

References

- ANDRETTI, G. D., CAVALCA, L. & MUSATTI, A. (1968). *Acta Cryst.* **B24**, 683.
- BIAGINI CINGI, M., DOMIANO, P., GUASTINI, C., MUSATTI, A. & NARDELLI, M. (1971). *Gazz. Chim. Ital.* **101**, 455.
- CAVALCA, L., FAVA, G., ANDRETTI, G. D. & DOMIANO, P. (1967). *Acta Cryst.* **22**, 90.
- CAVALCA, L., NARDELLI, M. & BRANCHI, G. (1960). *Acta Cryst.* **13**, 688.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321.
- CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
- CRUICKSHANK, D. W. J. (1950). *Acta Cryst.* **3**, 72.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
- FERRARI, A., BRAIBANTI, A., BIGLIARDI, G. & LANFREDI, A. M. (1965). *Acta Cryst.* **19**, 548.
- GHOSE, S. (1964). *Acta Cryst.* **17**, 1051.
- KUNCHUR, N. R. & TRUTER, M. R. (1958). *J. Chem. Soc.* p. 3478.
- LUNDBERG, B. K. S. (1966). *Acta Cryst.* **21**, 901.
- MONTGOMERY, H. & LINGAFELTER, E. C. (1964). *Acta Cryst.* **17**, 1295.
- NARDELLI, M. & FAVA, G. (1960). *Ric. Sci.* **30**, 898.
- NARDELLI, M., FAVA, G., BOLDRINI, P. & GIRALDI BATTISTINI, G. (1965). *Acta Cryst.* **19**, 491.
- NARDELLI, M., FAVA, G. & GIRALDI, G. (1963). *Acta Cryst.* **16**, 343.
- NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDRETTI, G. (1964). *Ric. Sci.* **34**, II-A, 711.
- NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDRETTI, G. D. (1965). *Ric. Sci.* **35**, II-A, 469, 477 & 807.
- ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
- VIJAYAN, M. & VISWAMITRA, M. A. (1966). *Acta Cryst.* **21**, 522.
- VIJAYAN, M. & VISWAMITRA, M. A. (1967). *Acta Cryst.* **23**, 1000.
- VIJAYAN, M. & VISWAMITRA, M. A. (1968). *Acta Cryst.* **B24**, 1067.
- WIESNER, J. R., SRIVASTAVA, R. C., KENNARD, C. H. L., DI VAIRA, M. & LINGAFELTER, E. C. (1967). *Acta Cryst.* **23**, 565.

Acta Cryst. (1972), **B28**, 672

The Crystal Structure of Lidocaine Hydrohexafluoroarsenate

BY A. W. HANSON

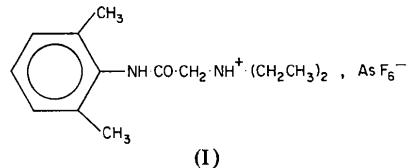
Biochemistry Laboratory, National Research Council of Canada, Ottawa, Canada K1A OR6

(Received 15 June 1971)

Crystals of lidocaine (2-diethylamino-2',6'-acetoxylidide) 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'-acetoxylidide), 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), $c=18.89$ (1) Å; $\beta=120.79$ (6)°; $V=3583$ Å³; $D_m=1.58$, $D_x=1.57$ g.cm⁻³; $Z=8$; $\mu=33.6$ cm⁻¹, ($Cu K\alpha$, $\lambda(\alpha_1)=1.54051$, $\lambda(\alpha_2)=1.54433$ 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 φ 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 β from the increments in φ for intense *a*- and *c*-axis reflexions. The relative intensities were measured in the θ - 2θ scan mode (scans of 2° from $2\theta < 100^\circ$, 3° 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

$$\begin{aligned} w_1 &= F_o/40 \text{ for } F_o \leq 40 \\ &= 40/F_o \text{ for } F_o > 40 \\ w_2 &= 2 \sin^2\theta \text{ for } \sin^2\theta < 0.5 \\ &= 1 \text{ for } \sin^2\theta \geq 0.5. \end{aligned}$$

(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. \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 ± 0.2 e. \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 \AA ; isotropic Debye-Waller factors B , in \AA^2 .

Table 2. Observed and calculated structure amplitudes, $\times 10$

An asterisk denotes the threshold value of an unobserved reflexion. A minus sign preceding $10 F_0$ means that the reflexion was omitted from the refinement.

