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## The Crystal Structure of Lidocaine Hydrohexafluoroarsenate

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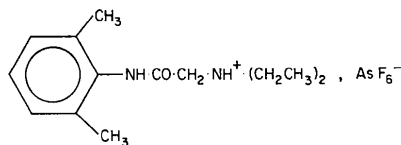
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Crystals of lidocaine (2-diethylamino-2',6'-acetoxyllidide) hydrohexafluoroarsenate,  $C_{14}H_{23}N_2OAsF_6$  are monoclinic,  $C2/c$ , with  $a=22.82$  (1),  $b=9.19$  (1),  $c=18.89$  (1) Å,  $\beta=120.79$  (6)°,  $D_m=1.58$ ,  $Z=8$ ,  $D_x=1.57$ . 2582 of a possible 3043 independent reflexions in the range  $\sin \theta/\lambda \leq 0.59$  were observed and measured diffractometrically. The crystal structure was determined by heavy-atom methods and refined by block-diagonal least-squares to a final  $R$  index of 0.044. The lidocaine moiety was found to be in the biologically active cationic form, with the amino nitrogen atom protonated. This atom is strongly hydrogen-bonded to the oxygen atom of an adjacent cation. Pairs of such bonds join pairs of cations across centres of symmetry. The amido nitrogen atom is weakly hydrogen-bonded to a fluorine atom of the hexafluoroarsenate anion.

### Introduction

It has been suggested that hydrogen bond donation is essential to the action of local anaesthetics (Sax & Pletcher, 1969). The hydrogen-bonding properties of lidocaine (2-diethylamino-2',6'-acetoxyllidide), a widely used local anaesthetic and nerve block, are thus of obvious interest. The infrared spectra of some crystalline salts of lidocaine have been studied by Neville & Regnier (1969), and one of their conclusions is that the hydrohexafluoroarsenate (I) is essentially free of hydrogen bonding. The X-ray analysis to be described is in conflict with this conclusion, demonstrating unequivocally that the amino nitrogen atom is strongly hydrogen bonded to the oxygen atom of a neighbouring cation.



### Experimental

Crystal data:  $C_{14}H_{23}N_2OAsF_6$ ; F.W. 424.3; monoclinic,  $a=22.82$  (1),  $b=9.19$  (1),  $c=19.89$  (1) Å;  $\beta=120.79$  (6)°;  $V=3583$  Å<sup>3</sup>;  $D_m=1.58$ ,  $D_x=1.57$  g.cm<sup>-3</sup>;  $Z=8$ ;  $\mu=33.6$  cm<sup>-1</sup>, (Cu  $K\alpha$ ,  $\lambda(\alpha_1)=1.54051$ ,  $\lambda(\alpha_2)=1.54433$  Å, all measurements at 20°C). Space group  $Cc$  or  $C2/c$ , from precession and Weissenberg photographs:  $C2/c$  is confirmed by the structure analysis.

The material supplied consisted of colourless needles elongated along **b**. The specimen used was a section of such a needle, 0.2 mm long. Its cross section was somewhat irregular, but was of extreme dimensions 0.15 and 0.2 mm. This was mounted on a four-circle diffractometer with **b** parallel to the  $\phi$  axis. The unit-cell parameters were measured using a narrow source and counter aperture. The axial lengths were determined from the Bragg angles of high-angle axial reflexions, and  $\beta$  from the increments in  $\phi$  for intense *a*- and *c*-axis reflexions. The relative intensities were measured in the  $\theta$ - $2\theta$  scan mode (scans of  $2^\circ$  from  $2\theta < 100^\circ$ ,  $3^\circ$  for  $2\theta \geq 100^\circ$ ) using nickel-filtered Cu  $K\alpha$  radiation with pulse-height discrimination. Background counts were measured at the beginning and end of each scan. Reflexions were considered to be unobserved if their net counts were less than 5 (deca) counts or 0.1 times the corresponding background count.

