

the dissertation of L.L.R. which was presented to the Graduate College of the University of Arizona in partial fulfillment of the requirements for the Ph.D. degree. Programs used in this investigation included Zalkin's *FORDAP* Fourier program, Busing's *ORFFE* and *ORFLS* programs, and Johnson's *ORTEP* plotting program. The necessary computations were performed on a CDC 6400 computer.

References

- CORFIELD, P. W. R., DOEDENS, R. L. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197.
 CORNFORTH, J. W., YOUHOTSKY, I. & POPJAK, G. (1954). *Nature, Lond.* **173**, 536.
 FIESER, L. F. & FIESER, M. (1959). *Steroids*, Chapter 3. New York: Reinhold.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
 HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. A.C.A. Monograph No. 3. Pittsburgh: Polycrystal Book Service.
 HAUPTMAN, H. & KARLE, J. (1965). *Acta Cryst.* **9**, 45.
 IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* **17**, 781.
International Tables for X-ray Crystallography (1962). Vol. III, Table 3.3.2B. Birmingham: Kynoch Press.
 JOHNSON, P. L. & SCHAEFER, J. P. (1971). Private communication.
 JULIAN, P. L., COLE, W., MAGNANI, A. & MEYER, E. W. (1945). *J. Amer. Chem. Soc.* **67**, 1728.
 KARLE, I. L. & KARLE, J. (1969). *Acta Cryst.* **B25**, 428.
 MATTOX, V. R., TURNER, R. B., MCKENZIE, B. F., ENGLE, L. L. & KENDALL, E. C. (1948). *J. Biol. Chem.* **173**, 283.
 RUZICKA, L., PLATTNER, P. A. & ENGLE, B. G. (1944). *Helv. Chim. Acta*, **27**, 1553.
 SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configurations in Molecules and Ions*. London: The Chemical Society.

Acta Cryst. (1972). **B28**, 1748

The Crystal Structure of 2-Amino-3-chloropyrazine, C₄H₂N₂ClNH₂

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The crystal structure of 2-amino-3-chloropyrazine, C₄H₂N₂ClNH₂, has been determined by single-crystal X-ray diffraction techniques. Crystals are orthorhombic, space group *Pbca*, with unit-cell dimensions $a = 13.880$ (4), $b = 10.685$ (4), $c = 7.196$ (4) Å; the cell contains 8 molecules. The observed and calculated densities are 1.60 and 1.612 g.cm⁻³ respectively. 648 unique intensities were obtained photometrically from film exposed to Cu *K*α radiation in an integrating Weissenberg camera. Phases were obtained by the symbolic addition method, and the structure was refined by least-squares techniques to a conventional *R* value of 7.7%. Pairs of planar molecules form centrosymmetric dimers through N-H...N hydrogen bonds [3.178 (8) Å]. The crystal consists of stacks of pleated sheets, formed from dimers linked with zigzag chains of other N-H...N bonds [3.275 (7) Å].

Introduction

Pyrazines are important in the synthesis of chemotherapeutic agents. They have not been studied as extensively as have the derivatives of the related diazine, pyrimidine, with which they have a number of important similarities. They possess interesting structural properties, especially when hydrogen bond networks are formed. This paper presents the crystal and molecular structure of 2-amino-3-chloropyrazine.

Crystal data

2-Amino-3-chloropyrazine: C₄H₂N₂ClNH₂
 F.W. 129.550
 $a = 13.880$ (4), $b = 10.685$ (4), $c = 7.196$ (4) Å
 $\text{Cu } K\alpha_1 = 1.54051$ Å
 White, acicular (*c*) crystals; $V = 1067$ (1) Å³
 $Z = 8$; $F(000) = 528$
 $D_x = 1.612$, $D_m = 1.60$ g.cm⁻³ (flotation in CH₃I/CCl₄/C₆H₆)
 Linear absorption coefficient: $\mu = 53$ cm⁻¹ (Cu *K*α)
 Space group: *Pbca* (No. 61)
 Absent spectra: $hk0$ for h odd; $0kl$ for k odd; $h0l$ for l odd.

