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9-Ethylguanine Hemihydrochloride: a Short Asymmetric N-H···N Hydrogen Bond*

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9-Ethylguanine hemihydrochloride, $C_7H_9N_5O.\frac{1}{2}HCl$, forms triclinic crystals, space group $P\bar{1}$, with $a=13{\cdot}277(3)$, $b=10{\cdot}303(1)$, $c=7{\cdot}987(1)$ Å, $\alpha=93{\cdot}78(1)$, $\beta=56{\cdot}58(1)$, $\gamma=105{\cdot}81(1)°$ and $Z=4$. Least-squares refinement led to an R index of 0·040 for 3615 reflections from a twinned crystal measured by a 2θ scan technique. Of the two ethylguanine moieties in the asymmetric unit, one is formally a cation while the other is neutral. However, they are joined by a hydrogen bond N(7)–H···N(7) across a pseudo center of symmetry, so that the two moieties are effectively indistinguishable. The N(7)···N(7) distance of 2·637(3) Å represents the shortest N–H···N hydrogen bond yet observed. It is a disordered, rather than a centrosymmetric, hydrogen bond, as the hydrogen atoms occupy – with perhaps slightly different population factors – sites close to one or the other of the N(7) atoms. Despite the partial positive charge on the ethylguanine moieties, they are closely stacked, with intermolecular spacings of about 3·2 Å.

Introduction

The base-stacking interactions and the hydrogen-bonding motifs exhibited by various purine and pyrimidine derivatives can be directly related to the molecular organizations of macromolecular nucleic acids. For this reason our laboratory, along with numerous others, has been studying the crystal structures of these derivatives and their complexes. We have also been interested in the geometric aspects of metal coordination to nucleic acid components.

While Dr Max R. Taylor, visiting from the Flinders University of South Australia, was attempting to prepare a series of zinc complexes of 9-ethylguanine, he obtained crystals which we identified as 9-ethylguanine hemihydrochloride, $C_7H_9N_5O.\frac{1}{2}HCl$. We report here the crystal structure of this latter compound, which has a number of interesting features.

Experimental

0·2 g of 9-ethylguanine was added to 5 ml of warm water containing 0·7 g of $ZnCl_2$; a suspension formed, which cleared upon addition of 3 ml of 4*N* HCl. When this solution was allowed to stand for several days, needle-shaped crystals formed, which have subsequently been characterized as a zinc salt. However, when 2 ml of the solution was diluted with 5 ml of water, warmed, and left to stand in a covered beaker, a large fused mass of colorless plates formed. These crystals have been identified as 9-ethylguanine hemihydrochloride.

Only two suitable crystals could be isolated from the fused mass. One was very small; the second, which was used for data collection, was twinned. It was a plate of approximate dimensions $0{\cdot}53\times0{\cdot}33\times0{\cdot}15$ mm, elongated along [100] and with principal faces {001}, {010}, {110}, and {$\bar{1}$10}. The minor twin fragment showed diffraction intensities about 10% those of the major fragment; twinning was across {010}, with the **c*** directions of the two fragments coincident.

Twinning information and approximate unit-cell dimensions were obtained from preliminary Weissenberg and precession photographs. More accurate cell dimensions were obtained from a least-squares fit to the $\sin^2\theta$ values of 15 high-angle reflections centered on a Datex-automated General Electric quarter-circle diffractometer equipped with a scintillation counter, pulse-height discriminator and Ni-filtered Cu $K\alpha$ radiation at room temperature. The density was measured by flotation in a CCl_4-ethanol solution. Crystal data are collected in Table 1. Our description of the structure is based on a non-reduced cell which conforms closely to the crystal morphology.

Table 1. *Crystal data*

The reduced cell has base vectors along [10$\bar{1}$], [010], [001], and dimensions $a=11{\cdot}102$, $b=10{\cdot}303$, $c=7{\cdot}987$ Å, $\alpha=93{\cdot}78$, $\beta=93{\cdot}48$, $\gamma=106{\cdot}16°$. Our results are based on a non-reduced cell which corresponds to the crystal morphology.