Using these criteria, 2582 of a possible 3043 reflexions were observed in the range  $2\theta \leq 130^\circ$ . Absorption corrections were not applied. However, the intense 020 reflexion, believed to be the most vulnerable to absorption error, was scanned for various rotations of the crystal about the diffraction vector. The spread between greatest and least intensities recorded in this way was found to be 8%. It was decided that the effect of absorption on the relative intensities could be ignored.

**Structure determination**

The position of the arsenic atom was deduced from a Patterson synthesis. A Fourier synthesis, phased on the contribution of the arsenic atom, indicated the positions of the remaining non-hydrogen atoms. Refinement was by block-diagonal least squares, using the program of Ahmed (Ahmed, Hall, Pippy & Huber, 1966). The quantity minimized was  $\sum w\Delta F^2$ , and the weighting scheme (chosen to give reasonable constancy of  $w\Delta F^2$  with  $F_o$  and  $\sin^2\theta$ ) was  $w = w_1 w_2$ , where

$$w_1 = F_o/40 \text{ for } F_o \leq 40$$

$$= 40/F_o \text{ for } F_o > 40$$

$$w_2 = 2 \sin^2\theta \text{ for } \sin^2\theta < 0.5$$

$$= 1 \text{ for } \sin^2\theta \geq 0.5.$$

(The nominal threshold value of  $F_o$  was 10.0.) The scattering factor curves used were those of Stewart, Davidson & Simpson (1965) for hydrogen and of Hanson, Herman, Lea & Skillman (1964) for the other atoms. The curve for arsenic was corrected for the real part of the anomalous scattering ( $\Delta f' = -1.2 e$ ). The hydrogen atoms were located from a difference synthesis, and their parameters (assuming isotropic thermal motion) were refined in subsequent cycles. The thermal parameters of the non-hydrogen atoms were allowed to vary anisotropically. The effect of extinction was detected by the method of Pinnock, Taylor & Lipson (1956), and an appropriate correction was applied to the 35 strongest reflexions. The amplitude of the strongest was thereby increased by 50%, that of another by 26%, and the amplitudes of the rest by 2 to 19%. (As the weighting scheme discriminates strongly against the intense, low-angle reflexions, the practical effect of this correction is rather small.) During refinement it was observed that the calculated amplitudes for sixteen rather weak reflexions were persistently below their estimated threshold values, and these reflexions were arbitrarily assigned zero weight. In the final cycle of refinement, no coordinate shift exceeded 17% of the corresponding e.s.d. The final parameters are given in Table 1.

**Assessment of analysis**

The agreement between observed and calculated structure amplitudes (Table 2) is satisfactory, and there can be no doubt of the essential correctness of the proposed structure. The final agreement residual ( $R = \sum |\Delta F| / \sum |F_o|$ ) is 0.044, for observed reflexions only. There are in the residual electron-density distribution some troughs and peaks of maximum amplitude  $0.6 e.\text{\AA}^{-3}$ . These occur in the neighbourhood of the fluorine atoms, and may result from anharmonicity of the very severe thermal motion of these atoms. Elsewhere the residual density lies between the limits  $\pm 0.2 e.\text{\AA}^{-3}$ . Chemically equivalent distances in the organic cation do not differ significantly. However, the thermal motion of the structure (specified in Table 1 and Fig. 1) is severe, and the resulting systematic errors in bond

Table 1. Final atomic parameters and their e.s.d.'s

Quantities given are: fractional coordinates  $\times 10^5$  for non-hydrogen,  $\times 10^3$  for hydrogen atoms [equivalent positions (0, 0, 0);  $\frac{1}{2}, \frac{1}{2}, 0 \pm (x, y, z); x, \bar{y}, \frac{1}{2} + z]$ ;  $U_{ij} \times 10^4 \text{ \AA}^2$  for non-hydrogen atoms:  
 $T.F. = \exp [-2\pi^2(U_{11}a^*2h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$ ;  
 R.m.s. displacements  $D_i$  along principal axes of vibration ellipsoids, in  $\text{\AA}$ ; isotropic Debye-Waller factors  $B$ , in  $\text{\AA}^2$ .