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC						
H+	0	L+	H+	20	L+	0	H+	7	68*	-65*	H+	21	L+	1	H+	8	-6	-2	H+	6	812	629	H+	7	L+	3						
2	880	902	0	663	-630	H+	9	L+	-1	H+	1	142	116	0	676	677	H+	18	L+	2	1	87*	839	H+	18	L+	3					
1	1289	-1300	2	290	-254	H+	4	324	-304	H+	3	78*	80	2	1456	1521	H+	20	L+	2	3	200	176	H+	3	374	-370					
8	443	-443	0	1291	-1383	H+	21	L+	0	H+	4	180	-149	1	167	131	H+	7	287	267	5	239	210	H+	6	265	252					
8	672	688	5	926	968	H+	21	L+	1	H+	2	141	-116	9	88*	88	H+	18	L+	2	9	88*	85	H+	10	213	229					
H+	1	L+	H+	1	89*	80	7	833	823	H+	1	93*	35	10	147	153	H+	19	L+	2	2	1020	1024	H+	7	317	311					
H+	2	L+	H+	3	83*	-80	9	209	-202	H+	3	123	151	H+	9	91	L+	2	4	217	242	H+	2	110	240							
1	1229	1143	2	22	L+	0	H+	10	101	L+	H+	22	L+	1	H+	1	166	-153	H+	3	271	-264	H+	3	197	190						
3	527	-549	0	122	L+	0	H+	10	101	L+	H+	22	L+	1	171	-162	H+	19	L+	3	5	420	-429	H+	17	L+	4					
5	109	-108	0	471	433	2	430	-414	2	426	415	3	808	-36	5	370	375	7	750	752	H+	9	107	106								
9	98*	55	2	191	165	2	733	730	H+	22	L+	-1	H+	9	177	-182	H+	2	220	210	3	209	276	H+	7	131	-104					
H+	2	L+	H+	0	101	L+	0	8	93	89	H+	2	354	-362	C	88*	-16	H+	8	L+	3	3	428	-356	H+	18	L+	4				
0	330	-456	2	3400	3784	H+	10	L+	-1	H+	23	L+	-1	H+	9	92	-2	2	830	-813	H+	19	L+	3								
0	592	-675	4	331	391	2	763	-750	1	644	-688	2	204	-201	2	101	140	5	566	563	H+	18	L+	5								
4	1394	1456	0	1822	-1320	2	763	-750	H+	10	101	L+	2	1118	1311	5	222	-195	0	409	-395	H+	18	L+	5							
8	166	-163	10	325	337	6	399	378	H+	0	101	L+	1	107	-88	6	100	135	7	285	-279	H+	2	210	226							
10	344	-340	8	144	-138	H+	0	101	L+	1	101	-101	7	481	-411	8	308	294	H+	8	181	-181										
H+	3	L+	H+	1	11*	L+	1	11*	11*	2	686	-221	4	460	-473	2	1131	-1139	H+	20	L+	3	0	548	619	H+	18	L+	5			
H+	3	151	0	1*	33*	8	81	717	-781	2	701	-656	6	75	-6	4	233	-237	H+	19	L+	2	0	500	-76	H+	18	L+	5			
3	985	1011	9	407	-421	3	1159	-1109	2	600	278	5	194	-190	9	810	-814	3	290	316	H+	12	L+	4								
5	335	422	7	93	93	3	391	309	8	268	-269	2	288	-311	8	166	166	H+	20	L+	3	8	345	340	H+	19	L+	5				
9	137	-128	9	97*	-111	10	177	-171	10	87	-88	6	282	258	1	113	-126	H+	9	94	-95	6	169	155	H+	18	L+	5				
H+	4	L+	H+	1	11*	L+	1	11*	11*	2	686	-221	3	308	294	H+	8	181	-181	0	1819	-1852	H+	18	L+	5						
H+	5	L+	H+	11	L+	1	H+	10	101	L+	2	675	-646	2	1131	-1139	2	80	284	H+	20	L+	3	0	578	592	H+	18	L+	5		
0	2339	2280	3	275	280	1	1177	1249	5	851	-863	H+	10	101	L+	2	1146	-1149	5	140	124	H+	20	L+	3	0	529	-568	H+	18	L+	5
2	462	-469	7	405	424	9	636	-659	2	747	-244	0	602	663	H+	21	L+	2	8	166	166	H+	20	L+	3							
6	732	-729	9	98*	-35	7	441	-461	9	163	150	4	495	455	H+	22	L+	2	2	357	-352	H+	7	181	-175							
10	132	116	H+	2	121	L+	1	H+	11	101	L+	2	610	-608	2	1113	-1126	H+	9	169	155	H+	18	L+	5							
H+	5	L+	H+	12	L+	1	H+	11	101	L+	2	675	-646	2	1120	-205	H+	11	101	L+	2	1	302	-293	H+	20	L+	3				
H+	6	L+	H+	2	214	-250	H+	12	L+	1	1-389	-234	H+	11	101	L+	2	1-248	-249	3	83	82	H+	21	L+	3						
1	1643	1553	6	1257	1328	1	182	-211	5	303	328	1	580	-501	H+	23	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
