1,2-*trans*-Diaminocyclohexane Hydrobromide

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Abstract. $C_6H_{15}N_2Br$, monoclinic, $P2_1/c$, $a = 7\cdot8818$ (7), $b = 22\cdot337$ (4), $c = 9\cdot5413$ (8) Å, $\beta = 91\cdot628$ (9)°, $Z = 8$, $D_o = 1\cdot56$ (by flotation), $D_c = 1\cdot543$ g cm^{-3}. The final R value was 0·052 for 2559 observed reflections. The two molecules in the asymmetric unit are both hydrogen bonded as dimers to their respective molecules related by centers of symmetry. N$\cdots$N hydrogen-bonded distances are 2·853 (6), 2·923 (5), 2·965 (6), and 3·321 (6) Å. $N^+\cdots Br^-$ hydrogen-bonded distances are 3·390 (4), 3·347 (4), 3·361 (4), and 3·395 (4) Å. The average of the two independent bond lengths for C–N is 1·485 (6) and for $C-N^+$ is 1·509 (6) Å.

Introduction. This compound, described by Einhorn & Bull (1897), was prepared by reaction of equimolar amounts of the diamine and conc. HBr, followed by recrystallization from methanol using ether vapor as a precipitating agent. The intensities were measured at 20°C with a $0\cdot15 \times 0\cdot20 \times 0\cdot25$ mm crystal using a Picker-Nuclear FACS-I diffractometer in θ–2θ scan mode, with 1° min^{-1} scan speed, Cu $K\alpha$ radiation, and a graphite crystal monochromator. All reflections for $5° \le 2\theta \le 125°$ were measured for the $hk\bar{l}$ and $h\bar{k}l$ octants of reciprocal space, with a 20 s count for each background and measurements of three standard reflections every 50 reflections. A total of 2675 unique reflections were measured, of which 2559 were considered as observed with F_{obs} greater than 2·3 standard deviations (counting statistics). The linear absorption coefficient $\mu(\text{Cu } K\alpha) = 69\cdot5$ cm^{-1} gives $\mu R = 0\cdot70$, using $R = 0\cdot1$ mm for the crystal employed. Spherical crystal absorption corrections and standard Lp correction factors were employed. Hydrogen atom scattering factors were those of Stewart, Davidson & Simpson (1965), carbon and nitrogen scattering factors were those of Hanson, Herman, Lea & Skillman (1964), and scattering factors for bromide ion were taken from *International Tables for X-ray Crystallography* (1968). Anomalous dispersion corrections were used for bromide and were those of Cromer & Liberman (1970).* The structure solution for the two molecules in the asymmetric unit was by the heavy-atom method. Isotropic block-diagonal least-squares refinement for the 18 non-hydrogen atoms gave $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0\cdot096$. The positions of the 20 hydrogen atoms bonded to carbon were calculated assuming tetrahedral carbon and a C–H bond length of 1·05 Å, and isotropic refinement of nitrogen atoms and anisotropic refinement of carbon atoms and bromide ions with these fixed hydrogens reduced R to 0·0588. All hydrogen atoms bonded to nitrogen, except for H(N12) and H(N32) were found in two successive difference Fourier syntheses. Further refinement with anisotropic

Table 1(*a*). *The positional* ($\times 10^4$) *and thermal* ($\times 10^4$) *parameters with their standard deviations*