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Experimental results

Samples of $C_4H_2N_2ClNH_2$ used in the experiments were prepared by the method of McDonald & Ellington (1947) and were kindly furnished by Dr A. Teass. Single crystals used in the diffraction study were obtained by recrystallization from water solution. Most crystals produced in this process were twins. The material was only moderately stable in air, and specimens used in diffraction experiments were sealed in Lindemann glass tubes. Preliminary precession photographs showed that the crystals are orthorhombic. Unit-cell dimensions were determined from Weissenberg photographs, obtained by exposing crystals to $Cu K\alpha$ radiation. Film shrinkage was determined from the locations of aluminum powder lines superimposed on the photographs. The positions of 30 reflections, with Bragg angles between 59 and 77° , were read on a Nikon comparator. These observations were used with the method of least-squares to determine the three cell constants.

Dimensions of the crystals used in the experiments are: $0.15 \times 0.15 \times 0.10$ mm (b axis rotation), and $0.12 \times 0.06 \times 1.62$ mm (c axis rotation). The first crystal was cut from a needle. Integrated multiple-film Weissenberg photographs were taken for levels 0–4 on rotation about the b axis, and for levels 0–4 on rotation about the c axis. Integration was performed in two directions. $Cu K\alpha$ radiation filtered through Ni foil was employed. Ilford Industrial G film was used in a Stoe integrating Weissenberg camera. Intensity data were obtained by scanning reflections in one direction with a Joyce–Loebl microdensitometer. Of the 1026 unique reflections accessible in the photographs, only 648 were sufficiently different from background for photometric measurement. Lorentz–polarization corrections were applied, but not absorption corrections. The absorption coefficient μ is 53 cm^{-1} . The maximum variation in $|F_o|$ ascribed to neglect of absorption correction is about 2% for the b axis data, if one assumes the crystal to be crude sphere with radius 0.007 cm. For c axis data, the maximum variation is about 1%,

if the crystal is considered a cylinder of radius 0.005 cm. Intersections of the b axis and c axis data were used to establish approximate factors, putting structure amplitudes on a common scale. Along with other variables, these scale factors were later refined by the method of least squares. The extremely intense reflection 020 appeared to be suffering badly from extinction, and it was not used in the least-squares refinement. Empirical extinction corrections taken from a plot of $I(\text{obs})$ versus $I(\text{calc})$ (Jeffrey & Jones, 1956) were applied to five strong reflections: 200, 002, 102, 112, and 202. No other allowance was made for extinction.

Structure determination

The symbolic addition method (Karle & Karle, 1966) was used to determine the phases. Normalized structure-factor magnitudes ($|E|$) were calculated and scaled (Hauptman & Karle, 1953) with $\epsilon=2$ for spectra with h or k or l zero, and $\epsilon=1$ for other spectra. Origin assignment was made by setting $\varphi(431)=\varphi(652)=\pi$ and $\varphi(722)=0$. The corresponding E values are 2.89, 2.07, and 1.69, respectively. The Σ_2 relationship of Hauptman & Karle (1953) was used to determine the phases of 59 reflections with $|E| > 1.2$. From the three dimensional E map calculated from these 59 values, the location of the molecules in the unit cell was directly evident, even though only six of the eight nonhydrogen atoms were seen as well-resolved peaks. All atoms occupy the general eightfold equipoint of the space group.

Structure factors calculated from the E map coordinates, the Wilson scale, and a uniform isotropic thermal factor $B=2.0$, produced a conventional $R = \frac{\sum ||F_o| - S|F_c||}{\sum |F_o|}$ of 56%. With the aid of a series of electron density and difference density calculations using 647 reflections, R was reduced to 17%. A modified version of the program *FORDAP* by A. Zalkin was used for the electron density calculations. Isotropic full-matrix least-squares refinement of nonhydrogen atoms, using the program *ORFLS* (Busing, Martin & Levy, 1962) was followed by anisotropic refinement,

Table 1. *Final fractional coordinates and thermal parameters*

Thermal factors are:

$$\exp [-2\pi^2(U_{11}a^*2h^2 + U_{22}b^*2k^2 + U_{33}c^*2l^2 + U_{12}a^*b^*hk + U_{13}a^*c^*hl + U_{23}b^*c^*kl)].$$

Standard deviations, given in parentheses, refer to the least significant digits.