$C_7H_9N_5O.\frac{1}{2}HCl$	F.W. 197·4
Triclinic	Space group $P\bar{1}$
$a=$ 13·277 (3) Å	$Z=4$; $F(000)=412$
$b=$ 10·303 (1)	$V=872{\cdot}6$ Å^3
$c=$ 7·987 (1)	$D_m=1{\cdot}50$ g cm^{-3}
$\alpha=$ 93·78 (1)°	$D_x=1{\cdot}503$ g cm^{-3}
$\beta=$ 56·58 (1)	λ(Cu $K\alpha$)=1·5418 Å
$\gamma=105{\cdot}81$ (1)	$\mu=22{\cdot}6$ cm^{-1}

Intensity data were collected from θ–2θ scans with scan speeds of 2° min^{-1}, scan widths varying from 2·0° at $2\theta=4{\cdot}0°$ to 4·0° at $2\theta=155°$, and 30s background counts. Two identical data sets were collected to a maximum 2θ value of 151° and were averaged to yield

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intensities for 3615 independent reflections. Three check reflections were monitored; they showed no appreciable trend. Observational variances, $\sigma^2(I)$, included counting statistics plus an additional term $(0{\cdot}02S)^2$, where S is the scan count. Intensities and their variances were corrected for Lorentz and polarization effects and also for absorption, using the method of Gaussian quadrature (Busing & Levy, 1957). The transmission factors ranged from 0·402 to 0·735.

A possible source of error in the intensity data would result from a coincidence of scattering angles for reflections from the two twin fragments. Accordingly, we determined the orientation of the smaller fragment, calculated the diffractometer angles 2θ, φ, and χ for all reflections, and compared these angles with those calculated for the major fragment. While in many instances different reflections from the two fragments showed quite similar scattering angles, we were unable to arrive objectively at a satisfactory criterion for presuming effective coincidence; eventually we were satisfied in assigning zero weights to the eight 00l reflections (which showed exact coincidence) and retaining the remaining observations.

Structure determination and refinement

A Howells, Phillips & Rogers (1950) plot of intensities (Fig. 1) indicated a hypersymmetric structure (Rogers & Wilson, 1953); thus the centrosymmetric space group $P\bar{1}$ was assumed. For this space group, the asymmetric unit contains one chloride ion and two 9-ethylguanine moieties. A three-dimensional sharpened Patterson map clearly indicated the position of the chloride ion, and showed images of the guanine groupings in the $w=0$ and $w=\frac{1}{2}$ sections. The positions of the terminal methyl groups C(10) were recovered from a subsequent electron density map and those of the hydrogen atoms from difference maps calculated

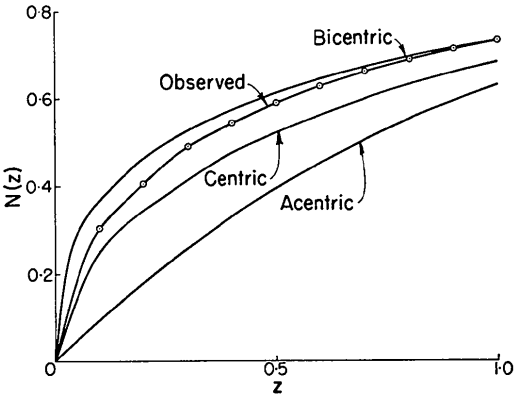

Fig. 1. Distribution plot for E^2 values (Howells, Phillips & Rogers, 1950). The curve for a 'bicentric' distribution is taken from Rogers & Wilson (1953).