The anisotropic temperature factor is of the form exp $[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	1131 (6)	1094 (2)	1418 (5)	149 (9)	12 (1)	68 (5)	−19 (5)	14 (10)	9 (4)
C(2)	1208 (6)	1144 (2)	−169 (5)	138 (8)	12 (1)	70 (5)	3 (4)	23 (10)	2 (3)
C(3)	2098 (7)	1715 (2)	−626 (5)	193 (10)	12 (1)	81 (6)	−7 (5)	47 (12)	9 (4)
C(4)	1169 (8)	2261 (2)	−54 (6)	223 (12)	14 (1)	102 (6)	18 (6)	22 (14)	1 (4)
C(5)	1065 (8)	2225 (2)	1518 (6)	243 (13)	15 (1)	84 (6)	8 (6)	25 (14)	−6 (4)
C(6)	225 (7)	1643 (2)	1981 (5)	177 (10)	17 (1)	77 (6)	−5 (5)	49 (12)	−9 (4)
C(7)	6311 (6)	996 (2)	4092 (5)	134 (8)	12 (1)	50 (5)	−9 (4)	25 (10)	2 (3)
C(8)	6190 (6)	1012 (2)	5689 (4)	117 (8)	12 (1)	57 (5)	2 (4)	1 (10)	−5 (3)
C(9)	6943 (7)	1596 (2)	6266 (5)	187 (10)	14 (1)	69 (5)	3 (5)	−21 (12)	−13 (4)
C(10)	5958 (8)	2130 (2)	5658 (6)	252 (12)	13 (1)	89 (6)	22 (6)	23 (14)	−20 (4)
C(11)	5966 (8)	2118 (2)	4060 (5)	261 (13)	12 (1)	75 (6)	3 (6)	9 (14)	0 (4)
C(12)	5333 (6)	1520 (2)	3489 (5)	165 (9)	13 (1)	56 (5)	6 (5)	4 (10)	2 (4)
Br(1)	6351 (1)	4218 (0)	4756 (1)	133 (1)	18 (0)	69 (1)	−3 (0)	20 (1)	−3 (0)
Br(2)	1301 (1)	738 (0)	5808 (1)	121 (1)	20 (0)	83 (1)	4 (0)	23 (1)	−3 (0)
N(1)	280 (6)	525 (2)	1772 (5)	205 (9)	13 (1)	104 (6)	−19 (5)	70 (11)	7 (4)
N(2)	2157 (6)	613 (2)	−733 (4)	165 (8)	13 (1)	74 (5)	6 (4)	36 (10)	6 (3)
N(3)	5596 (6)	427 (2)	3521 (4)	180 (8)	12 (1)	71 (4)	−12 (4)	9 (10)	−6 (3)
N(4)	7121 (5)	488 (2)	6347 (4)	125 (7)	14 (1)	64 (4)	3 (4)	−1 (8)	8 (3)

Table 1(b). *The hydrogen atom positional* ($\times 10^3$) *and isotropic thermal parameters* ($\mathring{A}^2$)

	x	y	z	B
H(1)	252 (6)	110 (2)	179 (5)	2·9 (11)
H(2)	2 (5)	113 (2)	−60 (4)	1·4 (8)
H(3)	328 (7)	171 (2)	−22 (6)	3·7 (12)
H(3P)	211 (6)	166 (2)	−170 (5)	2·8 (10)
H(4)	212 (8)	272 (3)	−18 (7)	5·3 (16)
H(4P)	10 (8)	223 (3)	−50 (6)	3·4 (14)
H(5)	222 (7)	228 (2)	198 (5)	2·5 (11)
H(5P)	31 (7)	259 (2)	187 (5)	3·3 (11)
H(6)	37 (7)	160 (3)	302 (6)	4·8 (13)
H(6P)	−101 (7)	170 (2)	165 (6)	3·6 (11)
H(7)	753 (5)	102 (2)	393 (4)	1·1 (8)
H(8)	501 (5)	92 (2)	602 (4)	1·4 (8)
H(9)	686 (6)	153 (2)	727 (5)	2·0 (10)
H(9P)	813 (9)	164 (3)	605 (7)	5·1 (17)
H(10)	489 (7)	212 (3)	607 (6)	3·7 (13)
H(10P)	668 (7)	252 (3)	607 (6)	4·3 (13)
H(11)	519 (7)	250 (3)	362 (6)	3·2 (12)
H(11P)	720 (8)	214 (3)	380 (6)	5·0 (13)
H(12)	399 (7)	148 (2)	369 (6)	3·7 (12)
H(12P)	534 (6)	149 (2)	242 (5)	2·7 (10)
H(N21)	346 (7)	65 (2)	−57 (6)	0·7 (10)
H(N22)	207 (10)	58 (4)	−181 (8)	2·2 (16)
H(N23)	197 (8)	28 (3)	−42 (6)	2·4 (12)
H(N41)	634 (7)	17 (3)	612 (6)	0·8 (11)
H(N42)	816 (7)	56 (2)	618 (6)	0·7 (10)
H(N43)	724 (12)	47 (4)	733 (9)	3·2 (21)
H(N11)	−92 (7)	59 (3)	145 (6)	4·3 (11)
H(N31)	622 (8)	14 (3)	364 (7)	4·8 (15)
H(N32)	523 (7)	46 (3)	254 (6)	5·1 (12)
H(N12)	49 (7)	46 (3)	281 (6)	6·1 (12)
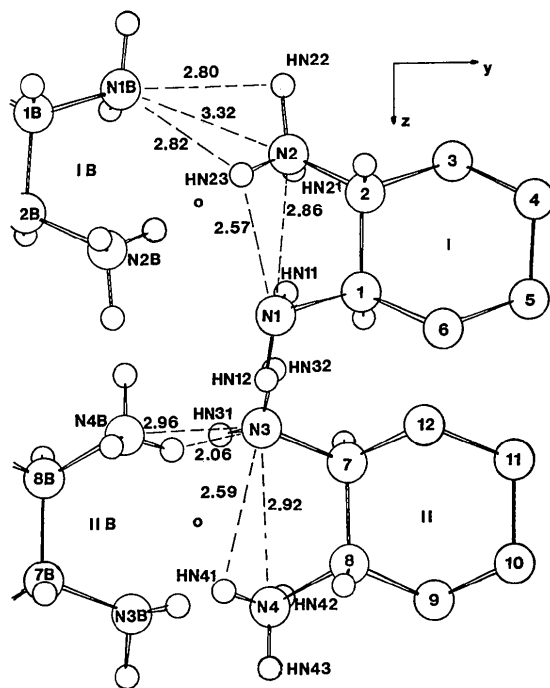
Fig. 1. The two molecules (I and II) in the asymmetric unit, and portions of the nearest neighbor molecules, related by centers of symmetry to I and II. View is in the *x* direction.

