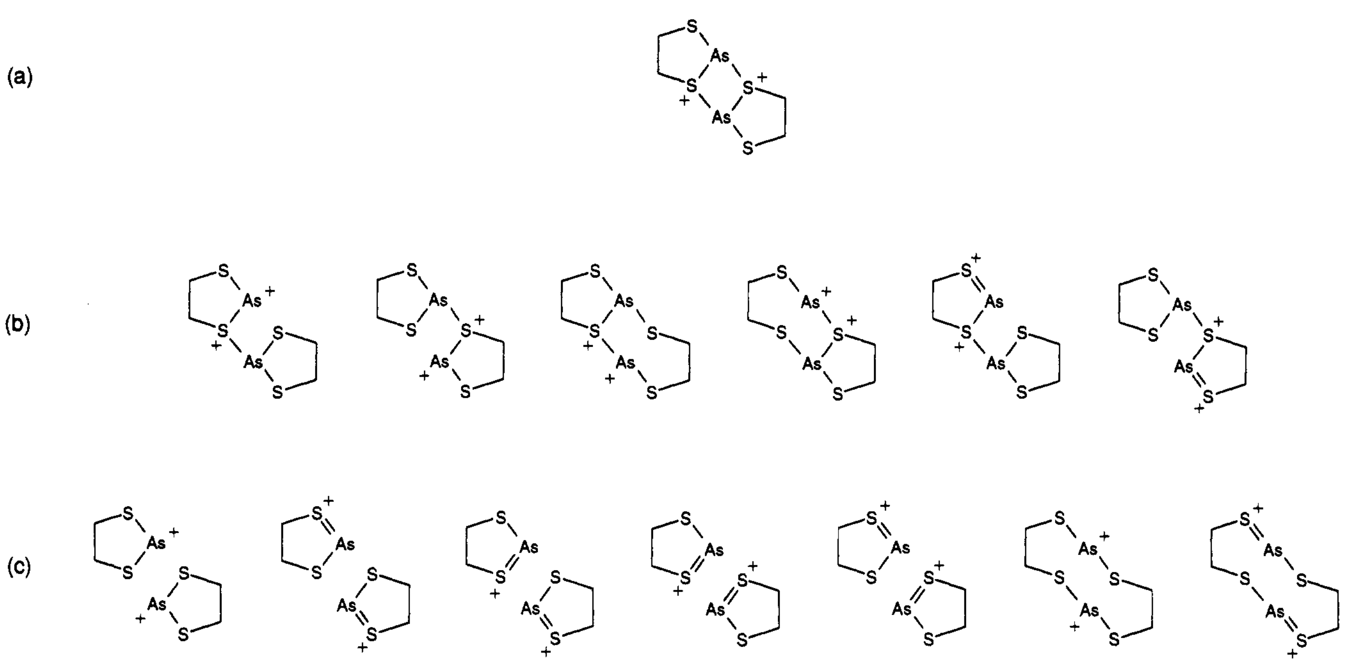


**Figure 6.** Principal resonance structures for $[\overline{SCH_2CH_2SAs}]_2^{2+}$ (**5b**).

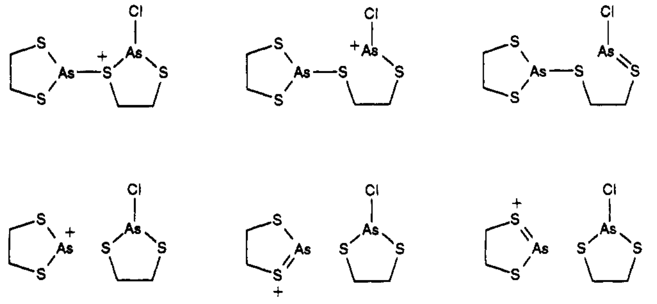


**Figure 7.** Principal resonance structures for $[\overline{SCH_2CH_2SAs}\overline{SAs(Cl)SCH_2CH_2}]^+$ (**6b**).

While assignment of the signals ($^1H$, 3.5–4.0 ppm, $CH_2$; 2.8–3.2 ppm $CH_3$) is straightforward, reasons for equivalence at room temperature and nonequivalence at low temperature are not so obvious, due to strong solvent interactions. Nevertheless, we envisage a process involving dissociation of the two rings. The interring contacts are noticeably weak in the solid state, especially in **6b**; however, the exchange process may well involve chloride transfer from the anion or from the solvent. This must certainly be the case for **6**, which requires two structural manipulations to render the methyl substituents (and methylene substituents) equivalent at room temperature: transfer of a chlorine atom from one arsenic center to another and shift of the interring connection to neighboring atoms on each ring. Moreover, in our experience tetrachloroaluminate and tetrachlorogallate salts readily exchange chloride ions with nonmetal cations and chlorinated solvents.[14] Further evidence for chloride ion exchange processes is provided by the $^1H$ NMR spectra of various nonequimolar mixtures of **5a** and **4a**, which show an average chemical shift corresponding to the relative amounts of each component. Consequently, we envisage the two coalescence points observed for **6a** on cooling as first retarding the chloride ion exchange, thereby distinguishing ring I from ring II, and second recognizing firm association between arsolidinium (ring I) and chloroarsolidine (ring II), as topologically illustrated in Figure 5. The methyl (and methylene) substituents of ring I are equivalent even at −90 °C.

**Arsenium Centers, Novel Carbenic Analogues.** Dimerization to an *alkenic* system is an obvious structural alternative for *carbenic* systems and is evident for carbenes,[1,37] germylenes,[38] and stannylenes.