Atom	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>	B	
										eq	max
C(1)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(2)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(3)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(4)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(5)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(6)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(7)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(8)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(9)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(10)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(11)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(12)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(13)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(14)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(15)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(16)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(17)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(18)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(19)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(20)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(21)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(22)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(23)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(24)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(25)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(26)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(27)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(28)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(29)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(30)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(31)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(32)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(33)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(34)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(35)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(36)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(37)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(38)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(39)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(40)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(41)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(42)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(43)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(44)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(45)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(46)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(47)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(48)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(49)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(50)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(51)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(52)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(53)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(54)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(55)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(56)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(57)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(58)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(59)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(60)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(61)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(62)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(63)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(64)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(65)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(66)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(67)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(68)	4307(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15
C(69)	4311(1)	370(1)	301(1)	0.011(1)	0.011(1)	0.011(1)	0.000(1)	0.000(1)	0.000(1)	0.15	0.15







errors are indeterminate. In view of the severity of the thermal motion – the maximum amplitude of libration is  $13.6^\circ$  – the errors may also be substantial.

Table 3. *Rigid-body thermal parameters*

(a) Atoms C(1)–C(8)

$$T(\sigma T) = \begin{pmatrix} 318 (13) & -76 (12) & -30 (11) \\ & 413 (14) & 91 (11) \\ & & 439 (11) \end{pmatrix} \times 10^{-4} \text{Å}^2$$

$$L(\sigma L) = \begin{pmatrix} 214 (18) & & & \\ & 7(18) & & 33 (20) \\ & 144 (3) & & -9 (24) \\ & & & 144 (22) \end{pmatrix} \times 10^{-1} (^\circ)^2$$

Unique origin 5.19, 3.52, 8.68 Å  
Position of C(1) 4.73, 3.46, 8.57 Å

Principal axes of T:

Eigenvalue	Direction cosines		
0.054 Å <sup>2</sup>	0.316	-0.665	-0.677
0.036	0.474	-0.507	0.720
0.027	0.822	0.548	-0.155

Principal axes of L:

Eigenvalue	Direction cosines		
22.7(°) <sup>2</sup>	0.929	0.038	0.369
15.0	0.156	0.861	-0.484
12.4	0.336	-0.506	-0.794

R.m.s. discrepancy between obs. and calc.  $U_{ij}$ : 0.002 Å<sup>2</sup>.

(b) Hexafluoroarsenate anion

$$T(\sigma T) = \begin{pmatrix} 539 (21) & & & \\ & 4 (19) & & -10 (19) \\ & 453 (23) & & -1 (18) \\ & & & 422 (22) \end{pmatrix} \times 10^{-4} \text{Å}^2$$

$$L(\sigma L) = \begin{pmatrix} 747 (40) & & & \\ & -308 (36) & & 198 (39) \\ & 1290 (4) & & 395 (28) \\ & & & 1562 (41) \end{pmatrix} \times 10^{-1} (^\circ)^2$$

Unique origin 4.40, 3.66, 3.35 Å  
Position of As 4.41, 3.53, 3.08 Å

Principal axes of T:

Eigenvalue	Direction cosines		
0.054 Å <sup>2</sup>	0.995	0.044	-0.086
0.045	0.044	-0.999	0.009
0.042	0.086	0.013	0.996

Principal axes of L:

Eigenvalue	Direction cosines		
184.4(°) <sup>2</sup>	0.018†	-0.587†	-0.809†
126.6	0.576	-0.656	0.489
48.9	0.818	0.475	-0.326

R.m.s. discrepancy between obs. and calc.  $U_{ij}$ : 0.003 Å<sup>2</sup>.

All positions and directions in this table are referred to the orthogonal axes  $x' \parallel \mathbf{a}$ ,  $y' \parallel \mathbf{b}$ ,  $z' \parallel \mathbf{c}^*$

†8° from vector  $\overrightarrow{\text{As}-\text{F}(1)}$ .

