The Crystal Structure of Aminoguanidine Hydrochloride*

By John H. Bryden

Chemistry Division, Research Department, U.S. Naval Ordnance Test Station, China Lake, California, U.S.A.

(Received 26 April 1957)

The structure of aminoguanidine hydrochloride has been determined by Fourier and least-squares methods. The crystals are monoclinic, having the unit-cell dimensions $a_0 = 7\cdot78$, $b_0 = 11\cdot07$, $c_0 = 6\cdot00$ Å, $\beta = 103° 5'$. There are four molecules per unit-cell, and the space group is $P2_1/n$. The guanidine part of the aminoguanidinium ion is planar, but the amino group is slightly displaced from this plane. Only one strong $Cl^- \cdots N$ hydrogen bond is to be found in this crystal.

Introduction

The crystal structure of the hydrochloride salt of aminoguanidine is one of several structure investigations being carried out in this laboratory on compounds which may be considered as derived from guanidine by substitution. While the dimensions of the guanidinium ion are reasonably well known from recent work (for instance that of Curtis & Pasternak (1955) on methylguanidinium nitrate), additional information on nitrogen–nitrogen bonds is desirable. In addition, the structure of the aminoguanidinium ion would provide information for a model of the triaminoguanidinium ion, the hydrochloride salt of which is one of the compounds under investigation.

Experimental

Aminoguanidine is commercially available as the bicarbonate salt. The hydrochloride salt was therefore easily obtained by neutralization with hydrochloride acid. When grown from water the crystals are in the form of needles elongated along [100]. When grown from ethyl alcohol they form small prisms. From rotation and Weissenberg photographs taken about the three crystallographic axes the unit-cell dimensions were found to be

$$a_0 = 7\cdot78\pm0\cdot02, \quad b_0 = 11\cdot07\pm0\cdot04, \quad c_0 = 6\cdot00\pm0\cdot02 \text{ Å},$$
$$\beta = 103° 5'\pm10'$$

(λ of Cu $K\alpha = 1\cdot5418$ Å). There are four molecules per unit cell (calculated density = $1\cdot457$ g.cm.$^{-3}$). The extinctions noted ($h0l$ present only with $h+l = 2n$ and $0k0$ present only with $k = 2n$) uniquely determined the space group as $P2_1/n$.

The intensity data used for the structure determination were estimated visually from Weissenberg photographs of the $hk0$ and $0kl$ reflections.

A C 10

Determination of the structure

From the Patterson projections on (001) and (100) the position of the chloride ion could be inferred with reasonable certainty. The contribution of this ion to the $hk0$ reflections determined a sufficient number of phases so that a Fourier projection calculated with these data was successfully interpreted. This projection was then partially refined by Fourier methods. However, two pairs of atoms projected so closely together as to prevent accurate Fourier refinement, and the final refinements were made by least squares, using the complete normal equations.

A Fourier projection on (100) based on phases determined by the chloride ion could not be successfully interpreted, and so a trial-and-error method was tried. Using the x and y parameters already obtained, two reasonable models of the molecule were moved parallel to the c axis, and the $0kl$ structure amplitudes were calculated at small increments of z. The sum of the squares of the residuals, $\Sigma(\Delta F)^2$, was determined at each point. The position giving the smallest value of $\Sigma(\Delta F)^2$ was then refined by least squares, again using the complete normal equations. The final least-squares parameters obtained from the $hk0$ and $0kl$ data after adjusting the temperature factor are listed in Table 1. The y parameters are averages from the two zones.

Table 1. *Final parameters and standard deviations*

Atom	x	y	z	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
Cl^-	0·5159	0·3347	0·1523	0·0053	0·0058	0·0066
N_1	0·4294	−0·1134	0·1950	0·019	0·019	0·025
N_2	0·2311	−0·0942	−0·1546	0·021	0·021	0·025
N_3	0·2412	0·0543	0·1058	0·020	0·021	0·024
N_4	0·3077	0·0969	0·3318	0·020	0·019	0·023
C	0·3038	−0·0534	0·0526	0·024	0·023	0·028

An isotropic temperature factor, $\exp[-B(\sin\theta/\lambda)^2]$, was used throughout the calculations. For the $hk0$ reflections the final value was $B = 2\cdot76$ Å^2. The reflections (020), (130), (220), (040), (310), (400), and

(260), as well as the unobserved reflections, were not included in the least-squares refinements. For the $0kl$ reflections the final value of the temperature factor was $B = 2\cdot70$ Å². All observed reflections were used in the least-squares refinement of this zone. In the final calculation of the $hk0$ and $0kl$ structure amplitudes the average temperature factor, $B = 2\cdot73$ Å², was used. The scattering factors of Hoerni & Ibers (1954) were used for the carbon and nitrogen atoms, and those given by Berghuis et al. (1955) were used for the chloride ion. The percentage discrepancy for the data used in the least-squares refinements was $14\cdot1\%$ for the $hk0$ reflections, $9\cdot3\%$ for the $0kl$ reflections, and $11\cdot6\%$ for all reflections. The observed and calculated values of the structure amplitudes are given in Table 4. While the $h0l$ intensities were not measured quantitatively, the calculated values of the $h0l$ structure amplitudes were compared with the intensities on the $h0l$ photograph and were found to be in complete agreement.

