Journal of Organometallic Chemistry, 354 (1988) 287–292
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The twist-boat conformation in a gallium-arsenic six-membered ring: crystal structure of $[(Me_3SiCH_2)_2AsGaBr_2]_3$

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(Received September 16th, 1987; in revised form April 6th, 1988)

Abstract

$[(Me_3SiCH_2)_2AsGaBr_2]_3$, the first trimeric mono(arsino)gallane to be structurally characterized by X-ray crystallographic analysis, has been shown to contain a $(Ga–As)_3$ ring in the twist-boat conformation. Crystals of the trimer are monoclinic, space group $P2/c$ (C_{2h}^4), with a 18.877(4), b 13.710(3), c 24.821(4) Å, β 122.24(2)°, U 5433.4 Å^3, and $Z = 4$. The Ga–As bond lengths (2.432(2)–2.464(1) Å) are all less than any of those found in the $(Ga\text{-}As)_2$ rings of dimeric arsinogallanes.

Introduction

The facile preparation of a number of new gallium-arsenic compounds, including $[(Me_3SiCH_2)_2AsGaBr_2]_3$ (**1**), using silylarsines was recently demonstrated by work in our laboratories [1], and **1** is one of a group of mono(arsino)gallanes now known to exist as trimers on the basis of NMR and cryoscopic molecular weight data. Some in this group are reported to be solely trimeric in solution, e.g., $(Me_2AsGaMe_2)_3$ [2], $[(Me_3SiCH_2)_2AsGaCl_2]_3$ [1a], and **1** [1b], whereas dimer-trimer equilibria have been shown to be present in solutions of others, e.g., $[(Ph)Me_3SiCH_2AsGaMe_2]_{2,3}$ [1d], $[(Ph)Me_3SiCH_2AsGaPh_2]_{2,3}$ [1d], $[(Me_3SiCH_2)_2AsGaMe_2]_{2,3}$ [1d], $[(Me_3SiCH_2)_2AsGaMe(Cl)]_{2,3}$ [1b], and $[(Me_3SiCH_2)_2\text{-}AsGaPh(Cl)]_{2,3}$ [1b]. Notwithstanding the preceding information, no structural details for a trimeric mono(arsino)gallane have appeared in the literature to date. Thus, a single-crystal X-ray analysis was performed on **1** to determine the geometrical features of the six-membered $(Ga\text{-}As)_3$ ring in this type of molecule.

Experimental

Preparation of $[(Me_3SiCH_2)_2AsGaBr_2]_3$ (1) [1b]

Compound **1** was prepared from the reaction of $(Me_3SiCH_2)_2AsSiMe_3$ (0.21 g, 0.65 mmol) with $GaBr_3$ (0.20 g, 0.65 mmol) in ligroin (~ 20 ml, b.p. 95–110 °C),

0022-328X/88/$03.50

rather than in pentane which was used in the initially reported synthesis [1b], and it precipitated from the solution as small, colorless crystals in contrast to the large crystals which separated from pentane [1b]. Removal of the mother liquor followed