[38] Nevertheless, the use of bulky substituents to prevent approach of two *carbenic* centers,[3,5,6,8,9] or the stabilization provided by intramolecular contacts to the coordinatively unsaturated center,[7] has made possible the isolation of systems containing these elements in dicoordinate environments. Although structural data is limited for phosphenium salts,[10,11,39] there is no evidence for dimerization of these carbene analogues. Bulky substituents do not appear to be a requirement for the stability of phosphenium derivatives and as π-electron donation from substituents to the phosphorus center is recognized as inferior to the C–N π-interaction, it is tempting to implicate the cationic molecular charge for the monomeric behavior. The new arsolidinium cations **3** described above are significant in this context in that they exist as dimers in the solid state but have an unusual, non-*alkenic*, four center associated structure.

The nature of the dimer structure **5** is reminiscent of some novel neutral main group systems.[40] However, in the context of the carbene analogy, the arsolidinium dications represent an alternative to the *alkenic* dimer arrangement **7**, which would require the formation of an As═As 4pπ-bond and localization of positive charges. The apparent weakness of the interring bonds in **5** and their lability in solution is not clearly understood, but might be an indication of a fine energetic balance between a coordinatively saturated σ-bonded dimer system (Figure 6a) and two *carbenic* centers involving As–X π-interaction (Figure 6e). We can interpret the observed structural features of the dimers using a simple Lewis resonance model, as illustrated in Figure 6, and the calculated bond orders [As–S(1), 0.93; As–S(2), 1.28; As–S(1)′, 0.50, labeling according to Figure 2] are consistent with the observed bond length trends in the solid state.

The structural features of the chloroarsolidine–arsolidinium complex can be interpreted in a similar fashion [calculated bond

---

(37) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 754. Quast, H.; Hunig, S. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 800.

(38) See, for example: Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387, and references therein.

(39) Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789. Litvinov, I. A.; Naumov, V. A.; Gryaznova, T. V.; Pudovik, A. N.; Kibardin, A. M. *Dokl. Akad. Nauk SSSR* **1988**, *298*, 369. Pohl, S. *Chem. Ber.* **1979**, *112*, 3159. Friedrich, P.; Huttner, G.; Luber, J.; Schmidpeter, A. *Chem. Ber.* **1978**, *111*, 1558. Pohl, S. *Z. Naturforsch.* **1975**, *32b*, 1342.

