1-1-1987

Structure of l,l-Diphenylarsenanium Bromide Monohydrate

J. A. Campbell
Montana State University - Bozeman

R. Larsen
Montana State University

C. Campana
Nicolet Analytical Instruments

Sheldon E. Cremer
Marquette University, sheldon.cremer@marquette.edu

A. Gamliel
Marquette University

Published version. *Acta Crystallographica Section C*, C43 (1987): 1912-1915. DOI.

Acta Cryst. (1987). C**43**, 1912–1915

Structure of 1,1-Diphenylarsenanium Bromide Monohydrate

BY J. A. CAMPBELL* AND R. LARSEN

Chemistry Department, Montana State University, Bozeman, Montana 59715, *USA*

C. CAMPANA

Nicolet Analytical Instruments, Madison, Wisconsin 53711, *USA*

AND S. E. CREMER AND A. GAMLIEL

Chemistry Department, Marquette University, Milwaukee, Wisconsin 53233, *USA*

(*Received* 17 *September* 1986; *accepted* 25 *August* 1987)

Abstract. $C_{17}H_{20}As^+.Br^-.H_2O$, $M_r = 397{\cdot}19$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}637\ (2)$, $b = 12{\cdot}168\ (4)$, $c = 16{\cdot}066\ (7)$ Å, $V = 1688{\cdot}44$ Å^3, $Z = 4$, $D_m = 1{\cdot}56$, $D_x = 1{\cdot}56$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 54{\cdot}8$ cm^{-1}, $F(000) = 800$, $T = 295$ K, $R = 0{\cdot}057$, $wR = 0{\cdot}061$, 1248 observed reflections. The arsenic heterocyclic ring is in the chair form and the torsion angles indicate that it is nearly symmetrical. The As—C bond

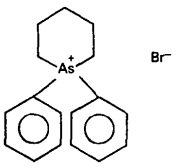
* To whom all correspondence should be addressed. Present address: Battelle, Pacific Northwest Laboratories, PO Box 999, Richland, Washington 99352, USA.

0108-2701/87/101912-04$01.50

distances are 1·911 (11), 1·916 (10), 1·902 (10) and 1·917 (11) Å. The bond angles around As are 103·5 (5), 109·4 (5), 109·9 (4), 109·6 (5), 112·0 (5) and 112·2 (5)°.

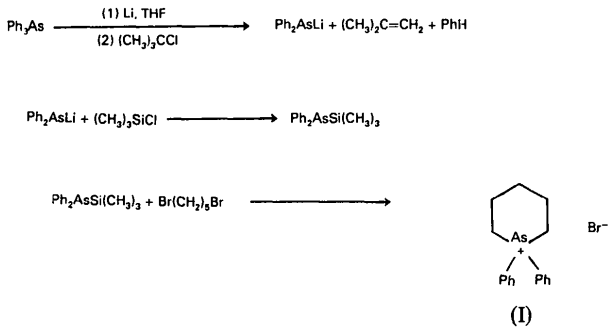
Introduction. The mechanism and stereochemical outcome involving the attack of nucleophiles at a phosphorus center (specifically phosphonium salts) have been actively pursued (Gallagher & Jenkins, 1968; Holmes, 1980). In contrast, very little has been reported regarding nucleophilic attack at an arsenic center. The primary reason for this is the short half-life of racemization of arsine oxides (Horner & Winkler, 1964; Horner & Hofer, 1965; Gatilov, Ionov & Molodtsov, 1972) which would result from hydroxide ion attack on arsenium salts with appropriate leaving groups. On the other hand, arsine sulfides are more stable to racemization and have occasionally served as substrates for stereochemical evaluation (Stackhouse, Cook & Mislow, 1973; Horner & Fuchs, 1963).

As part of a general program to probe the stereochemistry of nucleophilic attack at arsenic, we have incorporated the heteroatom into a ring system, since analogous substrates have been so useful in the evaluation of phosphorus stereochemistry (Gallucci & Holmes, 1980). The present investigation is concerned with a structural study of 1,1-diphenylarsenanium bromide monohydrate (I).