5	140	-103	10	181	-179	8	88*	-85	9	258	-264	5	610	-608	H+	24	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
7	397	384	9	160	160	H+	2	121	L+	1	H+	1	1-21	-21	0	191	195	H+	23	L+	2	1-202	-205	H+	18	L+	5					
H+	6	L+	H+	2	214	-250	H+	12	L+	1	1-389	-234	H+	11	101	L+	2	1-248	-249	3	83	82	H+	21	L+	3						
H+	7	T+	H+	1	226	220	1	1177	1249	5	851	-863	H+	10	101	L+	2	1-246	-249	5	140	124	H+	20	L+	3						
2	240	-247	0	155	155	2	240	-247	0	155	155	0	155	-165	H+	21	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
6	302	-298	6	130	130	H+	13	L+	1	1-92	-95	2	107	-87	2	808	-867	H+	22	L+	2	1-246	-249	H+	18	L+	5					
12	154	-129	1	150	-173	3	603	631	H+	12	L+	1	1-21	-21	0	191	195	H+	23	L+	2	1-202	-205	H+	18	L+	5					
H+	7	T+	H+	1	226	220	1	1177	1249	5	851	-863	H+	10	101	L+	2	1-246	-249	5	140	124	H+	20	L+	3						
3	340	339	2	245	-251	3	631	-646	2	747	-244	0	1100	-1105	H+	24	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
1	1108	-1153	7	619	-622	H+	13	L+	1	1-86	-816	2	820	-818	H+	25	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
3	342	295	8	619	-622	H+	13	L+	1	1-86	-816	2	820	-818	H+	25	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
7	629	-596	5	316	318	H+	3	L+	1	1-92	-95	2	808	-867	H+	26	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
9	311	-318	0	153	153	H+	13	L+	1	1-92	-95	2	808	-867	H+	27	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
H+	8	B+	H+	1	198	98*	7	833	198	H+	3	126	-122	0	101	101	H+	14	L+	2	1-246	-249	5	140	124	H+	20	L+	3			
0	855	-876	2	253	-267	9	75	-17	2	121	-127	0	101	101	H+	15	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
2	267	-297	2	130	124	H+	14	L+	1	1-92	-95	2	808	-867	H+	16	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
4	207	-224	10	103	103	H+	14	L+	1	1-92	-95	2	808	-867	H+	17	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
8	176	-170	8	104	107	H+	15	L+	1	1-92	-95	2	808	-867	H+	18	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
4	85*	63	H+	5	546	541	2	1108	-1094	7	359	-341	2	747	-244	H+	19	L+	2	1-246	-249	5	140	124	H+	20	L+	3				
0	193	-175	3	321	320	H+	14	L+	1	1-86	-816	2	808	-867	H+	20	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
3	104*	88	1	150*	88	H+	15	L+	1	1-86	-816	2	808	-867	H+	21	L+	2	1-246	-249	5	140	124	H+	20	L+	3					
8	122	-121	2	855	-864	2	760	771	9	94	100	H+	16	L+	2	1-246	-249	5	140	124	H+	20	L+	3								
1	823	-823	4	723	-737	4	93	-37	2	808	-867	H+	17	L+	2	1-246	-249	5	140	124	H+	20	L+	3								
H+	13	L+	H+	1	205	-103	4	808	-37	H+	17	L+	2	1-246	-249	H+	18	L+	2	1-246	-249	H+	18	L+	5							
H+	13	L+	H+	1	205	-103	4	808	-37	H+	17	L+	2	1-246	-249	H+	18	L+	2	1-246	-249	H+	18	L+	5							
H+	13	L+	H+	1	205	-103	4	808	-37	H+	17	L+	2	1-246	-249	H+	18	L+	2	1-246	-249	H+	18	L+	5							
H+	13	L+	H+	1	205	-103	4	808	-37	H+	17	L+	2	1-246	-249	H+	18	L+	2	1-246	-249	H+	18	L+	5							
H+	13	L+	H+	1	205	-103	4	808	-37	H+	17	L+	2	1-246	-249	H+	18	L+	2	1-246	-249	H+	18	L+	5							
H+	13	L+	H+	1	205	-103	4	808	-37	H+	17	L+	2	1-246	-249	H+	18	L+	2	1-246	-249	H+	18	L+	5							
H+	13	L+	H+	1	205	-103	4	808	-37	H+	17	L+	2	1-246	-249	H+	18	L+	2	1-246	-249											