Table 2. *Coordinates and anisotropic temperature factors*

Coordinates and U_{ij} values $\times 10^4$; standard deviations are given in parentheses. The anisotropic temperature coefficients are of the form $\exp(-2\pi^2)(h^2a^{*2}U_{11}\ldots+2klb^*c^*U_{23})$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	3250 (1)	780 (1)	2419 (1)	716 (3)	263 (2)	886 (4)	18 (2)	−529 (3)	−79 (2)
Molecule *A*									
N(1)	5004 (1)	3615 (1)	2396 (2)	296 (6)	210 (5)	466 (7)	83 (4)	−271 (5)	−60 (4)
C(2)	4362 (1)	4496 (1)	2487 (2)	265 (6)	248 (6)	381 (7)	82 (5)	−222 (6)	−36 (5)
N(2)	3331 (1)	3942 (1)	2492 (2)	347 (7)	259 (6)	672 (9)	84 (5)	−384 (7)	−72 (6)
N(3)	4720 (1)	5818 (1)	2573 (2)	243 (5)	248 (5)	411 (6)	90 (4)	−225 (5)	−30 (4)
C(4)	5775 (1)	6194 (1)	2579 (2)	237 (6)	217 (6)	341 (6)	62 (5)	−185 (5)	−20 (5)
C(5)	6460 (1)	5380 (1)	2512 (2)	241 (6)	244 (6)	373 (7)	69 (5)	−208 (5)	−27 (5)
C(6)	6088 (1)	3956 (1)	2419 (2)	280 (7)	262 (6)	376 (7)	113 (5)	−210 (6)	−39 (5)
O(6)	6580 (1)	3107 (1)	2384 (2)	412 (6)	282 (5)	612 (7)	179 (4)	−348 (6)	−69 (5)
N(7)	7445 (1)	6166 (1)	2615 (2)	257 (6)	268 (6)	437 (7)	80 (4)	−245 (5)	−34 (5)
C(8)	7357 (1)	7415 (1)	2732 (2)	275 (7)	261 (6)	469 (8)	61 (5)	−255 (6)	−37 (5)
N(9)	6361 (1)	7484 (1)	2705 (2)	257 (6)	210 (5)	438 (6)	73 (4)	−232 (5)	−33 (4)
C(9)	5936 (1)	8690 (1)	2811 (3)	365 (8)	238 (7)	648 (10)	126 (6)	−301 (8)	−41 (6)
C(10)	6861 (2)	9983 (2)	2619 (3)	576 (11)	258 (8)	906 (15)	107 (7)	−475 (12)	−57 (8)
Molecule *B*									
N(1)	1689 (1)	7866 (1)	2210 (2)	312 (6)	205 (5)	500 (7)	80 (4)	−292 (6)	−52 (5)
C(2)	2299 (1)	7016 (1)	2297 (2)	275 (7)	242 (6)	425 (7)	71 (5)	−243 (6)	−37 (5)
N(2)	3322 (1)	7609 (1)	2306 (2)	392 (7)	239 (6)	850 (11)	59 (5)	−474 (8)	−57 (6)
N(3)	1910 (1)	5679 (1)	2408 (2)	261 (6)	231 (5)	441 (6)	81 (4)	−255 (5)	−37 (4)
C(4)	844 (1)	5247 (1)	2432 (2)	235 (6)	238 (6)	358 (6)	73 (5)	−201 (5)	−46 (5)
C(5)	167 (1)	6023 (1)	2376 (2)	259 (6)	266 (6)	415 (7)	83 (5)	−239 (6)	−54 (5)
C(6)	599 (1)	7465 (1)	2199 (2)	314 (7)	269 (7)	435 (8)	121 (5)	−250 (6)	−52 (5)
O(6)	132 (1)	8289 (1)	2071 (2)	485 (7)	292 (5)	796 (9)	182 (5)	−471 (7)	−74 (5)
N(7)	−869 (1)	5188 (1)	2461 (2)	271 (6)	288 (6)	479 (7)	91 (5)	−275 (6)	−59 (5)
C(8)	−811 (1)	3948 (1)	2550 (2)	269 (7)	286 (7)	476 (8)	59 (5)	−266 (6)	−52 (6)
N(9)	217 (1)	3924 (1)	2525 (2)	266 (6)	213 (5)	424 (6)	81 (4)	−242 (5)	−49 (4)
C(9)	643 (1)	2746 (1)	2548 (2)	333 (7)	229 (6)	439 (8)	108 (5)	−248 (6)	−37 (5)
C(10)	−179 (2)	1426 (2)	2499 (3)	532 (11)	254 (7)	759 (13)	89 (7)	−427 (10)	−84 (7)

during the course of the refinement. The later difference maps (see Fig. 2) clearly indicated that H(7) is disordered, occupying with approximately equal probability sites adjacent to N(7) of the two molecules *A* and *B* in the asymmetric unit. The population parameters were set at 0·5 for both sites and were not further adjusted.