Table 1

Non-hydrogen atom fractional coordinates ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z
Molecule I			
As(1) [a]	0(–)	2200.9(11)	2500(–)
Ga(2)	–0.6(6)	3301.9(9)	1732.2(5)
As(3)	–658.5(6)	4919.9(8)	1521.7(4)
Ga(4) [a]	0(–)	5905.8(13)	2500(–)
Br(21)	–390.8(7)	2500.8(10)	789.6(5)
Br(22)	1393.4(6)	3837.4(10)	2286.2(6)
Br(41)	–1044.1(7)	6861.4(10)	2456.6(7)
Si(11)	–1229(2)	435(2)	2548(1)
Si(31)	–580(2)	6668(3)	571(2)
Si(32)	–2655(2)	4241(2)	482(1)
C(111)	–977(5)	1381(7)	2110(4)
C(112)	–1785(6)	1066(10)	2885(5)
C(113)	–1910(7)	–458(9)	1927(6)
C(114)	–283(7)	–181(10)	3211(6)
C(311)	–334(7)	5405(8)	950(5)
C(312)	431(8)	7219(10)	773(6)
C(313)	–1092(8)	7489(9)	877(6)
C(314)	–1261(10)	6489(12)	–308(6)
C(321)	–1869(5)	5073(8)	1109(5)
C(322)	–2533(7)	2996(9)	806(6)
C(323)	–3689(7)	4739(9)	260(6)
C(324)	–2570(7)	4235(10)	–224(5)
Molecule II			
As(1) [a]	5000(–)	–2364.5(10)	2500(–)
Ga(2)	4913.7(6)	–1254.7(9)	1702.7(5)
As(3)	4259.6(5)	357.9(8)	1517.6(4)
Ga(4) [a]	5000(–)	1343.6(12)	2500(–)
Br(21)	4486.8(8)	–2032.0(10)	746.4(5)
Br(22)	6302.4(6)	–707.8(10)	2224.1(6)
Br(41)	3900.2(7)	2292.4(9)	2515.1(6)
Si(11)	3820(2)	–4112(3)	2628(2)
Si(31)	4254(2)	2104(3)	540(1)
Si(32)	2257(2)	–341(2)	523(1)
C(111)	4016(5)	–3194(8)	2157(4)
C(112)	3362(8)	–3503(12)	3045(6)
C(113)	3059(8)	–4975(11)	2010(7)
C(114)	4768(8)	–4791(10)	3214(6)
C(311)	4508(6)	845(8)	895(4)
C(312)	5227(7)	2672(10)	688(6)
C(313)	3763(8)	2916(9)	867(6)
C(314)	3525(10)	1955(11)	–345(7)
C(321)	3075(5)	499(8)	1162(4)
C(322)	2407(7)	–1580(8)	854(6)
C(323)	1225(6)	121(9)	316(5)
C(324)	2317(7)	–347(9)	–201(5)

[a] Occupancy factor = 0.50.

by drying under vacuum resulted in a large number of small, uniformly sized crystals suitable for an X-ray study. The ^{1}H NMR spectrum of a sample of the latter crystals in C_6D_6 was identical to that of a sample of the large crystals [1b].

Crystal data. $C_{24}H_{66}As_3Br_6Ga_3Si_6$, $M = 1436.69$, monoclinic, space group $P2/c$ (C_{2h}^4), a 18.877(4), b 13.710(3), c 24.821(4) Å, β 122.24(2)°, U 5433.4 Å^3, $Z = 4$, D_c 1.756 g cm^{-3}, μ(Cu-K_α radiation, λ 1.5418 Å) 104.6 cm^{-1}, sample dimensions 0.15 × 0.25 × 0.54 mm (sealed inside a thin-walled capillary).

Crystallographic measurements. Preliminary unit-cell parameters and space group information were obtained from oscillation and Weissenberg photographs. Intensity data ($+h$, $+k$, $\pm l$, 9668 independent reflections) were recorded on an Enraf–Nonius CAD-4 diffractometer (Cu-K_α radiation, incident-beam monochromator; ω–2θ scans, $\theta_{max.}$ 67°). Those 4798 reflections with $I > 3.0\sigma(I)$ were retained for the structure analysis and corrected for the usual Lorentz and polarization effects. An empirical absorption correction, based on the ϕ-dependence of the

Table 2

Selected bond lengths (Å) and angles (deg.), with estimated standard deviations in parentheses