Table 2 (cont.)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
Hm - 5, L ₁ -6	5 440 451	5 459 -451	Hm 16, L ₁ -7	2 88 ^a -15	Hm 17, L ₁ -8	6 95 ^a -76	1 29 ^a -307	2 76 ^a -27	Hm 23, L ₁ -10	1 239 -244	1 101 101	7 215 -188														
3 1162 -1227	7 141 -110	7 852 -843	2 666 855	4 731 -698	Hm 17, L ₁ -8	8 185 -188	3 98 ^a -115	2 1367 1404	3 223 224	3 86 ^a -19	Hm 3, L ₁ -12															
3 330 326	Hm 16, L ₁ -6	9 809 -77	4 224 236	6 142 130	1 92 ^a -1	Hm 7, L ₁ -9	5 90 ^a -22	8 321 -313																		
9 149 -128			1 345 -353	8 140 -155	Hm 6, L ₁ -8	3 332 -143	1 606 623	Hm 9, L ₁ -10																		
9 152 137	0 449 -652	1 345 -353	1 148 155	4 230 -227	Hm 18, L ₁ -8	5 99 ^a -19	4 61 ^a -6	1 133 116	2 75 ^a -37	3 240 -263	7 97 ^a -98															
Hm - 6, L ₁ -6	4 266 272	5 933 -977	Hm 17, L ₁ -7	0 60 ^a -9	Hm 18, L ₁ -8	2 362 -223	Hm 18, L ₁ -8	5 151 -40	Hm 9, L ₁ -10	1 133 118	Hm 26, L ₁ -10	1 11, L ₁ -11	1 067 604													
0 431 -222	Hm 16, L ₁ -6	7 179 145	1 148 155	4 230 -227	Hm 17, L ₁ -7	0 60 ^a -9	0 1140 -1191	Hm 7, L ₁ -9	Hm 23, L ₁ -9	Hm 9, L ₁ -10	2 286 -283	0 556 -555														
6 292 -316	0 380 -391	9 934 -44	Hm 17, L ₁ -7	1 328 -306	Hm 7, L ₁ -8	4 329 321	1 106 -73	1 113 118	Hm 29, 269	6 133 101	2 319 -281															
6 374 -546	2 190 -40	Hm 6, L ₁ -7	4 92 ^a -47	9 99 ^a -61	Hm 16, L ₁ -7	0 164 -157	5 562 569	5 161 -171	5 455 -440	8 80 ^a -37	2 403 411	6 231 -241														
Hm - 6, L ₁ -6	8 170 -170	6 98 ^a -80	2 527 -527	3 248 -244	Hm 7, L ₁ -8	4 97 ^a -55	Hm 19, L ₁ -9	5 98 ^a -55	Hm 24, L ₁ -9	7 235 215	Hm 1, L ₁ -11	Hm 12, L ₁ -11	Hm 4, L ₁ -12													
0 66 26	Hm 17, L ₁ -6	8 114 -114	Hm 18, L ₁ -7	3 94 ^a -85	Hm 19, L ₁ -8	5 94 ^a -85	Hm 19, L ₁ -9	5 98 ^a -55	Hm 24, L ₁ -9	7 235 215	Hm 1, L ₁ -11	Hm 12, L ₁ -11	Hm 4, L ₁ -12													
2 864 -842	1 05 84	Hm 6, L ₁ -7	7 137 101	2 679 -677	Hm 18, L ₁ -7	0 170 -103	5 287 -270	2 1070 -1059	Hm 10, L ₁ -10	3 147 -142	4 189 158	0 1642 1618														
6 408 -402	3 88 -55	Hm 17, L ₁ -6	2 824 819	4 99 ^a -91	Hm 7, L ₁ -8	7 82 ^a -47	4 140 -143	Hm 25, L ₁ -9	0 772 -777	7 584 578	8 161 -166	4 1021 -1022														
10 224 -250	Hm 17, L ₁ -6	2 868 305	Hm 8, L ₁ -8	2 744 -244	Hm 20, L ₁ -7	1 60 ^a -20	Hm 20, L ₁ -8	1 443 -456	Hm 25, L ₁ -9	8 371 358	Hm 1, L ₁ -11	Hm 11, L ₁ -11	Hm 5, L ₁ -12													
Hm - 7, L ₁ -6	1 962 980	8 108 -113	Hm 19, L ₁ -7	2 662 -299	Hm 21, L ₁ -7	3 111 -117	Hm 21, L ₁ -8	2 662 -299	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
1 112 -759	5 479 -486	Hm 18, L ₁ -6	1 250 212	3 716 743	Hm 21, L ₁ -7	3 111 -117	Hm 21, L ₁ -8	2 662 -299	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
3 886 846	7 202 727	Hm 17, L ₁ -7	3 716 743	4 286 -302	Hm 21, L ₁ -7	3 111 -117	Hm 21, L ₁ -8	2 662 -299	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
9 586 -565	Hm 18, L ₁ -6	3 691 -726	Hm 21, L ₁ -7	3 112 -118	Hm 21, L ₁ -8	2 662 -299	Hm 21, L ₁ -9	1 724 -749	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