(40) Fisher, R. A.; Nielson, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 165. Bates, P. A.; Atwood, J. L.; Bott, S. G.; Jones, C.; Raston, C. L. *Inorg. Chem.* **1991**, *30*, 4868. Hursthouse, M. B.; Davies, A. G.; Slater, S. D. *J. Organomet. Chem.* **1989**, *363*, 45.

orders, As(1)-S(1), 0.67; As(2)-S(1), 0.5; As(1)-S(2), As(2)-S(3), and As(2)-S(4), 1.17], as illustrated in Figure 7. It is interesting to note that the heteroatom interring bonds in the complexes **6** are in contrast to the observations made for the analogous phosphine-phosphenium complexes, in which a phosphorus-phosphorus bond is evident.[11,41]

Our initial theoretical assessment of simple phosphenium and arsenium models at 6-31g* and sto-3g* levels, respectively, has shown an overwhelming energetic preference for the monomeric species in each case, with respect to dimers of various conformations.[42] While theoretical studies continue, at this time we view the dimers **5** in terms of a mutual intermonomer HOMO-LUMO donation, recognizing that the HOMO of the cation is a $\pi$-MO entirely nitrogen based and the LUMO is principally arsenic based (also consistent with the observed structure for the complex **6**). The apparent avoidance of association by phosphenium cations is perhaps an indication of the more effective P-X $\pi$-interaction in the monomer.

**Acknowledgment.** This work has been supported by grants from the Natural Sciences and Engineering Research Council of Canada (N.B.), the donors of the Petroleum Research Fund, administered by the American Chemical Society (N.B.), and Dalhousie University. We thank Dr. Don Hooper and the Atlantic Region Magnetic Resonance Centre for use of the NMR facilities, Mr. Jürgen Müller for construction of the custom glass apparatus, and Mr. Derek Gates for assistance with some of the preparative aspects.

**Supplementary Material Available:** Tables of positional parameters, thermal parameters, bond lengths, and bond angles for **5a**($\mathrm{AlCl_4}$)$_2$, **5a**($\mathrm{GaCl_4}$)$_2$, **5b**($\mathrm{GaCl_4}$)$_2$, **6b**($\mathrm{GaCl_4}$), and **4b** (13 pages); tables of observed and calculated structure factors (43 pages). Ordering information is given on any current masthead page.

---

[41] Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046. Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916. Baxter, S. G.; Collins, R. L.; Cowley, A. H.; Sena, S. F. *Inorg Chem.* **1983**, *22*, 3475.

[42] Boyd, R. J.; Burford, N.; MacKinnon, C. Unpublished results.

---

# Stereodynamics of Isopropyldimethylamine. $^{13}C\{^1H\}$ and $^1H$ Dynamic NMR Studies. Molecular Mechanics Calculations

**Jay H. Brown* and C. Hackett Bushweller***

*Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05405-0125.*

*Received February 10, 1992*

**Abstract:** Since it is the simplest tertiary aliphatic amine that has one isopropyl group, isopropyldimethylamine (IDMA) is an important member of a group of simple aliphatic amines. Both the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of IDMA are decoalesced into two subspectra at about 94 K due to slowing isolated rotation about the methine carbon-nitrogen bond. The major subspectrum is assigned to the enantiomeric conformations that have one isopropyl methyl group anti (A) and the other gauche (G) to the nitrogen lone pair (AG and GA forms). The minor subspectrum is assigned to the GG conformation that has both isopropyl methyl groups gauche to the lone pair. At about 94 K, there is a free energy preference for the AG (or GA) conformation over the GG equal to 0.070 ± 0.020 kcal/mol. Simulations of the exchange-broadened NMR spectra indicate that the AG (or GA) to GG conformational exchange occurs at a faster rate than the AG to GA process. The latter process is sufficiently slower that it contributes little to exchange broadening of the NMR line shape. The free energy of activation ($\Delta G^{\ddagger}$) for the faster NMR-visible AG (or GA) to GG conversion is 4.5 ± 0.1 kcal/mol at 95 K. This barrier is among the lowest measured by using the NMR method. The lower limit for $\Delta G^{\ddagger}$ associated with the AG to GA process is 5.2 kcal/mol at 95 K. Molecular mechanics calculations of conformational energies and rotation barriers agree well with the experimental data. The molecular mechanics calculations indicate a small enthalpy preference for the GG conformation (0.19 kcal/mol) and a barrier for the AG to GA conversion ($\Delta H^{\ddagger}$ = 7.84 kcal/mol) that is higher than that for the AG (or GA) to GG process (5.37 kcal/mol).