	10^4X	10^4Y	10^4Z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Cl	2973 (1)	8360 (1)	2386 (3)	40 (1)	58 (1)	49 (9)	9 (1)	-8 (2)	-6 (2)
N(1)	265 (3)	8353 (4)	770 (10)	36 (4)	45 (3)	38 (9)	-14 (4)	3 (6)	3 (6)
N(2)	1299 (4)	5 (4)	1341 (10)	45 (3)	38 (2)	57 (10)	-4 (4)	6 (6)	-16 (6)
N(4)	1715 (4)	6638 (4)	1738 (10)	40 (4)	44 (3)	40 (9)	-8 (4)	0 (6)	0 (6)
C(2)	1136 (4)	8745 (5)	1286 (10)	32 (3)	37 (3)	29 (9)	-4 (4)	14 (6)	-7 (6)
C(3)	1848 (4)	7852 (5)	1731 (11)	35 (3)	44 (3)	22 (10)	-8 (5)	-4 (6)	-1 (6)
C(5)	830 (4)	6246 (6)	1236 (11)	49 (5)	45 (3)	38 (11)	-4 (5)	-20 (7)	1 (7)
C(6)	121 (4)	7094 (6)	807 (11)	45 (5)	51 (3)	30 (10)	1 (5)	-14 (7)	12 (7)
H(21)	800	400	600						
H(24)	1928	354	1593						
H(6)	9573	6732	100						

which converged at $R=8.0\%$. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weight, w , given by the formula $w^{-1} = 0.810 + 0.0685|F_o| + 0.00144|F_o|^2$, was selected so that $\langle w\Delta^2 \rangle$ varied little with changing $|F_o|$. The 10 scale factors were treated as variables. Scattering factors for C, N, and Cl were taken from the tables of Hanson, Herman, Lea & Skillman (1964). Hydrogen scattering factors, used later in the calculations, were those given by Stewart, Davidson & Simpson (1965).

The hydrogen atom H(6), bonded to C(6), was readily located as the largest maximum ($0.56 \text{ e.}\text{\AA}^{-3}$) in the difference density calculated from the above least-squares refinement, but the hydrogen atom bonded to C(5) could not be seen in the difference density map. Two maxima (0.49 and $0.39 \text{ e.}\text{\AA}^{-3}$) near N(2) were identified as hydrogen atoms, H(21) and H(24), in the NH_2 group. H(6), H(21), and H(24) were included in the subsequent calculation of structure factors, but neither coordinates nor thermal parameters of these three atoms were treated as variables in the refinement. Each hydrogen atom was assigned the thermal parameter of the atom to which it is bonded. In the last cycle of refinement of this model, the largest coordinate shift was 2% of the standard deviation of that coordinate. The value of R is 7.7%. The inclusion of three hydrogen atoms decreased the weighted R , $[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$, from 10.87 to 10.28%. If the method of Hamilton (1965) is applied to the weighted R 's on the assumption that it is a reasonably good approximation to the ratio of the generalized R indices, Hamilton's tables show that the R ratio, 1.057, corre-

sponds to a significance parameter (α) well below 0.005, and the inclusion of the hydrogen atoms seems quite justified. Coordinates and temperature factors obtained from the final cycle of refinement are listed in

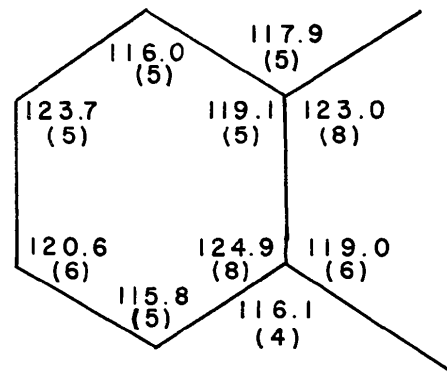
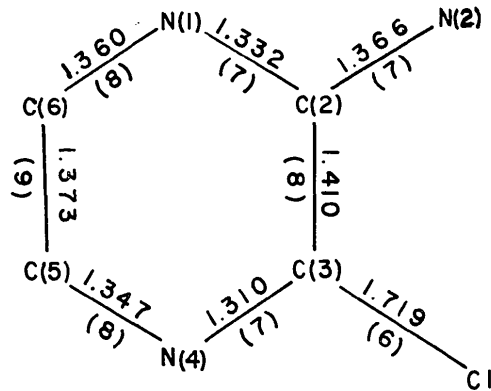