### Discussion

In this complex the lidocaine moiety is found to be in the physiologically active cationic form, with the amino nitrogen atom [N(13)] protonated. The conformation is illustrated in Figs. 1 and 2, and the planarity of some parts is specified in Table 4. The phenyl ring is planar, and the attached nitrogen and methyl carbon atoms lie close to its plane. The side chain from

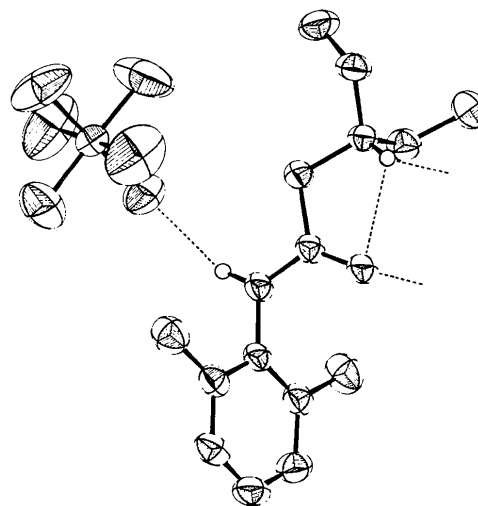


Fig. 1. Thermal motion ellipsoids of 50% probability. The hydrogen atoms involved in hydrogen bonding are shown as spheres.

N(9) to C(12) lies in a plane which is inclined at  $66^\circ$  to that of the ring. N(13) and H(131) lie quite close to this plane, an arrangement which appears to be stabilized by intramolecular hydrogen bonding [N(13)⋯O(11) = 2.682 (4) Å; H(131)⋯O(11) = 2.30 (4) Å; N(13)–H(131)–O(11) = 104 (3)°]. The configuration is not particularly favourable for hydrogen bonding, as the angle between C(10)–O(11) and O(11)⋯H(131) is only  $83^\circ$ . However, a weak bond is presumably better than none; if significant repulsion were involved it could readily be relieved by rotation about C(10)–C(12) or C(12)–N(13). H(131) participates also in a strong intermolecular hydrogen bond [N(13)⋯O(11') = 2.822 (4) Å, H(131)⋯O(11') = 1.96 (4) Å; N(13)–H(131)–O(11') = 160 (3)°]. Pairs of such bonds link adjacent cations across a centre of symmetry, as shown in Fig. 2. It is this conclusion which is in conflict with that of the infra-red study. In addition, the amido nitrogen atom [N(9)] is weakly hydrogen-bonded to F(1) of the anion [N(9)⋯F(1) = 3.040 (5) Å, H(91)⋯F(1) = 2.24 (5) Å, N(9)–H(91)–F(1) = 156 (3)°]. This conclusion is supported by the nature of the thermal motion

Table 4. *Mean planes of some parts of the lidocaine moiety, and the distances of some atoms therefrom*

(a) Benzene ring [C(1) to C(6)]:  $0.601x' + 0.693y' + 0.398z' - 1.837 = 0$

Distances (Å × 10<sup>3</sup>): C(1), 2; C(2), -2; C(3), 0; C(4), 2; C(5), -2; C(6), 0; C(7), 13; C(8), 32; N(9), 36.

(b) N(9) to C(12):  $0.214x' - 0.932y' - 0.292z' + 4.852 = 0$

Distances (Å × 10<sup>3</sup>): C(1), 138; N(9), 2; H(91), 7; C(10), -5; O(11), 2; C(12), 2; N(13), -300; H(131), 104.

The angle between planes (a) and (b) is  $66^\circ$ . Orthogonal coordinate system defined as in Table 3.

of the anion which is, as we have seen, consistent with rigid-body libration constrained at F(1). There is no

Table 5. Distances and angles involving the lidocaine cation. Values in square brackets have been corrected for thermal libration