Refinement was by least-squares minimization of the quantity $\sum w(F_o^2-F_c^2)^2$ with weights w equal to $\sigma^{-2}(F_o^2)$. Atomic form factors for C, N, and O were from *International Tables for X-ray Crystallography* (1962), for H from Stewart, Davidson & Simpson (1965) and for Cl^- from Cromer & Waber (1965) corrected by 0·33 *e* to compensate for the real component of anomalous dispersion (Cromer, 1965). In the final cycles, 325 parameters were adjusted. Two matrices were collected: coordinates of the 27 heavy atoms in one, coordinates and isotropic temperature parameters of the 20 hydrogen atoms, anisotropic temperature parameters of the heavy atoms, a scale factor and an isotropic extinction parameter (Larson, 1967) in the second. Convergence was presumed when the maximum shift, in a hydrogen-atom coordinate, was $0{\cdot}6\sigma$. Atomic parameters are given in Tables 2 and 3; the final value for the extinction parameter g was $(5{\cdot}8\pm0{\cdot}2)\times10^{-6}$.

The final R index, $\sum||F_o|-|F_c||/\sum|F_o|$, was 0·040 for 3550 reflections showing positive net intensity; the good-

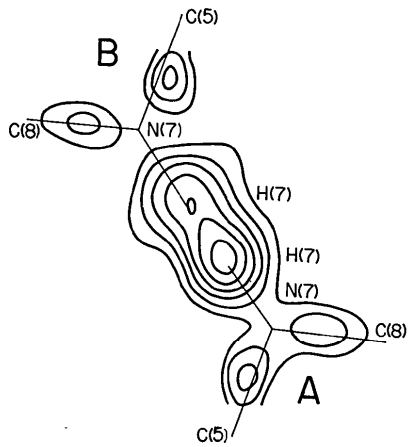

Fig. 2. A difference map, calculated at the conclusion of the refinement in the region of the N(7)···N(7) hydrogen bond. Coefficients were F_o-F_c', where values of F_c' were based on all atoms except H(7). Contours are at 0·1, 0·2, ..., 0·6 e Å^{-3}. Note the residual electron density along the C(5)–N(7) and N(7)–C(8) bonds.

Table 3. *Coordinates* ($\times10^3$) *and isotropic temperature coefficients for the hydrogen atoms*

	x	*y*	*z*	*B*
Molecule *A*				
H(1)	468 (2)	268 (2)	235 (3)	4·7 (5)
H(2)	287 (2)	446 (2)	258 (3)	3·8 (4)
H(2′)	311 (2)	312 (2)	252 (3)	4·8 (5)
H(7)	799 (3)	582 (3)	263 (4)	1·3 (5)
H(8)	794 (2)	812 (2)	277 (2)	2·9 (3)
H(9)	509 (2)	853 (2)	409 (3)	4·3 (4)
H(9′)	587 (2)	875 (2)	159 (3)	4·8 (5)
H(10)	653 (2)	1076 (2)	259 (3)	4·8 (5)
H(10′)	704 (2)	1002 (2)	369 (4)	6·9 (6)
H(10″)	773 (2)	1013 (2)	135 (4)	6·7 (6)
Molecule *B*				
H(1)	202 (2)	878 (2)	214 (3)	4·5 (4)
H(2)	380 (2)	708 (2)	236 (3)	4·0 (4)
H(2′)	357 (2)	847 (2)	220 (3)	3·9 (4)
H(7)	−152 (4)	553 (4)	245 (6)	4·1 (9)
H(8)	−142 (2)	320 (2)	262 (2)	2·6 (3)
H(9)	66 (2)	269 (2)	378 (2)	2·7 (3)
H(9′)	154 (2)	289 (2)	132 (3)	3·3 (4)
H(10)	10 (2)	64 (2)	251 (3)	4·8 (5)
H(10′)	−106 (2)	122 (2)	363 (3)	4·1 (4)
H(10″)	−21 (2)	142 (2)	132 (3)	4·7 (5)