Table 2. Observed and calculated structure amplitudes, in electrons

h	k	l	$ F_o $	$ F_c $	$ F_o - F_c $	$ F_o + F_c $	$ F_o / F_c $
0	0	0	100	100	0	200	1.00
0	0	1	10	10	0	20	1.00
0	0	2	10	10	0	20	1.00
0	0	3	10	10	0	20	1.00
0	0	4	10	10	0	20	1.00
0	0	5	10	10	0	20	1.00
0	0	6	10	10	0	20	1.00
0	0	7	10	10	0	20	1.00
0	0	8	10	10	0	20	1.00
0	0	9	10	10	0	20	1.00
0	0	10	10	10	0	20	1.00
0	0	11	10	10	0	20	1.00
0	0	12	10	10	0	20	1.00
0	0	13	10	10	0	20	1.00
0	0	14	10	10	0	20	1.00
0	0	15	10	10	0	20	1.00
0	0	16	10	10	0	20	1.00
0	0	17	10	10	0	20	1.00
0	0	18	10	10	0	20	1.00
0	0	19	10	10	0	20	1.00
0	0	20	10	10	0	20	1.00
0	0	21	10	10	0	20	1.00
0	0	22	10	10	0	20	1.00
0	0	23	10	10	0	20	1.00
0	0	24	10	10	0	20	1.00
0	0	25	10	10	0	20	1.00
0	0	26	10	10	0	20	1.00
0	0	27	10	10	0	20	1.00
0	0	28	10	10	0	20	1.00
0	0	29	10	10	0	20	1.00
0	0	30	10	10	0	20	1.00
0	0	31	10	10	0	20	1.00
0	0	32	10	10	0	20	1.00
0	0	33	10	10	0	20	1.00
0	0	34	10	10	0	20	1.00
0	0	35	10	10	0	20	1.00
0	0	36	10	10	0	20	1.00
0	0	37	10	10	0	20	1.00
0	0	38	10	10	0	20	1.00
0	0	39	10	10	0	20	1.00
0	0	40	10	10	0	20	1.00
0	0	41	10	10	0	20	1.00
0	0	42	10	10	0	20	1.00
0	0	43	10	10	0	20	1.00
0	0	44	10	10	0	20	1.00
0	0	45	10	10	0	20	1.00
0	0	46	10	10	0	20	1.00
0	0	47	10	10	0	20	1.00
0	0	48	10	10	0	20	1.00
0	0	49	10	10	0	20	1.00
0	0	50	10	10	0	20	1.00
0	0	51	10	10	0	20	1.00
0	0	52	10	10	0	20	1.00
0	0	53	10	10	0	20	1.00
0	0	54	10	10	0	20	1.00
0	0	55	10	10	0	20	1.00
0	0	56	10	10	0	20	1.00
0	0	57	10	10	0	20	1.00
0	0	58	10	10	0	20	1.00
0	0	59	10	10	0	20	1.00
0	0	60	10	10	0	20	1.00
0	0	61	10	10	0	20	1.00
0	0	62	10	10	0	20	1.00
0	0	63	10	10	0	20	1.00
0	0	64	10	10	0	20	1.00
0	0	65	10	10	0	20	1.00
0	0	66	10	10	0	20	1.00
0	0	67	10	10	0	20	1.00
0	0	68	10	10	0	20	1.00
0	0	69	10	10	0	20	1.00
0	0	70	10	10	0	20	1.00
0	0	71	10	10	0	20	1.00
0	0	72	10	10	0	20	1.00
0	0	73	10	10	0	20	1.00
0	0	74	10	10	0	20	1.00
0	0	75	10	10	0	20	1.00
0	0	76	10	10	0	20	1.00
0	0	77	10	10	0	20	1.00
0	0	78	10	10	0	20	1.00
0	0	79	10	10	0	20	1.00
0	0	80	10	10	0	20	1.00
0	0	81	10	10	0	20	1.00
0	0	82	10	10	0	20	1.00
0	0	83	10	10	0	20	1.00
0	0	84	10	10	0	20	1.00
0	0	85	10	10	0	20	1.00
0	0	86	10	10	0	20	1.00
0	0	87	10	10	0	20	1.00
0	0	88	10	10	0	20	1.00
0	0	89	10	10	0	20	1.00
0	0	90	10	10	0	20	1.00
0	0	91	10	10	0	20	1.00
0	0	92	10	10	0	20	1.00
0	0	93	10	10	0	20	1.00
0	0	94	10	10	0	20	1.00
0	0	95	10	10	0	20	1.00
0	0	96	10	10	0	20	1.00
0	0	97	10	10	0	20	1.00
0	0	98	10	10	0	20	1.00
0	0	99	10	10	0	20	1.00
0	0	100	10	10	0	20	1.00