(I)

Experimental. The synthesis is based on analogous reactions of α,ω-dihaloalkanes with diphenyltrimethylsilylphosphine (Haque, Horne, Cremer, Kremer & Mast, 1980) and is illustrated in the following scheme



(I)

Colorless crystals of the title compound suitable for X-ray analysis obtained by recrystallization from acetonitrile, D_m by flotation in ethanol and methyl iodide, crystal size 0·3 × 0·4 × 0·4 mm, Nicolet *R*3*m* diffractometer, graphite monochromator, precise unit-cell parameters (Campana, 1981) from least-squares refinement of 25 reflections (θ range 10–20°), Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å); three standard reflections (057, 434, 623) measured every 120 minutes, average intensity variation <3%. Range of *hkl*: $0 \le h \le 10$, $0 \le k \le 14$, $0 \le l \le 18$, data collected by θ–2θ scan, 1800 unique data measured, $3 \le 2\theta \le 55°$, 1248 observed reflections, $I \ge 2\sigma(I)$, Lorentz, polarization, and absorption corrections. Absorption corrections by numerical Gaussian integration method from crystal dimensions and indexed faces. Maximum and minimum transmission coefficients 0·66 and 0·59, respectively. Br^- position from Patterson map, full-matrix least squares, $\sum w(|F_o|-|F_c|)^2$ minimized where $w = 1/[\sigma^2(F) + G(F)^2]$ and $G = 0{\cdot}001$; non-hydrogen atoms anisotropic, H atoms located in ΔF map, idealized coordinates calculated and not refined, isotropic thermal parameters for H's assigned as 0·06 Å^2, $R = 0{\cdot}057$ and $wR = 0{\cdot}061$, scattering factors for As, C, Br, O and H from *International Tables for X-ray Crystallography* (1962), $S = 1{\cdot}28$. In the final cycle, largest shift in any parameter was $0{\cdot}06\sigma$. Final difference map showed no peaks larger than 0·50 e Å^{-3} (at 0·90 Å from Br). Calculations carried out with *SHELXTL* package on Nicolet *R*3*m* crystallographic system (Sheldrick, 1980).

Discussion. The final atomic parameters are given in Table 1, and the structure and numbering scheme are shown in Fig. 1.* Table 2 is a list of selected interatomic distances and angles with their e.s.d.'s in parentheses. A projection of the structure along **c** is shown in Fig. 2.

The bond angles around the As atom vary from 103·5 to 112·2° and the average is 109·4°, which is not significantly different from the tetrahedral angle of 109·5°. The As–C bond lengths vary from 1·902 to 1·917 Å with an average bond length of 1·911 (10) Å, which is similar to other published values, *e.g.* 1·915 (8) Å in tetraphenylarsonium trichloride (Bogaard, Peterson & Rae, 1981) and 1·923 (13) and 1·941 (36) Å in tetramethylarsonium dichlorodimethylgallate and tetramethylarsonium trichloromonomethylgallate, respectively (Hausen, Guder & Schwarz, 1977).

The As–C distances are 1·911 (11), 1·916 (10), 1·902 (10) and 1·917 (11) Å. The C–C distances of

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43807 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the heterocyclic ring are 1·557 (17), 1·521 (18), 1·517 (17) and 1·528 (17) Å. In comparison, the P–C distances in the isomorphous analog, 1,1-diphenylphosphorinanium bromide (Campbell, Larsen, Ekeland & Cremer, 1986), are 1·794 (9), 1·806 (10), 1·796 (9), and 1·783 (10) Å and C–C distances are 1·544 (13), 1·524 (14), 1·516 (15) and 1·542 (15) Å for the phosphorus analog. The bond angles around the As atom are 103·5 (5), 109·4 (5), 109·6 (5), 112·0 (5), 112·2 (5) and 109·9 (4)°. The bond angles around the P atom in the phosphorus analog are similar: 103·7 (5), 111·7 (4), 110·5 (4), 109·8 (4), 111·0 (4) and 109·9 (4)°.

Table 1. *Atom coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å² × 10^3)

	x	*y*	*z*	U_{eq}*
Br	5131 (2)	8376 (1)	5845 (1)	63 (1)
As	9053 (1)	8928 (1)	7519 (1)	36 (1)
C(1)	9415 (13)	8322 (11)	6439 (6)	47 (4)
C(2)	10010 (14)	9264 (10)	5866 (7)	55 (4)
C(3)	8933 (17)	10249 (10)	5800 (7)	59 (4)
C(4)	8679 (17)	10862 (10)	6611 (8)	56 (5)
C(5)	7849 (16)	10217 (6)	7294 (7)	45 (4)
C(6)	10974 (12)	9339 (9)	8006 (6)	35 (3)
C(7)	11017 (14)	10156 (10)	8628 (7)	44 (4)
C(8)	12417 (16)	10447 (12)	8970 (7)	58 (4)
C(9)	13742 (16)	9934 (12)	8700 (8)	57 (5)
C(10)	13727 (14)	9113 (10)	8113 (8)	50 (4)
C(11)	12322 (14)	8818 (12)	7762 (7)	56 (4)
C(12)	7989 (13)	7916 (9)	8233 (6)	41 (3)
C(13)	7016 (14)	7144 (11)	7900 (7)	52 (4)
C(14)	6310 (15)	6397 (9)	8392 (8)	53 (4)
C(15)	6588 (16)	6407 (10)	9255 (9)	62 (5)
C(16)	7529 (20)	7193 (12)	9584 (8)	73 (6)
C(17)	8246 (16)	7942 (11)	9082 (7)	61 (4)
O	7369 (12)	8488 (9)	4118 (7)	76 (4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