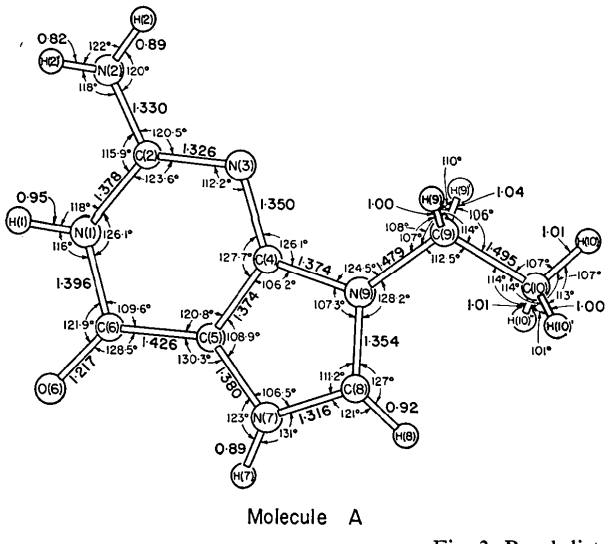

Fig. 3. Bond distances (Å) and angles (°).

ness-of-fit, $[\sum w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$, was 4·04 for $p=325$ parameters and $n=3606$ observations of non-zero weight.* The somewhat high value of the goodness-of-fit may be partly due to intensity errors caused by the presence of the small twin. In part, though, it must be a result of the high scattering power of the relatively large crystal which led to excellent counting statistics and low observational variances that, especially for the weaker reflections, do not adequately reflect errors due to the neglect of bonding electrons (see Fig. 2), incorrect form factors, and the like.

Discussion

Bond distances and angles are shown in Fig. 3. The e.s.d.'s in these values, as evaluated from the coordinate uncertainties in Tables 2 and 3, are 0·002–0·003 Å and 0·1–0·2° for bonds involving only C, N, and O atoms and about ten times larger for bonds involving H atoms. Agreement between corresponding bond lengths in the two molecules is good. The largest discrepancy involves the C(9)–C(10) bond, where the difference of 0·013 Å is slightly greater than three e.s.d.'s of that difference. Here, the apparent discrepancy can be blamed on out-of-plane thermal motions of these two atoms, which are appreciably greater in molecule *A* than in *B*. Excluding this bond, the goodness-of-fit value $\{\sum[\Delta d/\sigma(\Delta d)]^2/13\}^{1/2}$ for the 13 pairs of equivalent C–C, C–N, and C–O bonds is 1·15. Agreement among the N–H and C–H bond lengths is equally satisfactory; the average values of 0·91 and 0·99 Å are typical X-ray diffraction values.

The bond lengths in this 'hemi-protonated' species agree well with values found in the neutral 9-ethylguanine molecule (Destro, Kistenmacher & Marsh, 1974), its 1:1 complex with 1-methylcytosine (O'Brien, 1967), and in guanosine (Thewalt, Bugg & Marsh, 1970). The largest difference involves the C(6)–O(6), bond, which is significantly shorter in the present compound. There can be little doubt that the shortening of this bond is a consequence of the absence of the strong hydrogen bond to O(6) that is a feature of the other structures, leaving O(6) free to donate more bonding power to C(6). Concomitantly, the adjacent C(5)–C(6) bond [but not the N(1)–C(6) bond] is marginally longer in the present compound.