## Introduction

Any successful attempt to elucidate a comprehensive picture of the stereodynamics of an aliphatic amine requires identification of the equilibrium conformations and the preferred pathways for conformational exchange.[1] Two different types of internal motion are relevant. One is pyramidal inversion at nitrogen.[2] The other involves isolated rotation about various bonds in the amine.[3] In many simple aliphatic amines, the rotation-inversion dichotomy is clearly delineated; the energy barrier for inversion is significantly greater than that for any isolated rotation process.[4] Infrared spectroscopy, microwave spectroscopy, and molecular orbital calculations have shed considerable light on the stereodynamics of simple aliphatic amines including methylamine,[5] dimethylamine,[5a,6] trimethylamine,[5a,7] ethylamine,[8] isopropylamine,[8d,9]

---

[1] Bushweller, C. H. In *Acyclic Organonitrogen Stereodynamics*; Lambert, J. B., Takeuchi, Y., Eds.; VCH Publishers: New York, 1992.

[2] Lambert, J. B. *Top. Stereochem.* **1971**, *6*, 19. Lehn, J. M. *Fortschr. Chem. Forsch.* **1970**, *15*, 311. Payne, P. W.; Allen, L. C. In *Applications of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4.

[3] Orville-Thomas, W. J., Ed. *Internal Rotation in Molecules*; J. Wiley and Sons: New York, 1974.

[4] Bushweller, C. H.; Fleischman, S. H.; Grady, G. L.; McGoff, P.; Rithner, C. D.; Whalon, M. R.; Brennan, J. G.; Marcantonio, R. P.; Domingue, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 6224.

[5] (a) Eades, R. A.; Weil, D. A.; Dixon, D. A.; Douglass, C. H., Jr. *J. Phys. Chem.* **1981**, *85*, 976. (b) Flood, E.; Pulay, P.; Boggs, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 5570. (c) Tsuboi, M.; Hirakawa, A. Y.; Takamitsu, I.; Sasaki, T.; Tamagake, K. *J. Chem. Phys.* **1964**, *41*, 2721. (d) Tsuboi, M.; Hirakawa, A. Y.; Tamagake, K. *J. Mol. Spectrosc.* **1967**, *22*, 272. (e) Nishikawa, T.; Itoh, T.; Shimoda, K. *J. Chem. Phys.* **1955**, *23*, 1735.

[6] Wollrab, J. E.; Laurie, V. W. *J. Chem. Phys.* **1968**, *48*, 5058. Wollrab, J. E.; Laurie, V. W. *J. Chem. Phys.* **1971**, *54*, 539.

[7] Weston, R. E., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 2645. Lide, D. R.; Mann, D. E. *J. Chem. Phys.* **1958**, *28*, 572.

[8] (a) Durig, J. R.; Li, Y. S. *J. Chem. Phys.* **1975**, *63*, 4110. (b) Tsuboi, M.; Tamagake, K.; Hirakawa, A. Y.; Yamaguchi, J.; Nakagawa, H.; Manocha, A. S.; Tuazon, E. C.; Fateley, W. G. *J. Chem. Phys.* **1975**, *63*, 5177. (c) Hamada, Y.; Hashiguchi, K.; Hirakawa, A. Y.; Tsuboi, M.; Nakata, M.; Tasumi, M.; Kato, S.; Morokuma, K. *J. Mol. Spectrosc.* **1983**, *102*, 123. (d) Alsenoy, C. V.; Scarsdale, J. N.; Williams, J. O.; Schaefer, L. J. *J. Mol. Struct.* **1982**, *86*, 365. (e) Krueger, P. J.; Jan, J. *Can. J. Chem.* **1970**, *48*, 3229.

[9] Bohlmann, F. *Chem. Ber.* **1958**, *91*, 2157. Hamlow, H. P.; Okada, S.; Nakagawa, N. *Tetrahedron Lett.* **1964**, 2553.