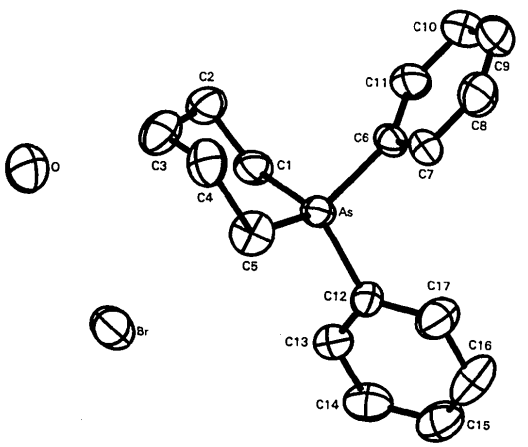


Fig. 1. The structure and numbering scheme for 1,1-diphenylarsenanium bromide monohydrate. Non-hydrogen atoms are represented as thermal ellipsoids scaled to enclose 50% probability. The hydrogen atoms are omitted for clarity.

The heterocyclic ring is in the chair form and only slightly distorted from that observed for cyclohexane. The angle between the normal to the least-squares plane through C(1), C(2), C(4) and C(5) and the normal to the plane defined by C(5), As, and C(1) is 46·9°. The angle for this same normal to the least-squares plane of C(1), C(2), C(4), C(5) with the normal to the plane C(2), C(3) and C(4) is 55·4°. For the cyclohexane structure determined by electron diffraction (Davis & Hassel, 1963), the above dihedral angles are 49·2°. Thus, the arsenic portion of the ring is slightly flattened. The Br–O distance is 3·385 (5) Å which indicates hydrogen bonding between the anion and the water molecule.

The torsion angles for the heterocyclic ring are listed in Table 3 and indicate the heterocyclic ring has near-mirror-plane symmetry. The torsion angles are quite similar to those of the phosphorus analog which are also listed in Table 3.

Table 2. *Bond lengths* (Å) *and angles* (°)

As–C(1)	1·911 (11)	As–C(5)	1·916 (10)
As–C(6)	1·902 (10)	As–C(12)	1·917 (11)
C(1)–C(2)	1·557 (17)	C(2)–C(3)	1·521 (18)
C(3)–C(4)	1·517 (17)	C(4)–C(5)	1·528 (17)
C(6)–C(7)	1·410 (16)	C(6)–C(11)	1·382 (16)
C(7)–C(8)	1·374 (18)	C(8)–C(9)	1·373 (19)
C(9)–C(10)	1·375 (18)	C(10)–C(11)	1·386 (17)
C(12)–C(13)	1·369 (17)	C(12)–C(17)	1·382 (15)
C(13)–C(14)	1·350 (17)	C(14)–C(15)	1·408 (19)
C(15)–C(16)	1·362 (20)	C(16)–C(17)	1·365 (19)

C(1)–As–C(5)	103·5 (5)	C(1)–As–C(6)	109·4 (5)
C(5)–As–C(6)	109·6 (5)	C(1)–As–C(12)	112·0 (5)
C(5)–As–C(12)	112·2 (5)	C(6)–As–C(12)	109·9 (4)
As–C(1)–C(2)	107·9 (8)	C(1)–C(2)–C(3)	114·8 (10)
C(2)–C(3)–C(4)	114·6 (10)	C(3)–C(4)–C(5)	115·6 (10)
As–C(5)–C(4)	107·6 (9)	As–C(6)–C(7)	120·0 (8)
As–C(6)–C(11)	119·8 (8)	C(7)–C(6)–C(11)	120·1 (10)
C(6)–C(7)–C(8)	119·2 (11)	C(7)–C(8)–C(9)	119·3 (12)
C(8)–C(9)–C(10)	122·7 (12)	C(9)–C(10)–C(11)	118·4 (12)
C(6)–C(11)–C(10)	120·2 (12)	As–C(12)–C(13)	120·0 (8)
As–C(12)–C(17)	119·9 (9)	C(13)–C(12)–C(17)	120·0 (11)
C(12)–C(13)–C(14)	120·7 (11)	C(13)–C(14)–C(15)	119·6 (12)
C(14)–C(15)–C(16)	119·3 (12)	C(15)–C(16)–C(17)	120·7 (12)
C(12)–C(17)–C(16)	119·6 (12)		