It is particularly surprising that the presence of a proton on N(7) in one-half of the molecules has failed to have a significant effect on the lengths of the C(5)–N(7) and N(7)–C(8) bonds. On the other hand, it *has* had an effect on the bond angle C(5)–N(7)–C(8), enlarging it by about 2° compared with the neutral molecule. Other bond angles that show variations are N(1)–C(6)–C(5), which is smaller in the present compound as a result of the additional C(6)–O(6) bond character already discussed, and the angles to the substituent group at N(9), which are undoubtedly sensitive to the conformational and packing features of the substituent.

Planarities of the molecules are described in Table 4. The ethyl groups are approximately in the planes of the purine rings, with the C(9)–C(10) bonds *cis* to C(8). The same conformation is found in crystalline complexes of 9-ethylguanine with 1-methylcytosine and with 1-methyl-5-fluorocytosine (O'Brien, 1967); how-

Table 4. *Deviations from the planes of the purine rings*

Least-squares planes were passed through N(2), O(6), and the nine ring atoms N(1)–N(9), all weighted equally. The dihedral angles between the planes of molecules *A* and *B* is 6·7°.

	Deviation (Å)			Deviation (Å)	
	A	*B*		*A*	*B*
N(1)	−0·012	0·008	H(1)	0·01	0·02
C(2)	0·000	−0·004	H(2)	0·05	0·01
N(2)	0·028	0·024	H(2′)	0·09	0·01
N(3)	−0·010	−0·015	H(7)	0·04	0·06
C(4)	−0·021	−0·010	H(8)	0·01	0·01
C(5)	−0·020	0·018	H(9)	0·85	0·71
C(6)	−0·010	−0·008	H(9′)	−0·80	−0·92
O(6)	0·012	−0·028	H(10)	−0·25	−0·26
N(7)	0·011	0·035	H(10′)	0·52	0·54
C(8)	0·024	0·008	H(10″)	−1·03	−0·99
N(9)	−0·002	−0·028	Cl*	0·141	0·317
C(9)	0·004	−0·101	N(3)†	−0·122	0·053
C(10)	−0·185	−0·209	N(7)‡	−0·034	0·234

* Acceptor of hydrogen bonds from N(1) and N(2).
† Acceptor of hydrogen bond from N(2).
‡ Acceptor of hydrogen bond from N(7).

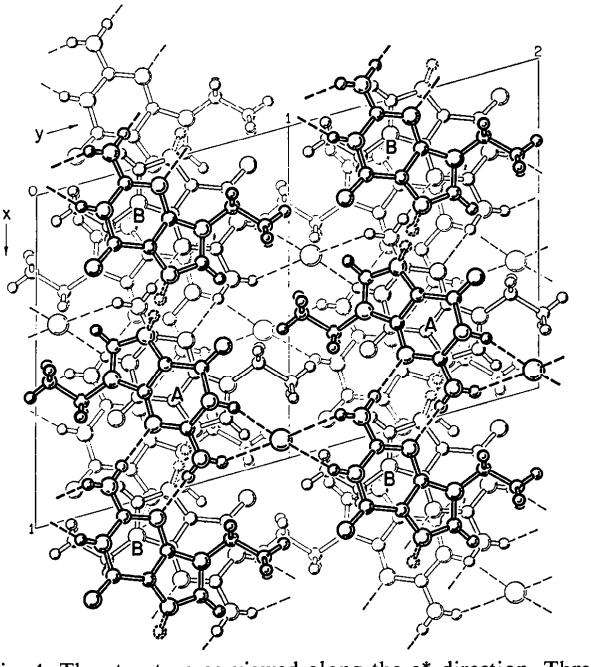

Fig. 4. The structure as viewed along the **c*** direction. Three layers of molecules are shown.

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31113 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ever, in crystals of 9-ethylguanine itself (Destro *et al.*, 1974) the C(9)–C(10) bonds are oriented approximately perpendicular to the planes of the purine rings.