9 446 -243	0 387 397	2 307 307	Hm 20, L ₁ -7	3 134 -136	Hm 21, L ₁ -8	2 662 -299	Hm 21, L ₁ -9	1 724 -749	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
Hm - 7, L ₁ -6	2 70+ 64	3 398 398	Hm 20, L ₁ -7	3 134 -136	Hm 21, L ₁ -8	2 662 -299	Hm 21, L ₁ -9	1 724 -749	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
1 1291 -1273	Hm 18, L ₁ -6	Hm 7, L ₁ -7	2 702 711	4 560 560	Hm 21, L ₁ -7	3 134 -136	Hm 21, L ₁ -8	2 662 -299	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
3 1235 1258	Hm 18, L ₁ -6	4 565 565	Hm 21, L ₁ -7	3 134 -136	Hm 21, L ₁ -8	2 662 -299	Hm 21, L ₁ -9	1 724 -749	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
5 416 -396	0 476 482	1 677 664	Hm 21, L ₁ -7	3 134 -136	Hm 21, L ₁ -8	2 662 -299	Hm 21, L ₁ -9	1 724 -749	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
7 779 -779	0 476 482	1 677 664	Hm 21, L ₁ -7	3 134 -136	Hm 21, L ₁ -8	2 662 -299	Hm 21, L ₁ -9	1 724 -749	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
9 202 -202	4 727 -744	6 905 -905	Hm 21, L ₁ -7	3 134 -136	Hm 21, L ₁ -8	2 662 -299	Hm 21, L ₁ -9	1 724 -749	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
Hm - 8, L ₁ -6	2 638 236	7 905 -905	Hm 21, L ₁ -7	3 134 -136	Hm 21, L ₁ -8	2 662 -299	Hm 21, L ₁ -9	1 724 -749	Hm 26, L ₁ -9	1 724 -749	1 709 34	Hm 5, L ₁ -12														
0 88+ -23	Hm 19, L ₁ -6	5 98+ -587	Hm 21, L ₁ -7	3 134 -313	Hm 21, L ₁ -8	0 04+ -384	1 251 -187	Hm 11, L ₁ -10	1 724 -749	1 709 34	Hm 5, L ₁ -12															
4 603 -621	1 355 -373	2 199 203	Hm 22, L ₁ -7	0 326 -307	Hm 22, L ₁ -8	5 98+ -587	Hm 22, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	
4 112 -141	3 406 383	2 199 203	Hm 22, L ₁ -7	0 326 -307	Hm 22, L ₁ -8	5 98+ -587	Hm 22, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	
8 150 -154	7 124 -190	Hm 22, L ₁ -7	0 326 -307	Hm 22, L ₁ -8	5 98+ -587	Hm 22, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098		
Hm - 8, L ₁ -6	20, L ₁ -6	Hm 23, L ₁ -7	0 326 -307	Hm 23, L ₁ -8	5 98+ -587	Hm 23, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098		
1 059 255	0 908 -923	Hm 24, L ₁ -7	0 326 -307	Hm 24, L ₁ -8	5 98+ -587	Hm 24, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098		
1 060 255	4 414 -427	Hm 24, L ₁ -7	0 326 -307	Hm 24, L ₁ -8	5 98+ -587	Hm 24, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098		
1 108 255	Hm 23, L ₁ -6	0 954 -954	Hm 24, L ₁ -7	0 326 -307	Hm 24, L ₁ -8	5 98+ -587	Hm 24, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	
9 876 -667	Hm 23, L ₁ -6	0 954 -954	Hm 23, L ₁ -7	0 326 -307	Hm 23, L ₁ -8	5 98+ -587	Hm 23, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	
8 798 -667	Hm 23, L ₁ -6	0 954 -954	Hm 23, L ₁ -7	0 326 -307	Hm 23, L ₁ -8	5 98+ -587	Hm 23, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	
Hm - 11, L ₁ -6	1 011 -111	4 814 -12	Hm 23, L ₁ -7	0 326 -307	Hm 23, L ₁ -8	5 98+ -587	Hm 23, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	0 098 -098	
1 021 -120	1 021 -120	4 814 -12	Hm 23, L ₁ -7	0 326 -307	Hm 23, L ₁ -8	5 98+ -587	Hm 23, L ₁ -9	0 103 -103	Hm 11, L ₁ -10	0 430 446	3 251 -352	0 290 -24	Hm 15, L ₁ -11	0 098 -098	0											