The standard deviations of the atomic coordinates were calculated from the sum of the squares of the residuals and the normal equations by the expression

$$\sigma^2(x_i) = \frac{\Sigma(\Delta F)^2}{(s-m)} \cdot \frac{A_{ii}}{D}$$

(Whittaker & Robinson, 1944).

These values are also listed in Table 1. The values of $\sigma(y)$ are again the averages from the two zones.
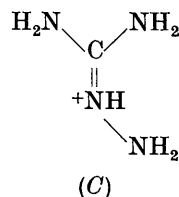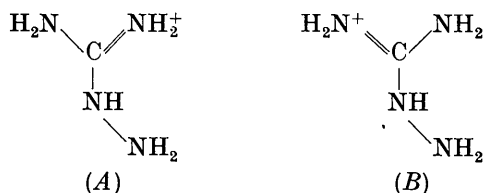
Discussion

To determine the dimensions and the degree of planarity of the aminoguanidinium ion the coordinates listed in Table 1 were converted to orthogonal coordinates by the relations $x' = x+z\cos\beta$ and $z' = z\sin\beta$. The bond lengths and bond angles calculated are listed in Table 2. The three carbon–nitrogen bond

Table 2. *Intramolecular distances and bond angles*

C–N$_1$	1·32 Å	N$_1$–C–N$_2$	122·1°
C–N$_2$	1·32	N$_2$–C–N$_3$	115·0
C–N$_3$	1·35	N$_1$–C–N$_3$	122·9
N$_3$–N$_4$	1·42	C–N$_3$–N$_4$	116·5
N$_1$–N$_4$	2·71		

lengths are in good agreement with those found by Mendel & Hodgkin (1954) and Jensen (1955) in creatine monohydrate and by Curtis & Pasternak (1955) in methylguanidinium nitrate. Three chief resonance structures can be written for the aminoguanidinium ion:

H$_2$N$\diagdown$C$\diagup$NH$_2^+$
|
NH
$\diagdown$NH$_2$
(A)

H$_2$N$^+\diagdown$C$\diagup$NH$_2$
|
NH
$\diagdown$NH$_2$
(B)

H$_2$N$\diagdown$C$\diagup$NH$_2$
‖
$^+$NH
$\diagdown$NH$_2$
(C)

On the basis of the bond lengths found, it appears that structures (A) and (B) contribute somewhat more to the structure of the ion than does structure (C). Weighting (A) and (B) at 40% each and (C) at 20%, and applying the bond character curve suggested by Donohue, Lavine & Rollett (1956), bond lengths of 1·335, 1·335 and 1·364 Å are calculated for C–N$_1$, C–N$_2$ and C–N$_3$, respectively. Allowing a correction of about 0·015 Å for the effect of formal charge (Pauling, 1940), excellent agreement is obtained between the observed and calculated bond lengths.

The N$_3$–N$_4$ bond is probably a single bond. The shortening of nitrogen–nitrogen bonds due to charge has been observed in hydrazinium chloride (Sakurai & Tomiie, 1952) and in the hydrazine salt of 5-aminotetrazole (Bryden, 1957). The present value agrees particularily well with the value of 1·42 Å found by Donohue & Lipscomb (1947) in hydrazonium dichloride.

A least-squares plane was calculated through the (orthogonal) atomic coordinates of the four atoms forming the guanidine part of the ion. In the normal form the equation of this plane is

$$0\cdot7993X+0\cdot4748Y-0\cdot3683Z = 1\cdot442 .$$

The average deviation of the four atoms from this plane is 0·002 Å, the largest deviation being 0·003 Å. The degree of planarity found is much greater than might be expected from the standard deviations of the atomic coordinates. The amino group, N$_4$, was found to be 0·093 Å out of the plane. This significantly larger deviation is probably due to the close approach (2·71 Å) of N$_1$ and N$_4$, resulting is a slight bending of the N$_3$–N$_4$ bond which has little or no double-bond character.