Fig. 2. One molecule and its hydrogen bonded neighbors, viewed down the c axis. E.s.d.'s in units of the last decimal place are given in parentheses.

Table 1, and a list of observed and calculated structure factors is given in Table 2.

Discussion of the structure

The four carbon atoms and two nitrogen atoms, which form the six-membered ring, are almost exactly coplanar. The least-squares plane defined by these atoms is $-0.2865P + 0.03944Q + 0.9573R = 0.7924$, where P , Q , and R are cartesian coordinates in Å along a , b , and c respectively. Perpendicular distances of atoms from the plane are given in Table 3.

Table 3. *Distance of atoms from least-squares plane calculated from ring atom positions*

E.s.d.'s in parentheses refer to the last significant digit.

N(1)	-0.015 (7) Å
C(2)	+0.010 (7)
C(3)	-0.004 (8)
N(4)	+0.003 (7)
C(5)	-0.008 (8)
C(6)	+0.014 (8)
N(2)	+0.036 (7)
Cl	+0.022 (2)

Intramolecular bond distances and angles calculated from the final coordinates in Table 1 are shown in Fig. 1. Ring dimensions closely resemble those found for pyrazine by Wheatley (1957), but the asymmetry produced by ring substituents is reflected in small variations from corresponding bond distances in pyrazine. The four C–N distances in the 2-amino-3-chloropyrazine ring average 1.337 (8) Å, which is also the average of ring C–N distances reported by Sutton (1958) for conjugated heterocyclic systems. The mean of the two C–N distances involving carbon atoms with substituents is 0.033 Å ($\sigma = 0.011$) smaller than the mean of the other two C–N distances in the ring; this difference is significant at the 0.1% level. It is likely that bonds C(2)–N(1) and C(3)–N(4) may have slightly greater double bond character than do the other two C–N bonds in the ring, since enlargement of the C(2)–C(3) separation beyond the usual aromatic value could mean that the resonance form with C(2)–C(3) a single bond is somewhat more important than other forms.

The difference between the two C–C ring distances, 1.410 (8) and 1.373 (9) Å, is significant at the 0.1% level. Steric interaction of chloro and amino groups on adjacent carbon atoms is doubtless responsible for the lengthening of the C(2)–C(3) distance over the C(5)–C(6) distance of 1.373 (9) Å, which is almost identical to the corresponding distance, 1.38 Å, found in pyrazine itself (Wheatley, 1957). Cromer (1957) observed a symmetrical lengthening of the ring C–C separations to 1.43 Å in tetramethylpyrazine. Monosubstitution in pyrazine-2-carboxamide (Takaki, Sasada & Watanabe, 1960), complex formation between AgNO_3 and pyrazine (Vranka & Amma, 1966), and the formation of adducts of pyrazine with tetrabromo- and tetra-

iodoethylene (Dahl & Hassel, 1968), do not change the C–C distance from that of pyrazine.

The chlorine atom is only 0.022 (2) Å distant from the plane of the ring, so that the configuration at C(3) is essentially planar. The C(3)–Cl distance, 1.719 (6) Å, is frequently encountered in other compounds (Sutton, 1958). The C(2)–N(2) separation, 1.366 (7) Å, is considerably shorter than the single bond value, 1.41 Å, estimated by Trueblood, Goldish & Donohue (1961) for the bond between trigonal carbon and trigonal nitrogen atoms. The distance 1.37 Å for C(ring)–NH₂ is also encountered in 4-nitroaniline (Trueblood, Goldish & Donohue, 1961), in 2-amino-3-methylbenzoic acid (Brown & Marsh, 1963), and in 2-amino-5-propyl-7-methyl-*s*-triazolo[2,3-*c*]pyrimidine hydrochloride (Owston & Rowe, 1962). In 4,4'-diamino-1,1'-biantroquinone (Ogawa & Scheel, 1969) and in *p*-aminobenzoic acid (Lai & Marsh, 1967), the corresponding distances are 1.36 and 1.38 Å respectively. In all of these structures the bond is thought to have a considerable amount of double-bond character, introduced through an important resonance form which has $>\text{C}=\text{N}^+\text{H}_2$. In 2-amino-3-chloropyrazine, N(2) is only 0.036 (7) Å distant from the plane of the ring and the configuration at C(2) is essentially planar. These features are consistent with a considerable amount of double-bond character of the C(2)–N(2) bond. The corresponding C–N bond in the aminopurine structures reviewed by Voet & Rich (1970) has even greater double-bond character, as the average length 1.34 Å indicates.