treatment for all non-hydrogen atoms and isotropic treatment for the hydrogens was made using an occupancy factor of 0·7 for the three hydrogens on each of the quaternary nitrogen atoms. This occupancy factor was used to compensate for the partial positive charge on each of these hydrogen atoms needed to balance the transfer of electronic charge to chlorine. This charge transfer is implicit in the use of chloride ion scattering factors. The last two hydrogen atoms were located in a final difference synthesis, and further refinement included all 48 atoms. The final R was 0·052 for the 2559 observed reflections and 0·053 when using the full data set of 2675 reflections. Refinement minimized $\sum w(|F_o| - |F_c|)^2$ with $w = (2·20 + 0·279 F_o)^{-1/2}$ chosen to give uniform average values of $w(|F_o| - |F_c|)^2$ over intervals spanning the range of F_o values. Tables 1(a) and 1(b) give the atomic coordinates and thermal parameters. Tables 2, 3, and 4 give interatomic distances, bond angles, and torsion angles. Fig. 1 shows the numbering system and some aspects of the N$\cdots$N–H hydrogen bonding arrangement for the two molecules in the asymmetric unit.

Table 2. *Interatomic distances* ($\mathring{A}$)

N(1)–N(2)	2·853 (6)	N(3)—N(4)	2·923 (5)
C(1)–N(1)	1·482 (6)	C(7)—N(3)	1·487 (6)
C(2)–N(2)	1·509 (6)	C(8)—N(4)	1·510 (6)
C(1)–C(2)	1·521 (6)	C(7)—C(8)	1·530 (6)
C(2)–C(3)	1·527 (7)	C(8)—C(9)	1·528 (7)
C(3)–C(4)	1·531 (8)	C(9)—C(10)	1·528 (8)
C(4)–C(5)	1·507 (8)	C(10)–C(11)	1·525 (8)
C(5)–C(6)	1·530 (8)	C(11)–C(12)	1·522 (7)
C(6)–C(1)	1·527 (7)	C(12)–C(7)	1·507 (7)
N(1)–N(2B)	3·321 (6)	N(3)–N(4B)	2·965 (6)
C——H	1·04 (8) (average)		
N——H	0·94 (12) (average)		

Table 3. *Bond angles* (°)

C(1)–C(2)–C(3)	112·2	C(7)—C(8)—C(9)	110·1
C(2)–C(3)–C(4)	109·6	C(8)—C(9)—C(10)	109·9
C(3)–C(4)–C(5)	110·7	C(9)—C(10)–C(11)	110·5
C(4)–C(5)–C(6)	111·6	C(10)–C(11)–C(12)	111·2
C(5)–C(6)–C(1)	111·8	C(11)–C(12)–C(7)	112·8
C(6)–C(1)–C(2)	108·9	C(12)–C(7)—C(8)	108·4
N(1)–C(1)–C(2)	108·7	N(3)—C(7)—C(8)	110·6
N(1)–C(1)–C(6)	113·0	N(3)—C(7)—C(12)	109·9
N(2)–C(2)–C(1)	109·4	N(4)—C(8)—C(7)	109·5
N(2)–C(2)–C(3)	108·5	N(4)—C(8)—C(9)	110·6

Table 4. *Torsion angles* (°)