There appears to be only one well defined Cl$^-$ $\cdots$ N hydrogen bond: the distance between N$_3''$ and Cl$^-$ (see Fig. 1) is 3·13 Å, the chloride ion is only 0·13 Å out of the plane of the molecule containing N$_3''$, and the angle C''–N$_3''$–Cl$^-$ is 107·5°. This arrangement should form a strong hydrogen bond. The chloride ion, Cl$^-$, is equidistant from N$_1'$ and N$_2'$ at 3·31 Å and is 0·30 Å out of the plane of this molecule. It is probable that hydrogen bonds are formed here, but they are weak. Other Cl$^-$–N distances range from 3·39 Å to

Table 3. *Interatomic distances from the chloride ion*

Cl$^-$ to N$_3'$	3·13 Å	Cl$^-$ to N$_4$	3·39 Å
Cl$^-$ to N$_1'$	3·31	Cl$^-$ to N$_3''$	3·65
Cl$^-$ to N$_2'$	3·31	Cl$^-$ to N$_3$	3·74
Cl$^-$ to N$_2''$	3·39	Cl$^-$ to Cl$^{-'}$	4·07

Table 4. *Observed and calculated structure amplitudes*

The left column is the h or l index, the middle column is the observed structure amplitude, and the right column is the calculated structure amplitude. The values have been multiplied by ten.

$h00$		
0	—	2080
2	69	−46
4*	460	546
6	80	73
8	34	50

$h10$		
1	< 8	50
2	117	−134
3*	245	322
4	213	−250
5	79	88
6	107	−92
7	101	103
8	53	−84
9	50	75

$h20$		
0	265	265
1	15	22
2*	472	−585
3	33	34
4	< 16	−5
5	< 19	−16
6	105	−123
7	93	−110
8	39	−50
9	59	−80

$h30$		
1*	311	−424
2	57	−52
3	312	−322
4	129	−150
5	241	−251
6	< 21	4
7	112	−138
8	19	−2
9	47	−68

$h40$		
0	614	−614
1	23	30
2	153	−158
3	155	143
4	147	−162
5	88	88
6	59	−37
7	99	103
8	< 19	−7
9	18	37

$h50$		
1	298	324
2	42	40
3	96	94
4	175	184
5	83	80
6	37	53
7	< 21	21
8	58	84
9	12	−11

$h60$		
0	34	−24
1	69	−60
2*	421	489
3	26	−16
4	140	115
5	131	−111
6	140	167
7	67	73
8	73	87

$h70$		
1	164	150
2	87	−82
3	100	78
4	102	107
5	137	116
6	132	−130
7	49	57
8	27	−30

$h80$		
0	153	−152
1	43	−48
2	28	30
3	62	−45
4	134	−132
5	139	−146
6	47	−52
7	< 16	−3
8	21	−46

$h90$		
1	256	−251
2	40	−49
3	189	−186
4	61	41
5	79	−88
6	26	−43
7	51	−54

$h,10,0$		
0	70	−63
1	31	26
2	77	−75
3	85	69
4	100	−82
5	69	62
6	49	−52

$h,11,0$		
1	72	60
2	27	22
3	64	50
4	26	−21
5	28	42
6	39	57

$h,12,0$		
0	105	106
1	19	15
2	142	102
3	< 16	4
4	82	92
5	40	54

$h,13,0$		
1	102	88
2	14	20
3	52	49
4	59	−80

$h,14,0$		
0	63	−74
1	14	−6

$00l$		
2	353	−310
4	334	−339
6	168	171

$01l$		
1	248	255
2	329	−340
3	104	91
4	101	85
5	47	−38
6	116	112
7	53	−65

$02l$		
1	177	208
2	129	112
3	< 29	−25
4	< 34	19
5	65	−48
6	61	−58
7	40	46

$03l$		
1	364	412
2	< 25	−6
3	254	−252
4	50	−51
5	55	−35
6	91	90
7	80	83

$04l$		
1	462	−499
2	280	268
3	114	−116
4	132	128
5	219	244
6	124	−124
7	< 21	−10

$05l$		
1	163	−173
2	172	170
3	170	177
4	57	−68
5	41	−21

$06l$		
6	< 33	−14
7	27	−30
1	69	−59
2	46	−27
3	42	20
4	86	−75
5	< 37	19
6	50	52

$07l$		
1	170	−182
2	250	−259
3	102	99
4	146	155
5	42	36
6	37	38

$08l$		
1	203	244
2	53	−65
3	72	65
4	54	78
5	128	−143
6	< 21	1

$09l$		
1	54	42
2	38	−2
3	172	−186
4	< 36	7
5	40	53

$0,10,l$		
1	65	−55
2	60	−65

$0,10,l$		
3	47	−38
4	48	39
5	52	53

$0,11,l$		
1	70	−83
2	145	152
3	55	43
4	90	−90

$0,12,l$		
1	< 34	−21
2	50	−56
3	31	−12
4	51	−74

$0,13,l$		
1	54	−54
2	49	−61
3	48	59

$0,14,l$		
1	27	28

* Reflections which were not used in either least-squares refinement.