The interior bond angles of the ring of 2-amino-3-chloropyrazine are essentially the same as the corresponding angles in pyrazine (Wheatley, 1957) and in the pyrazine derivatives described above. The bond angles C(6)–N(1)–C(2) and C(5)–N(4)–C(3) are 116.0 (5) and 115.8 (5)° respectively, whose values, according to Singh's (1965) rule, correspond to ring nitrogen atoms without substituents. The difference synthesis confirms that these nitrogen atoms have no substituents. This evidence that the molecule is in the amino rather than the imino form is consistent with indications from magnetic resonance spectra that 2-aminopyrazine and 2-amino-3-methylpyrazine are in the amino form (Cox & Bothner-By, 1968*a, b*).

In the crystal, pairs of $\text{C}_4\text{H}_2\text{N}_2\text{ClNH}_2$ molecules are held together by N(2)–H(21)–N(1') hydrogen bonds (Fig. 2 and Table 4). This centric pair of hydrogen bonds is closely similar to the centric pairs of N–H...N bonds observed in certain purine-pyrimidine complexes, and in dimers formed from self-pairing of purines or pyrimidines (Voet & Rich, 1970). Of the many different kinds of N–H...N centric pairing given by Voet & Rich (1970) in their review, those most nearly like that found in 2-amino-3-chloropyrazine involve $-\text{NH}_2$ and a ring N with the bonding relationship $\cdots\text{H}-\text{NH}-\text{C}=\text{N}\cdots$. Typical of the substances showing this hydrogen bonding arrangement are 9-ethylguanine-1-methylcytosine

(O'Brien, 1967), 1-methyluracil-9-ethyl-8-bromo-2,6-diaminopurine (Simundza, Sakore & Sobell, 1970), and 4-amino-2,6-dichloropyrimidine (Clews & Cochran, 1949). N...N distances in these hydrogen bond systems are 3.01, 3.11, and 3.09 Å respectively, all somewhat shorter than the 3.178 (8) Å distance found in 2-amino-3-chloropyrazine. In the substance 2-amino-4,6-dichloropyrimidine (Clews & Cochran, 1948), the shorter of the two centric pairs of N-H...N bonds has a length 3.21 Å, which is close to the value found in the present study.

Table 4. Bond distances and angles associated with hydrogen bonds

E.s.d.'s in parentheses refer to the last significant digit.

N(2) ... N(1')	3.178 (8) Å
N(2) — H(21)	0.97 (5)
N(1') ... H(21)	2.22 (5)
∠ N(2) — H(21) ... N(1')	168 (4)°
N(2) ... N(4')	3.275 (7) Å
N(2) — H(24)	0.97 (5)
N(4') ... H(24)	2.33 (5)
∠ N(2) — H(24) ... N(4')	165 (4)°

Each dimer is linked to four neighbors by N(2)-H(24)...N(4') hydrogen bonds (Fig. 2 and Table 4), which form zigzag chains in both *a* and *b* directions. They link molecules to form corrugated sheets, which stack in the *c* direction so that the pyrazine rings in neighboring sheets are essentially parallel and in van der Waals contact. Accordingly, the *c* spacing is almost exactly double the aromatic ring thickness, 3.6 Å. Pyrazine rings in contact are rotated about 21° with respect to one another (Fig. 3). The packing in quite efficient as the density of 1.612 g.cm⁻³ suggests. Parallel close packing of heterocyclic rings is often observed with purines and pyrimidines. An example is 5-fluorouracil.cytosine (Voet & Rich, 1969), which consists of cyclic dimers linked by infinite chains of hydrogen bonds and packed parallel to one another with a spacing of 3.50 Å. Table 5 lists the closest contacts of nonbonded atoms, excluding hydrogen. None of these contacts is smaller than the sum of the van der Waals radii. Fig. 4 shows an ellipsoidal representation of atomic thermal vibration (75% probability).