	Molecule I	Molecule II
(a) Bond lengths		
As(1)–Ga(2)	2.431(2)	2.432(2)
As(1)–C(111)	1.923(9)	1.945(9)
Ga(2)–As(3)	2.458(2)	2.453(2)
Ga(2)–Br(21)	2.320(2)	2.319(2)
Ga(2)–Br(22)	2.344(1)	2.343(1)
As(3)–Ga(4)	2.459(1)	2.468(1)
As(3)–C(311)	1.939(14)	1.956(13)
As(3)–C(321)	1.954(9)	1.926(9)
Ga(4)–Br(41)	2.321(2)	2.325(2)
(b) Bond angles		
Ga(2)–As(1)–Ga(2′)	103.22(7)	102.54(7)
Ga(2)–As(1)–C(111)	111.7(3)	112.1(3)
C(111)–As(1)–C(111′)	108.5(4)	108.4(4)
As(1)–Ga(2)–As(3)	121.06(7)	121.65(7)
As(1)–Ga(2)–Br(21)	111.33(7)	112.41(6)
As(1)–Ga(2)–Br(22)	101.76(5)	100.44(5)
As(3)–Ga(2)–Br(21)	111.11(5)	110.92(5)
As(3)–Ga(2)–Br(22)	97.11(6)	96.78(6)
Br(21)–Ga(2)–Br(22)	113.14(8)	112.82(8)
Ga(2)–As(3)–Ga(4)	110.74(5)	110.20(5)
Ga(2)–As(3)–C(311)	98.3(4)	98.4(3)
Ga(2)–As(3)–C(321)	121.7(3)	121.4(3)
Ga(4)–As(3)–C(311)	110.1(3)	110.2(3)
Ga(4)–As(3)–C(321)	107.0(3)	107.8(3)
C(311)–As(3)–C(321)	108.5(5)	108.2(4)
As(3)–Ga(4)–As(3′)	113.32(8)	113.59(7)
As(3)–Ga(4)–Br(41)	107.16(4)	109.12(4)
Br(41)–Ga(4)–Br(41′)	111.26(9)	111.94(8)
As(1)–C(111)–Si(11)	125.0(4)	125.2(5)
As(3)–C(311)–Si(31)	125.7(7)	125.1(7)
As(3)–C(321)–Si(32)	124.1(6)	123.3(6)

intensities of 4 reflections with χ ca. 90°, was also applied to the data. Refined unit-cell parameters were derived from the diffractometer setting angles for 25 reflections ($40° < \theta < 55°$) widely separated in reciprocal space.

Structural analysis. The structure was solved by direct methods. Full-matrix least-squares adjustment of non-hydrogen atom positional and anisotropic thermal parameters, with hydrogen atoms included at their calculated positions in the later iterations, converged to $R = 0.045$ ($R_w = 0.060$) ($R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$). For the structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 3. In the least-squares iterations, $\Sigma w\, \Delta^2$ ($w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$) was minimized. All crystallographic calculations were performed on a PDP11/44 computer by use of the Enraf–Nonius SDP suite of programs incorporating the direct methods program MULTAN 11/82. Final non-hydrogen atom positional parameters are in Table 1 and selected bond lengths and angles are in Table 2. Tables of interatomic distances and angles, torsion angles, thermal parameters, hydrogen atom parameters, and observed and calculated structure factors are available from the authors (R.L.W.).

Discussion

Crystals of **1** contain two crystallographically independent, but structurally identical, discrete molecules having the constitution illustrated in Fig. 1. Each of the molecules lies across a crystallographic C_2 axis of symmetry passing through As(1)