3·74 Å (see Table 3). The $Cl^{-\prime}$ distance through the inversion center at $(\frac{1}{2}, \frac{1}{2}, 0)$ is 4·07 Å.
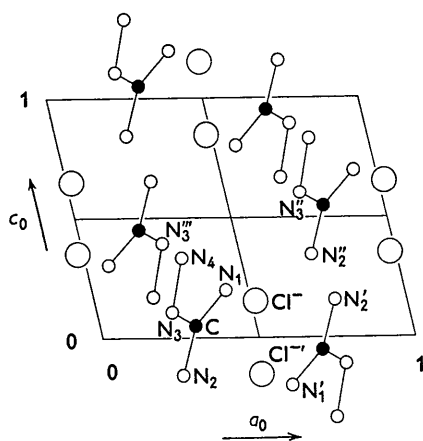

Fig. 1. Aminoguanidine hydrochloride viewed along the *b* axis.

Figs. 2(*a*) and 2(*b*) are schematic drawings of the structure viewed along the *a* and *c* axes respectively. On Fig. 2(*a*) the two aminoguanidinium ions related by the inversion center at the origin appear to be quite close together. The perpendicular distance between the planes of the two ions is indeed only 2·88 Å. However, the two ions are sufficiently offset so that the shortest interatomic distance is 3·87 Å from N_3 to its inverse counterpart.

This paper is published with the approval of the Technical Director, U.S. Naval Ordnance Test Station.

Fig. 2. Aminoguanidine hydrochloride viewed (*a*) along the *a* axis, (*b*) along the *c* axis.

References

BERGHUIS, J. *et al.* (1955). *Acta Cryst.* **8**, 478.

BRYDEN, J. H. (1957). *Acta Cryst.* In the Press.

CURTIS, R. M. & PASTERNAK, R. A. (1955). *Acta Cryst.* **8**, 675.

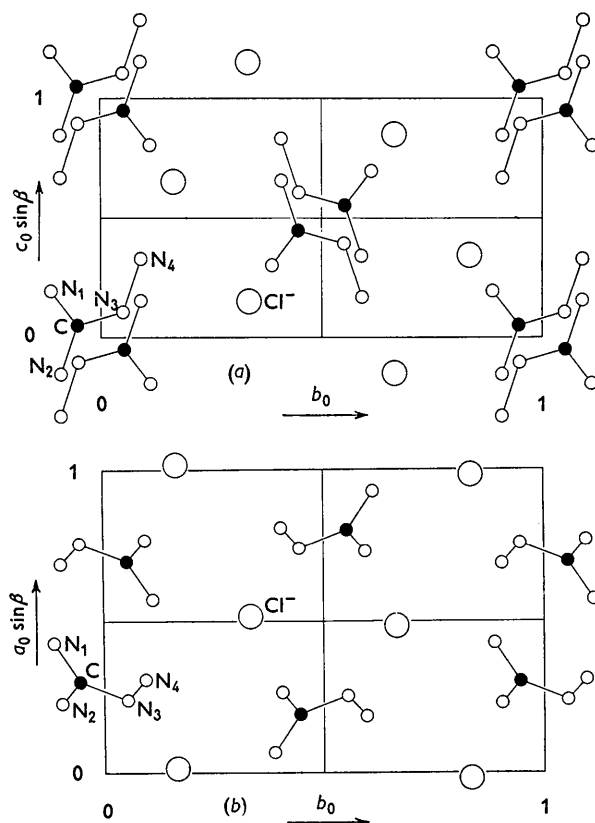DONOHUE, J., LAVINE, L. R. & ROLLETT, J. S. (1956). *Acta Cryst.* **9**, 655.

DONOHUE, J. & LIPSCOMB, W. N. (1947). *J. Chem. Phys.* **15**, 115.

HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.

JENSEN, L. H. (1955). *Acta Cryst.* **8**, 237.

MENDEL, H. & HODGKIN, D. C. (1954). *Acta Cryst.* **7**, 443.

PAULING, L. (1940). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.

SAKURAI, K. & TOMIIE, Y. (1952). *Acta Cryst.* **5**, 293.

WHITTAKER, E. T. & ROBINSON, G. (1944). *The Calculus of Observations*, 4th ed. Glasgow: Blackie.