Confirmation of the presence of hydrogen bonding in the solid was obtained from its infrared spectrum. The spectra of KBr pellets containing 2-amino-3-chloropyrazine were provided by Dr A. Teass. The N-H stretching band shows three prominent peaks at 3175, 3290, and 3380 cm⁻¹ and has a width of about 400 cm⁻¹. The absorption maxima are very close to those observed by Pimentel & Sederholm (1956) for CH₃NH₂, namely 3196, 3285, and 3340 cm⁻¹. Similarly, the N...N separations of 3.18 and 3.23 Å observed by Atoji & Lipscomb (1953) for CH₃NH₂ are very near the values of 3.178 (8) and 3.275 (7) Å found in 2-amino-3-chloropyrazine. The spectral features of the molecules that are hydrogen-bonded in

the solid offer the expected contrast with those molecules free from such bonding. Infrared spectra of the compound in dilute CHCl₃ solution were provided by Dr R. Rieke. The N-H stretching band shows peaks at 3415 and 3518 cm⁻¹. These are close to the 3395 cm⁻¹ symmetric and 3480 cm⁻¹ asymmetric N-H stretching frequencies observed for aniline in dilute CCl₄ solution (Fuson, Josien, Powell & Utterback, 1952). The presence of three prominent absorption maxima in the solid as opposed to two for the solution, the greatly enhanced intensity and band width, along with the shift of the peaks to somewhat lower frequencies in the solid are typical indications of hydrogen bonding (Hamilton & Ibers, 1968).

The empirical equation of Pimentel & Sederholm (1956), $\Delta\nu_s = 1.05 \times 10^3 (3.38 - R) \text{ cm}^{-1}$, where *R* is the

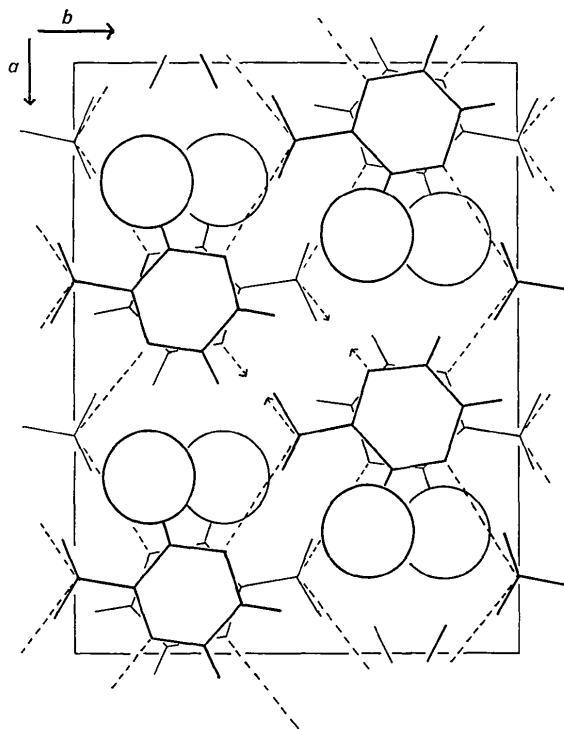


Fig. 3. Unit-cell contents, viewed down the *c* axis.

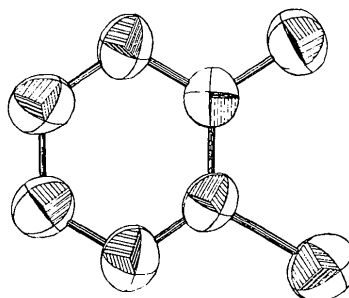


Fig. 4. Thermal vibration ellipsoids scaled to enclose 75% probability. Atoms are identified in Fig. 1.

Table 5. *Closest contacts of nonbonded atoms, excluding hydrogen*

E.s.d.'s in parentheses refer to the last significant digit.