Table 2 (cont.)

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC			
H+	151	L+	-12	7	113	76	1	95	71	0	190	-169	H+	3	L+	15	4	93	-41	7	125	-133	0	313	-314	2	305	273	
5	675	664	H+	6	L+	13	5	91	-95	H+	10	L+	-14	1	98	-57	6	197	-252	H+	12	L+	-16	1	631	-618	2	422	442
7	929	167	2	98	24	H+	24	L+	-13	0	189	171	H+	3	L+	-10	5	95	-53	H+	12	L+	-16	3	433	-419	4	202	214
H+	161	L+	-12	6	92	91	2	143	70	2	146	-151	H+	3	L+	-14	1	98	-8	H+	12	L+	-16	0	809	-781	2	315	343
0	928	-30	2	345	-382	H+	6	L+	-13	0	215	219	H+	25	L+	-13	0	83	-40	3	315	-296	H+	6	L+	-17	4	317	-327
4	130	-141	4	138	-152	H+	25	L+	-13	0	83	-219	H+	25	L+	-16	3	94	-23	H+	12	L+	-16	4	317	-310			
6	117	-137	2	1588	1582	H+	25	L+	-13	0	83	-40	H+	25	L+	-16	4	88	-261	H+	12	L+	-16	4	206	196			
8	776	-37	4	216	323	1	250	-240	H+	11	L+	-14	7	281	-302	H+	2	452	-466	1	618	-371	H+	11	L+	-16	0	206	176
H+	17x	L+	-12	6	277	-287	3	78	-17	1	705	692	H+	4	L+	15	4	86	-60	H+	1	533	-175	4	206	-306			
H+	8	87	-91	H+	26	L+	-13	3	914	-978	H+	4	L+	15	H+	23	L+	-15	7	181	-149	H+	4	L+	16	1	411	-404	
1	452	418	H+	7	L+	13	5	804	-608	2	659	-466	H+	4	L+	16	H+	12	L+	-16	3	409	-412	1	324	319			
3	565	-881	1	270	-180	H+	6	L+	14	7	934	64	H+	4	L+	17	2	771	-274	H+	4	L+	18	0	294	-287			
7	140	142	3	342	-380	H+	6	L+	14	7	124	-142	H+	4	L+	16	2	255	-252	H+	4	L+	17	3	216	-218			
5	279	273	H+	1	L+	14	7	167	-172	H+	24	L+	-15	0	719	-604	H+	8	L+	-17	0	317	-329						
H+	18	L+	-12	6	593	-697	0	90	-56	2	397	380	H+	4	L+	16	4	638	-667	H+	4	L+	17	2	550	599			
0	96	-90	7	120	912	H+	7	L+	13	6	88	-53	H+	4	L+	17	6	207	-188	H+	4	L+	18	0	379	374			
2	124	-75	6	190	209	H+	8	L+	13	8	139	137	H+	5	L+	16	6	143	-137	H+	3	L+	-19	2	121	-107			
4	98	-23	6	92	-103	H+	1	L+	14	6	97	-96	H+	1	L+	14	2	255	-245	H+	1	L+	15	4	375	-387			
H+	19	L+	-12	H+	8	L+	13	1	294	-277	3	227	-196	H+	3	L+	-14	5	135	-134	H+	3	L+	-19	3	210	-205		
1	485	-491	H+	8	L+	13	5	143	-117	3	182	-752	H+	4	L+	16	7	180	-150	H+	4	L+	17	3	176	-170			
5	263	-294	2	92	-40	7	101	-105	5	521	-515	H+	5	L+	-16	0	1061	-1072	H+	6	L+	-16	2	350	-367				
7	70	-76	2	63	-84	H+	1	L+	14	7	167	-212	H+	1	L+	14	2	255	-217	H+	1	L+	15	4	362	-367			
H+	20	L+	-12	H+	8	L+	13	1	135	-152	1	847	-867	H+	4	L+	16	0	649	-659	H+	4	L+	17	0	577	-587		
0	108	-86	4	242	256	5	98	-108	2	376	-383	H+	4	L+	16	2	133	-108	H+	4	L+	17	1	258	-230				
2	209	-209	7	109	-30	H+	6	L+	15	6	96	-104	H+	6	L+	16	6	308	-360	H+	6	L+	17	5	180	-187			
4	106	103	8	89	72	H+	1	L+	14	8	77	73	H+	2	323	319	3	94	-80	H+	17	L+	-16	1	282	-280			
6	93	55	H+	9	L+	13	H+	2	L+	14	8	77	73	H+	4	L+	16	H+	17	L+	-16	H+	9	L+	-19	1	258	-230	
H+	21	L+	-12	0	669	670	H+	15	L+	-14	H+	6	L+	15	H+	1	160	-157	3	309	-312	H+	11	L+	-17	1	258	-230	
1	340	368	1	236	282	709	-729	1	827	759	H+	6	L+	15	H+	1	160	-157	3	320	-301	H+	11	L+	-17	1	282	-280	
3	230	-231	3	452	522	0	351	-351	3	816	-876	2	153	-114	H+	1	170	-281	3	132	-101	H+	17	L+	-17	1	258	-230	
5	214	-211	H+	9	L+	13	H+	2	L+	14	7	101	-152	H+	1	160	-157	0	379	-345	H+	8	L+	-19	1	258	-230		
H+	22	L+	-12	1	351	-331	H+	1	L+	14	7	101	-152	H+	1	160	-157	0	379	-345	H+	12	L+	-17	1	258	-230		
0	132	116	2	349	368	1	365	-351	2	153	-114	H+	1	160	-157	0	379	-345	H+	12	L+	-17	1	258	-230				
2	97	78	7	267	218	4	612	-628	0	314	-269	H+	1	160	-157	5	171	-178	H+	8	L+	-19	2	493	-485				
4	142	-119	6	182	-181	2	106	-105	1	105	152	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
6	93	-62	H+	10	L+	13	7	371	-420	5	166	-166	H+	2	153	-261	5	161	-161	H+	10	L+	-13	0	379	-345			
H+	23	L+	-12	2	220	194	H+	3	L+	14	H+	7	L+	15	H+	2	L+	15	H+	1	160	-157	H+	9	L+	-19	1	258	-230
1	279	-293	H+	10	L+	13	3	355	346	H+	17	L+	-14	1	515	-520	0	449	-443	H+	10	L+	-14	1	258	-230			
3	211	237	3	312	328	1	312	-312	1	859	-827	3	211	-218	H+	2	153	-261	2	305	-324	H+	10	L+	-14	1	258	-230	
5	188	215	2	416	-115	5	108	-124	5	346	-345	7	522	-540	H+	8	L+	15	0	320	-325	H+	10	L+	-14	1	258	-230	
H+	24	L+	-12	6	259	-247	H+	3	L+	14	7	824	-10	H+	8	L+	15	H+	1	160	-157	H+	12	L+	-16	1	258	-230	
0	321	-313	8	134	-122	H+	1	L+	14	1	92	-37	H+	16	L+	-14	0	379	-345	H+	13	L+	-20	1	258	-230			
2	89	-78	7	267	218	4	612	-628	0	314	-269	H+	2	153	-261	7	198	-179	H+	8	L+	-19	2	493	-485				
4	201	236	7	267	218	4	612	-628	2	161	-191	H+	1	160	-157	0	379	-345	H+	11	L+	-17	1	258	-230				
H+	25	L+	-12	1	329	-322	H+	3	L+	14	7	703	-739	H+	8	L+	15	0	379	-345	H+	10	L+	-14	1	258	-230		
0	125	-125	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
2	250	-250	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
4	183	-183	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
H+	26	L+	-12	1	326	-322	H+	1	L+	14	1	326	-322	H+	1	160	-157	0	379	-345	H+	10	L+	-14	1	258	-230		
0	126	-126	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
2	257	-257	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
4	184	-184	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
H+	27	L+	-12	1	326	-322	H+	1	L+	14	1	326	-322	H+	1	160	-157	0	379	-345	H+	10	L+	-14	1	258	-230		
0	127	-127	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
2	258	-258	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
4	185	-185	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
H+	28	L+	-12	1	326	-322	H+	1	L+	14	1	326	-322	H+	1	160	-157	0	379	-345	H+	10	L+	-14	1	258	-230		
0	128	-128	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
2	259	-259	1	326	-322	1	326	-322	0	284	-286	H+	2	153	-261	7	198	-179	H+	8	L+	-19	1	258	-230				
4	186	-186	1	326</td																									