A view down **c*** is shown in Fig. 4. The basic motif is a planar array of ethylguanine moieties, held together along the **a** direction by N(2)–H(2)···N(3) and N(7)–H(7)···N(7) hydrogen bonds and in the **b** direction by N–H···Cl hydrogen bonds. The base pairing through the N(2)···N(3) hydrogen bonds is also found in crystals of guanine hydrochloride (Broomhead, 1951); the pairing through the N(7)···N(7) bond has apparently not been previously observed. Since this latter feature involves only one hydrogen atom for each pair of N(7) atoms, it can occur only in cases involving different tautomeric forms of the guanine group or, as in the present case, when only half of the guanine groups are protonated.

The planar arrays, taken by themselves, are almost exactly centrosymmetric; the approximate centers of symmetry lie on the chloride ions, on the midpoints of the N(7)–H···N(7) bonds, midway between pairs of N(2)–H···N(3) bonds, and between pairs of terminal methyl groups C(10). As a result of these additional centers, the intensity distribution (Fig. 1) lies very close to that predicted by Lipson & Woolfson (1952) and Rogers & Wilson (1953) for a 'bicentric' motif. While these additional centers define a two-dimensional lattice in a plane parallel to (001), they do not define a lattice in the **c** direction; if this were the case, the structure could be described by a unit cell one-half as large.

Although the presence of halogen ions frequently disrupts the normal stacking pattern of purine bases (Bugg, 1970), in this case there is intimate stacking along the [001] direction (Fig. 4). The shortest contacts between stacked molecules are: O(6)*A*···C(2)*B* 3·181; C(6)*A*···N(3)*B* 3·230; C(2)*A*···N(7)*A* 3·263; O(6)*A*···N(3)*B* 3·323; C(4)*A*···C(6)*A* 3·330; N(7)*B*···N(7)*B* 3·350; and O(6)*A*···N(1)*B* 3·352 Å.

Details of the hydrogen bonds are given in Table 5. As far as we are aware, the N(7)···N(7) distance of 2·637 (3) Å represents the shortest N–H···N hydrogen bond yet observed. In a survey of the crystal structures of purines and pyrimidines, Voet & Rich (1970) find an average N–H···N distance of about 2·90 Å when the acceptor atom is N(7) of a purine derivative, the shortest distance reported being 2·73 Å in the intermolecular complex 5-fluorouracil-9-ethylhypoxanthine (Kim & Rich, 1967). Thus, the distance we find here is nearly 0·1 Å shorter than any analogous distance, and would represent a severe discontinuity in the histogram of N···N distances in purines and pyrimidines presented by Voet & Rich (1970) as well as in the earlier histogram of *all* N···N distances presented by Pimentel & McClellan (1960).

We believe that the primary cause for the pronounced shortening of this N–H···N bond is the additional ionic character resulting from the two molecules, donor and acceptor, having different formal charge. Within this hydrogen-bonded pair of 9-ethylguanine molecules [which are indistinguishable because of disorder in the location of H(7)] one molecule is protonated and is formally a cation; a large portion of the charge on this molecule must be concentrated near N(7) (Marsh, 1968). The second molecule of the pair is a neutral species, and Voet & Rich (1970) as well as Marsh (1968) have noted that an unprotonated N(7) atom in a purine ring acquires a partial negative charge and is an excellent hydrogen-bond acceptor.

Table 5. *Details of the hydrogen bonds, D–H···A*

D	H	*A*	*D*···*A*	H···*A*	*D*–H···*A*
N(1)*A*	H(1)*A*	Cl	3·195 Å	2·31 Å	156°
N(1)*B*	H(1)*B*	Cl	3·203	2·34	157
N(2)*A*	H(2′)*A*	Cl	3·227	2·46	157
N(2)*B*	H(2′)*B*	Cl	3·288	2·50	154
N(2)*A*	H(2)*A*	N(3)*B*	2·960	2·08	173
N(2)*B*	H(2)*B*	N(3)*A*	3·041	2·09	176
N(7)*A*	H(7)*A*	N(7)*B*	2·637	1·75	176
N(7)*B*	H(7)*B*	N(7)*A*	2·637	1·61	174