	Distance, Å	Sum of van der Waals radii, Å
Cl, N(2)	3·489 (7)	3·3
Cl, N(4)	3·559 (5)	3·3
Cl, Cl	4·040 (4)	3·6
C(2), N(4)	3·39 (1)	3·3
C(2), C(5)	3·59 (1)	3·6
C(3), N(4)	3·64 (1)	3·3
C(3), C(3)	3·68 (1)	3·6
C(5), N(1)	3·38 (1)	3·3
C(5), N(2)	3·82 (1)	3·3
C(6), N(1)	3·61 (1)	3·3
C(6), C(6)	3·70 (1)	3·6
N(2), N(4)	3·79 (1)	3·0

N···N separation in a N-H···N hydrogen bond and $\Delta\nu_s$ is the difference between mean values of the N-H stretching frequency in the solution and in the solid, gives a satisfactory correlation of the data for 2-amino-3-chloropyrazine. For nitrogen atoms separated by 3·18 Å, the equation predicts a shift of 210 cm⁻¹, which is close to the 183 cm⁻¹ observed shift of the mean frequency from 3465 to 3282 cm⁻¹.

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References

- ATOJI, M. & LIPSCOMB, W. N. (1953). *Acta Cryst.* **6**, 770.
 BROWN, G. M. & MARSH, R. E. (1963). *Acta Cryst.* **16**, 191.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 CLEWS, C. J. B. & COCHRAN, W. (1948). *Acta Cryst.* **1**, 4.
 CLEWS, C. J. B. & COCHRAN, W. (1949). *Acta Cryst.* **2**, 46.
 COX, R. H. & BOTHNER-BY, A. A. (1968a). *J. Phys. Chem.* **72**, 1642.
 COX, R. H. & BOTHNER-BY, A. A. (1968b). *J. Phys. Chem.* **72**, 1646.
 CROMER, D. T. (1957). *J. Phys. Chem.* **61**, 254.
 DAHL, T. & HASSEL, O. (1968). *Acta Chem. Scand.* **22**, 2851.
 FUSON, N., JOSEIN, M. L., POWELL, R. L. & UTTERBACK, E. (1952). *J. Chem. Phys.* **20**, 145.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
 HAMILTON, W. C. & IBERS, J. (1968). *Hydrogen Bonding in Solids*. New York: Benjamin.
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
 HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem, I: The Centrosymmetric Crystal*. ACA Monograph No. 3.
 JEFFREY, G. A. & JONES, D. W. (1956). *Acta Cryst.* **9**, 286.
 KARLE, I. L. & KARLE, J. (1966). *Acta Cryst.* **21**, 849.
 LAI, T. F. & MARSH, R. E. (1967). *Acta Cryst.* **22**, 885.
 McDONALD, F. S. & ELLINGTON, R. C. (1947). *J. Amer. Chem. Soc.* **69**, 1034.
 O'BRIEN, E. J. (1967). *Acta Cryst.* **23**, 92.
 OGAWA, K. & SCHEEL, H. J. (1969). *Z. Kristallogr.* **130**, 405.
 OWSTON, P. G. & ROWE, J. M. (1962). *Acta Cryst.* **15**, 231.
 PIMENTEL, G. C. & SEDERHOLM, C. H. (1956). *J. Chem. Phys.* **24**, 639.
 SIMUNDZA, G., SAKORE, T. D. & SOBELL, H. M. (1970). *J. Mol. Biol.* **48**, 263.
 SINGH, C. (1965). *Acta Cryst.* **19**, 861.
 STEWART, R. G., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 SUTTON, L. E. (1958). *Tables of Interatomic Distances and Configurations in Molecules and Ions*. Special Publication No. 11. London: The Chemical Society.
 TAKAKI, Y., SASADA, Y. & WATANABE, T. (1960). *Acta Cryst.* **13**, 693.
 TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009.
 VOET, D. & RICH, A. (1969). *J. Amer. Chem. Soc.* **91**, 3069.
 VOET, D. & RICH, A. (1970). *Progr. Nucleic Acid Res. Mol. Biol.* **10**, 183.
 VRANKA, R. G. & AMMA, E. L. (1966). *Inorg. Chem.* **5**, 1020.
 WHEATLEY, P. J. (1957). *Acta Cryst.* **10**, 182.