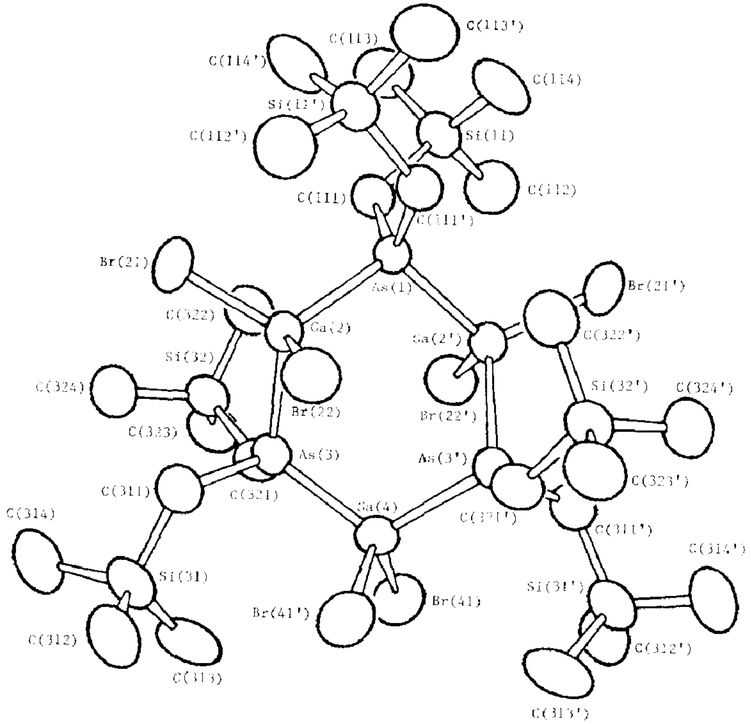

Fig. 1. Atomic arrangement in $[(Me_3SiCH_2)_2AsGaBr_2]_3$ (**1**) (hydrogen atoms omitted for clarity).

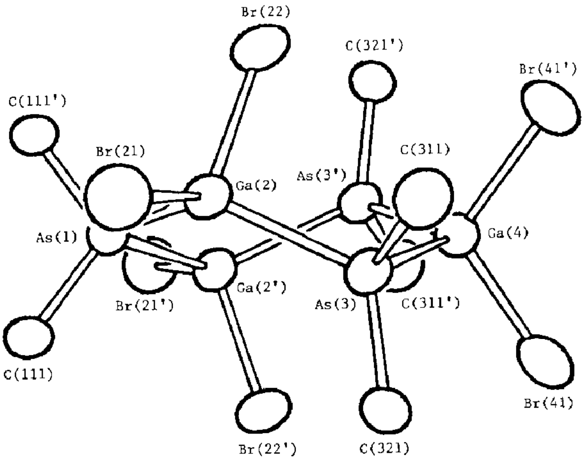

Fig. 2. The twist-boat conformation of the $(Ga-As)_3$ ring of $[(Me_3SiCH_2)_2AsGaBr_2]_3$ (**1**).

and Ga(4) and, with the endocyclic torsion angles also related by an approximate C_2 axis passing through the mid-points of the Ga(2)–As(3) and Ga(2′)–As(3′) bonds, the $(Ga-As)_3$ ring adopts the somewhat rare twist-boat conformation (Fig. 2). The torsion angles of -30.2, $+59.9$, and $-25.0°$ * (Ga(2′)–As(1)–Ga(2)–As(3), As(1)–Ga(2)–As(3)–Ga(4), and Ga(2)–As(3)–Ga(4)–As(3′), respectively) compare favorably to the theoretical values of -31, $+65$, and $-31°$ for equivalent torsion angles in the twist-boat form of cyclohexane [4]. In $(t\text{-}Bu_2SbGaCl_2)_3$, the $(Ga-Sb)_3$ ring has a somewhat irregular boat conformation, whereas in $(Me_2AsInMe_2)_3$, the $(In-As)_3$ ring is found to be both planar and puckered [5].

Endocyclic bond angles at As (102.88(7), 110.47(5)°) differ significantly and both are smaller than those subtended at Ga (113.46(8), 121.36(7)°) which are also unequal. Exocyclic Br–Ga–Br angles (112.98(8), 111.60(9)°) differ only slightly and the C–As–C angles (108.5(4), 108.4(5)°) are equal. Ga–As bond lengths (2.432(2)–2.464(1) Å) are all less than any of the distances found thus far between four-coordinate Ga and four-coordinate As centers in dimeric organogallium compounds [1b, 6–8] for which the shortest (2.513(1)°) occurs in the planar $(Ga-As)_2$ ring of $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$ [1b] and the longest (2.581(1) Å) is present in $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$ which contains a nonplanar $(Ga-As)_2$ ring [7]. Interestingly, the shortest Ga–As distance in **1** (2.432(2) Å) is not significantly different from the shortest previously reported length for an organogallium-arsenic compound, viz., the Ga-*exo*-As distance (2.437(1) Å) between four-coordinate Ga and three-coordinate As in the dimer $\{[(Me_3SiCH_2)_2As]_2GaBr\}_2$ [1b].

Acknowledgement

We thank the Office of Naval Research and the Duke University Research Council for financial support.

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* Averages for the two crystallographically-independent molecules are cited; similarly, all other numbers in the discussion section pertaining to **1** are average values. Where different, the higher of two estimated standard deviations are quoted.

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