The N···N distance of 2·637 Å is nearly 0·4 Å shorter than the van der Waals contact distance (Pauling, 1960). In the system O–H···O, a shortening of 0·4 Å below the O···O van der Waals distance of 2·8 Å would result in a distance so short as to probably correspond to a symmetric O···H···O hydrogen bond (Hamilton & Ibers, 1968). Thus, there is reason to expect that the N(7)–H(7)···N(7) bond in the present compound might be symmetric. However, we do not believe this to be the case. Each of the two fractional hydrogen atoms refined to satisfactory positions, and difference maps continuingly suggested two separate atoms (Fig. 2). Whether or not the N–H···N system is symmetric – and a definitive answer to that question must await neutron diffraction studies – it seems clear that the potential barrier to transfer of the proton from one molecule to the other must be quite small, perhaps even approaching the ground-state vibrational level of the proton (see Hamilton & Ibers, 1968, pp. 94–104).

Finally, although we have assigned equal population factors of 0·5 to both H(7) sites, the relative peak heights on the difference map (Fig. 2) and the values of the isotropic temperature factor *B* (Table 3) suggest that the site of H(7*A*) might have greater occupancy than that of H(7*B*). We note that the site of H(7*A*) is slightly more favorable to the geometry of the N(7)–H···N(7) hydrogen bond, since the acceptor atom N(7*B*) is closer to the plane of molecule *A* (0·034 Å) than N(7*A*) is to the plane of molecule *B* (0·234 Å; see Table 4).

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A Refined Model for *N*-Acetyl-α-D-glucosamine

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A set of counter data has been collected for *N*-acetyl-α-D-glucosamine and the model refined by full-matrix least-squares calculations. For 1230 reflections 98·4% of all data within the Cu $K\alpha$ limit, $R(F)=0{\cdot}0237$, $R_w(F)=0{\cdot}0280$. Except for differences at the anomeric carbon the molecular conformation is similar to that of *N*-acetyl-α-D-glucosamine in the complex with triclinic lysozyme. The conformation found in a previous study of the compound [Johnson, *Acta Cryst.* (1966), **21**, 885–891] is generally confirmed. There are, however, systematic and in part significant differences between the two sets of bond lengths and valency angles. The present values for the glucopyranose structure are normal. The C–N bond of 1·346 (2) Å in the *N*-acetyl group is a long peptide-type C–N bond, all other structure parameters in this part of the molecule agree closely with averaged values for the peptide group. Most intermolecular hydrogen bonds are involved in helical chains running in the polar direction. These and a number of van der Waals interactions lead to tight packing and low thermal motion. The present study provides some evidence for a small amount of β sugar in the crystal as was suggested in the original analysis.

Introduction

N-acetylglucosamine (NAG) inhibits the enzymatic function of lysozyme (Wenzel, Lenk & Schütte, 1961; Rupley, 1964). Since it binds to lysozyme in both the tetragonal and triclinic forms, its structure in the crystalline state is of considerable interest. An analysis based on film data has already been reported (Johnson, 1966).

NAG is a derivative of D-glucose and it is a major constituent of a number of biological polymers such as chitin, hyaluronic acid, bacterial cell-wall polysaccharides, and some of the blood group polysaccharides. Thus, its structure is important in its own right, and a precise model would be useful for comparative purposes. We report such a model here based on counter data.

Experimental

A commercial sample of NAG was recrystallized from aqueous methanol containing a small amount of acetone. A prismatic crystal of dimensions 0·15 × 0·28 × 0·78 mm was mounted with its *b* axis (longest dimension) tilted *ca* 3° from the diffractometer φ axis and used for the X-ray measurements.

Crystallographic data are given in Table 1 together with those of Johnson (1966) (referred to hereinafter as J). Cell dimensions were determined from the setting angles of 20 reflections. The reciprocal vector $\mathbf{R}_{00l}$ chosen by J corresponds to $\mathbf{R}_{h0\bar{h}}$ in the present analysis. Transformation of our values according to the matrix

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