		Distance (Å)	Mean (Å)
C(1)	C(2)	1.386 (5)	1.390 [1.398]
		[1.394]	
C(1)	C(6)	1.394 (5)	
		[1.401]	
C(2)	C(3)	1.396 (6)	1.395 [1.401]
		[1.402]	
C(5)	C(6)	1.394 (6)	
		[1.400]	
C(3)	C(4)	1.376 (6)	1.370 [1.376]
		[1.382]	
C(4)	C(5)	1.364 (6)	
		[1.371]	
C(2)	C(8)	1.505 (7)	1.500 [1.505]
		[1.510]	
C(6)	C(7)	1.494 (6)	
		[1.499]	
C(1)	N(9)	1.437 (5)	1.505 1.497
N(9)	C(10)	1.331 (5)	
C(10)	O(11)	1.214 (4)	
C(10)	C(12)	1.519 (5)	
C(12)	N(13)	1.490 (5)	
N(13)	C(14)	1.503 (5)	
N(13)	C(16)	1.507 (5)	
C(14)	C(15)	1.497 (7)	
C(16)	C(17)	1.496 (6)	
N(9)	H(91)	0.85 (5)	
N(9)	F(1)	3.040 (5)	
H(91)	F(1)	2.24 (5)	
N(13)	H(131)	0.89 (4)	
O(11)	H(131)	2.30 (4)	
O(11)	N(13)	2.682 (4)	
O(11)	N(13')	2.822 (4)	
O(11)	H(131')	1.96 (4)	

The C-H distances range from 0.90 to 1.07 Å

			Angle (°)
C(6)	C(1)	C(2)	122.3 (3)
C(2)	C(1)	N(9)	119.6 (3)
C(6)	C(1)	N(9)	118.1 (3)
C(1)	C(2)	C(3)	117.7 (4)
C(5)	C(6)	C(1)	117.6 (3)
C(2)	C(3)	C(4)	120.4 (4)
C(4)	C(5)	C(6)	121.2 (4)
C(1)	C(2)	C(8)	122.0 (4)
C(1)	C(6)	C(7)	121.8 (4)
C(3)	C(4)	C(5)	120.4 (4)
C(1)	N(9)	C(10)	122.8 (3)
N(9)	C(10)	O(11)	124.3 (3)
N(9)	C(10)	C(12)	114.8 (3)
O(11)	C(10)	C(12)	120.9 (3)
C(10)	C(12)	N(13)	109.6 (3)
C(12)	N(13)	C(14)	111.8 (3)
C(12)	N(13)	C(16)	111.7 (3)
C(14)	N(13)	C(16)	113.6 (3)
N(13)	C(14)	C(15)	113.9 (3)
N(13)	C(16)	C(17)	113.3 (3)
N(9)	H(91)	F(1)	156 (3)
N(13)	H(131)	O(11)	104 (3)
C(10)	O(11)	H(131)	83 (2)
N(13)	H(131)	O(11')	160 (3)

obvious way in which such a constraint could be applied, other than by the hydrogen bond. Apart from the hydrogen bonds specified, contacts between ions are consistent with van der Waals interaction. Minimum values are: F...H, 2.59; O...H, 2.60; H...H, 2.49 Å.

Bond lengths and angles for the lidocaine cation are given in Table 5. Although the distances may be significantly underestimated as a result of thermal motion, all values appear to be consistent with the assumed formulation.

The configuration of the hexafluoroarsenate anion is nominally octahedral, with no angle deviating by more than 3° from the ideal value of 90 or 180°. As indicated in Table 6, however, the As-F distances vary appreciably. This is undoubtedly a result of the very severe thermal motion of the anion. Corrections for rigid-body motion have been applied, but without much improvement in consistency. However, it seems unlikely that the anion is entirely rigid. Distances corrected for riding motion (Busing & Levy, 1964) are given also, chiefly to indicate the magnitude of possible systematic errors. It is clear that a reliable value for the As-F distance is not given by this analysis. Similar severe thermal motion has been observed in other structures for the hexafluoride anions of arsenic and other group VA elements (Calleri & Speakman, 1969; Copeland, Connor & Meyers, 1966; Davis & Ibers, 1970; Roof, 1955). Lower temperatures are obviously required for the accurate study of these anions.