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

Table 3. Rigid-body thermal parameters

(a) Atoms C(1)–C(8)

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

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

Unique origin
Position of C(1)
Principal axes of T:

Eigenvalue	Direction cosines		
0.054 \AA^2	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		
$22.7(\text{°})^2$	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. $U_{ij}: 0.002 \text{ \AA}^2$.

(b) Hexafluoroarsenate anion

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

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

Unique origin
Position of As

Eigenvalue	Direction cosines		
0.054 \AA^2	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 T:

Eigenvalue	Direction cosines		
$184.4(\text{°})^2$	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. $U_{ij}: 0.003 \text{ \AA}^2$.

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

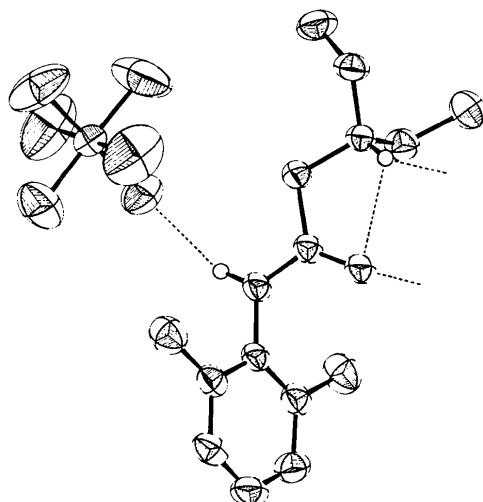


Fig. 1. Thermal motion ellipsoids of 50% probability. The hydrogen atoms involved in hydrogen bonding are shown as spheres.