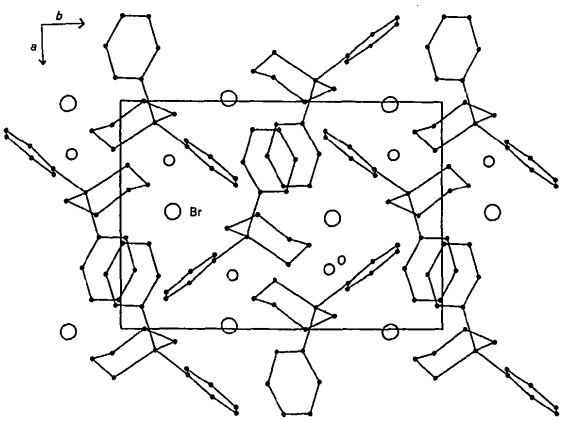


Fig. 2. Crystal structure viewed along the *c* axis.

Table 3. *Comparison of the torsion angles* (°) *in the* As *heterocyclic ring and corresponding phosphorus analog*

	X = As	X = P
X–C(1)–C(2)–C(3)	−57·1 (11)	−58·0 (9)
C(2)–C(3)–C(4)–C(5)	−64·9 (16)	−64·0 (12)
C(1)–C(2)–C(3)–C(4)	63·4 (14)	63·0 (11)
C(5)–X–C(1)–C(2)	49·1 (8)	52·2 (7)
C(4)–C(5)–X–C(1)	−49·5 (9)	−52·9 (8)
C(3)–C(4)–C(5)–X	58·5 (13)	59·6 (10)

References

BOGAARD, M. P., PETERSON, J. & RAE, A. D. (1981). *Acta Cryst.* B**37**, 1357–1359.

CAMPANA, C. F. (1981). Editor. *Nicolet P3/R3 Data Collection Manual.* Nicolet Analytical Instruments, Madison, Wisconsin.

CAMPBELL, J. A., LARSEN, R., EKELAND, R. & CREMER, S. E. (1986). *Acta Cryst.* C**42**, 251–252.

DAVIS, M. & HASSEL, O. (1963). *Acta Chem. Scand.* **17**, 1181–1184.

GALLAGHER, M. J. & JENKINS, I. D. (1968). In *Topics in Stereochemistry,* Vol. 3, edited by E. L. ELIEL & N. ALLINGER, pp. 1–96. New York: John Wiley.

GALLUCCI, J. C. & HOLMES, R. R. (1980). *J. Am. Chem. Soc.* **102**, 4379–4386.

GATILOV, YU. F., IONOV, L. B. & MOLODTSOV, S. S. (1972). *Zh. Obshch. Khim.* **42**, 1535–1538.

HAQUE, M., HORNE, W., CREMER, S. E., KREMER, D. W. & MAST, J. T. (1980). *J. Chem. Soc. Perkin Trans.* 2, pp. 1467–1472.

HAUSEN, H. D., GUDER, H. J. & SCHWARZ, W. (1977). *J. Organomet. Chem.* **132**, 37–43.

HOLMES, R. R. (1980). In *Pentacoordinated Phosphorus,* Vol. II, *ACS Monogr.* 176, ch. 2. Washington, DC: American Chemical Society.

HORNER, L. & FUCHS, H. (1963). *Tetrahedron Lett.* pp. 203–204.

HORNER, L. & HOFER, W. (1965). *Tetrahedron Lett.* pp. 3281–3285.

HORNER, L. & WINKLER, H. (1964). *Tetrahedron Lett.* pp. 3265–3269.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

SHELDRICK, G. M. (1980). Editor. *Nicolet SHELXTL Structure Determination Manual.* Nicolet Analytical Instruments, Madison, Wisconsin.

STACKHOUSE, J., COOK, R. J. & MISLOW, K. (1973). *J. Am. Chem. Soc.* **95**, 953–955.