Table 6. Bond distances in hexafluoroarsenate anion

	Uncorrected length	Corrected 'rigid-body'	Corrected 'riding motion'
As-F(1)	1.705 (3) Å	1.732 Å	1.732 Å
As-F(2)	1.695 (3)	1.723	1.758
As-F(3)	1.687 (5)	1.716	1.757
As-F(4)	1.696 (5)	1.739	1.764
As-F(5)	1.697 (4)	1.734	1.771
As-F(6)	1.673 (4)	1.713	1.747

In the interpretation of the infrared spectrum a sharp band at 3367 cm<sup>-1</sup> is assigned to the stretching vibration of the N<sup>+</sup>-H group (Neville & Regnier,

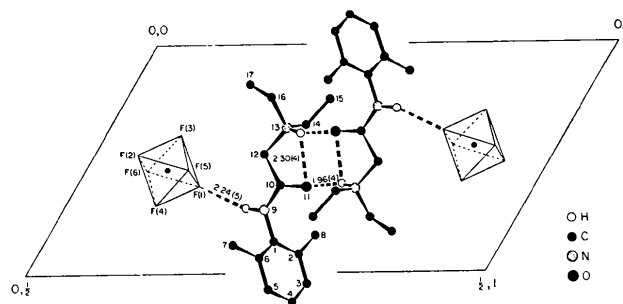


Fig. 2. A part of the structure viewed along *b*, showing hydrogen bonding. The only hydrogen atoms shown are those which participate in hydrogen bonding.

1969). In retrospect it is clear that this band should instead be assigned to the N-H group which is, as we have seen, weakly bonded to a fluorine atom. In Table 7 it is shown that the N...F distance and N-H stretching frequency fit very well into the approximately linear relationship demonstrated by Nakamoto, Margoshes & Rundle (1955). This N-H...F bond must, incidentally, be one of the weakest ever reported, and yet its authenticity seems assured. It does not seem possible to identify the band corresponding to N<sup>+</sup>-H stretching. It should presumably be rather broad, and may be lost in the region of C-H stretching.

Table 7. Bond distance and stretching frequency for N-H...F bonds

(Adapted from Nakamoto, Margoshes & Rundle, 1955). Non-bonded N-H frequency, 3400 cm<sup>-1</sup>.

	Bond distance	Stretching frequency	$\Delta\nu$
N <sub>2</sub> H <sub>4</sub> .2HF	2.62 (2) Å	2548 cm <sup>-1</sup>	852 cm <sup>-1</sup>
NH <sub>4</sub> HF <sub>2</sub>	2.80 (3)	2910	490
NH <sub>3</sub> BF <sub>3</sub>	3.01 (3)	3338	62
This work	3.040 (5)	3367	33

Computer programs used in this work are those of Ahmed, Hall, Pippy & Huber (1966), Gantzel & Trueblood (*MGTLS*, thermal motion analysis) and C. K. Johnson (*ORTEP*, thermal ellipsoid plot). The specimen material was supplied by Dr G. A. Neville, with

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## The Crystal Structure of Strontium Di-iodate(V) Monohydrate

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The crystals of strontium di-iodate(V) monohydrate, Sr(IO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O, are monoclinic, with unit-cell constants  $a=13.156$  (16),  $b=7.741$  (6),  $c=8.914$  (15) Å,  $\beta=132.9$  (3)°, space group *C2/c* and  $Z=4$ . The structure consists of pyramidal anions IO<sub>3</sub><sup>-</sup> with bond distances I-O=1.786, 1.806 and 1.825 Å, of Sr<sup>2+</sup> cations and of water molecules. The environment of each iodine atom is completed by four oxygen atoms of three different pyramidal anions and the resulting coordination polyhedron can be described as a distorted pentagonal bipyramid. Sr<sup>2+</sup> cations are surrounded by nine oxygen atoms (one from the water molecule): the coordination polyhedron is a trigonal prism with non-basal faces centred. The bond distances Sr-O are in the range 2.531–3.136 Å.

### Introduction

In connexion with researches on salts of oxyacids of iodine(V) and iodine(VII), the crystal structure of strontium diiodate(V) monohydrate, Sr(IO<sub>3</sub>)<sub>2</sub>.H<sub>2</sub>O, has been determined by X-ray diffraction methods.

### Experimental

#### Preparation

The crystals were prepared in the form of stable, shiny, colourless prisms by concentrating solutions obtained by dissolving strontium carbonate in aqueous iodic acid.