N(9) to C(12) lies in a plane which is inclined at 66° 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 [$\text{N}(13) \cdots \text{O}(11) = 2.682 (4) \text{ \AA}$; $\text{H}(131) \cdots \text{O}(11) = 2.30 (4) \text{ \AA}$; $\text{N}(13)-\text{H}(131)-\text{O}(11) = 104 (3)^\circ$]. 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° . 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 [$\text{N}(13) \cdots \text{O}(11') = 2.822 (4)$, $\text{H}(131) \cdots \text{O}(11') = 1.96 (4) \text{ \AA}$; $\text{N}(13)-\text{H}(131)-\text{O}(11') = 160 (3)^\circ$]. 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 [$\text{N}(9) \cdots \text{F}(1) = 3.040 (5)$, $\text{H}(91) \cdots \text{F}(1) = 2.24 (5) \text{ \AA}$, $\text{N}(9)-\text{H}(91)-\text{F}(1) = 156 (3)^\circ$]. 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

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

Distances ($\text{\AA} \times 10^3$): 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.

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

Distances ($\text{\AA} \times 10^3$): 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° .

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) [1.394]	1.390
C(1)	C(6)	1.394 (5) [1.401]	[1.398]
C(2)	C(3)	1.396 (6) [1.402]	1.395
C(5)	C(6)	1.394 (6) [1.400]	[1.401]
C(3)	C(4)	1.376 (6) [1.382]	1.370
C(4)	C(5)	1.364 (6) [1.371]	[1.376]
C(2)	C(8)	1.505 (7) [1.510]	1.500
C(6)	C(7)	1.494 (6) [1.499]	[1.505]
C(1)	N(9)	1.437 (5)	
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)	1.505
C(14)	C(15)	1.497 (7)	
C(16)	C(17)	1.496 (6)	1.497
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⁻¹ is assigned to the stretching vibration of the N⁺-H group (Neville & Regnier,

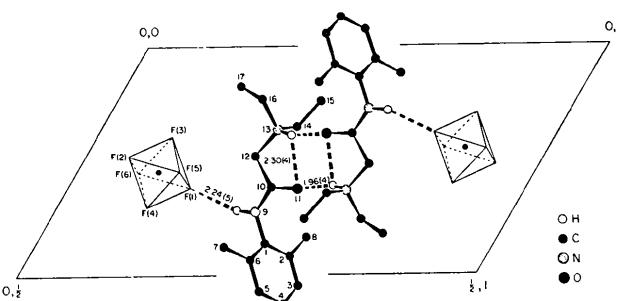


Fig. 2. A part of the structure viewed along \mathbf{b} , showing hydrogen bonding. The only hydrogen atoms shown are those which participate in hydrogen bonding.

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⁺–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⁻¹.

	Bond distance	Stretching frequency	$\Delta\nu$
N ₂ H ₄ .2HF	2.62 (2) Å	2548 cm ⁻¹	852 cm ⁻¹
NH ₄ HF ₂	2.80 (3)	2910	490
NH ₃ BF ₃	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

whom the author acknowledges much helpful discussion.

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. IUCr *World List of Crystallographic Computer Programs*. Second Edition, Appendix, page 52.
- BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
- CALLERI, M. & SPEAKMAN, J. C. (1969). *J. Chem. Soc. (A)*, p. 1644.
- COPELAND, R. F., CONNER, S. H. & MEYERS, E. A. (1966). *J. Phys. Chem.* **70**, 1288.
- DAVIS, B. R. & IBERS, J. A. (1970). *Inorg. Chem.* **9**, 2768.
- GANTZEL, P. K. & TRUEBLOOD, K. N. (1966). *MGTLs, thermal motion analysis*. Personal communication.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- NAKAMOTO, K., MARGOSHES, M. & RUNDLE, R. E. (1955). *J. Amer. Chem. Soc.* **77**, 6480.
- NEVILLE, G. A. & REGNIER, Z. R. (1969). *Canad. J. Chem.* **47**, 4229.
- PINNOCK, P. R., TAYLOR, C. A. & LIPSON, H. (1956). *Acta Cryst.* **9**, 173.
- ROOF, R. B. (1955). *Acta Cryst.* **8**, 739.
- SAX, M. & PLETCHER, J. (1969). *Science*, **166**, 1546.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Acta Cryst. (1972). **B28**, 679

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

BY A. M. MANOTTI LANFREDI, M. A. PELLINGHELLI, A. TIRIPICCHIO AND M. TIRIPICCHIO CAMELLINI
Istituto di Chimica Generale, Università di Parma, Parma, Italy

(Received 17 May 1971)

The crystals of strontium di-iodate(V) monohydrate, Sr(IO₃)₂.H₂O, are monoclinic, with unit-cell constants $a=13.156$ (16), $b=7.741$ (6), $c=8.914$ (15) Å, $\beta=132.9$ (3) $^\circ$, space group $C2/c$ and $Z=4$. The structure consists of pyramidal anions IO₃⁻ with bond distances I–O = 1.786, 1.806 and 1.825 Å, of Sr²⁺ 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. Sr²⁺ 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(IO₃)₂.H₂O, 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.