C(1)–C(2)–C(3)–C(4)	−58·4	C(7)–C(8)–C(9)–C(10)	60·7
C(2)–C(3)–C(4)–C(5)	56·6	C(8)–C(9)–C(10)–C(11)	−56·9
C(3)–C(4)–C(5)–C(6)	−55·8	C(9)–C(10)–C(11)–C(12)	53·6
C(4)–C(5)–C(6)–C(1)	55·9	C(10)–C(11)–C(12)–C(7)	−55·1
C(5)–C(6)–C(1)–C(2)	−55·4	C(11)–C(12)–C(7)–C(8)	57·4
C(6)–C(1)–C(2)–C(3)	57·6	C(12)–C(7)–C(8)–C(9)	−60·0
N(1)–C(1)–C(2)–C(3)	178·9	N(3)–C(7)–C(8)–C(9)	179·5
N(2)–C(1)–C(2)–C(4)	179·5	N(4)–C(8)–C(9)–C(10)	177·4
N(1)–C(1)–C(2)–N(2)	−58·5	N(3)–C(7)–C(8)–N(4)	58·3
H(N11)–N(1)–C(1)–C(6)	52	H(N31)–N(3)–C(7)–C(12)	165
H(N12)–N(1)–C(1)–C(6)	−71	H(N32)–N(3)–C(7)–C(12)	37

Discussion. The acid salts of carboxylic acids are relatively common, and the occurrence of extremely short hydrogen bonds in some cases, with the proton equally distant from both oxygen atoms, has been of structural interest. This has been discussed most thoroughly in a review by Speakman (1972). However, the preparations of only a few of the basic analogs, *i.e.* basic salts of amines or diamines, have been reported. Structure determinations are rare. One such case is the structure of *o*-phenylenediamine hydrochloride (Stålhandske, 1972). We chose to investigate the compound reported here as part of a program to study the structures of basic amine salts.

The view in the $+x$ direction in Fig. 1 shows that each of the molecules in the asymmetric unit is hydrogen-bonded to an equivalent molecule related by the center of symmetry nearest the nitrogen atoms, at $(0,0,0)$ for molecule I and at $(\frac{1}{2},0,\frac{1}{2})$ for molecule II. The quaternary nitrogen of each molecule is also hydrogen-bonded to two symmetry-unrelated bromide ions. The cyclohexane rings are essentially parallel to the *b* axis and the centers of all bromide ions and nitrogen atoms in the cell are within two 3·5 Å thick slabs centered at $y=0·0$ and $y=0·5$. Br(1) and Br(2) are 4·224 (1) and 4·155 (1) Å, respectively, away from equivalent bromide ions related by the nearest centers of symmetry. These distances are slightly longer than the value of 3·86 Å expected as the sum of ion radii using the value of 1·93 Å for bromide favored by Baughan (1973). The $N^+\cdots Br^-$ distances found for the four non-equivalent $N^+-H\cdots Br^-$ hydrogen bonds are 3·390 (4), 3·347 (4), 3·361 (4), and 3·395 (4) Å and are similar to values previously reported. For example Sobel & Tomita (1962) find 3·36, 3·39 and 3·40 Å for methylcytosine hydrobromide and 3·30 and 3·39 for 9-methylguanine hydrobromide (Sobel & Tomita, 1964).

The C–N bond lengths, 1·482 (6) and 1·487 (6) Å, to the amine nitrogen atoms N(1) and N(3) are significantly shorter than the values of 1·509 (6) and 1·510 (6) found for the bonds to the positive quaternary nitrogen atoms N(2) and N(4). This substantiates the observation of Trefonas & Couvillion (1963) that the C–N$^+$ bond is about 0·03 Å longer than the C–N bond for non-aromatic amines. Larger differences are well known for aromatic amines; for example 0·08 Å in the case of *o*-phenylenediamine hydrochloride (Stålhandske, 1972). The ring C–C bond lengths and angles and the torsion angles for the carbon and nitrogen atoms are in essential agreement with the values obtained for cyclohexylamine hydrochloride (Rao & Sundaralingam, 1969) and for 1,4-*trans*-diaminocyclohexane dihydrochloride (Dunitz & Strickler, 1966). All NH$_3^+$ and NH$_2$ groups have close to staggered conformations with respect to the substituents of the attachment carbon atoms, but the NH$_2$ group of molecule I must be rotated by 120° to make this molecule similar to molecule II (or its mirror image). The difference between the shortest intermolecular N$\cdots$N distance of 2·965 Å for II and the corresponding value of 3·321 for I may readily be understood in terms of the more effective packing of II with its mirror image which is possible for the orientation of the NH$_2$ group involving N(3). The hydrogen-bonded N$\cdots$N distances range from 2·853 to 3·321 Å and are in the 'normal' range for the N–H$\cdots$N system, as summarized by Donohue (1968) and much earlier by Pimentel (1960). There is no evidence for symmetric hydrogen bonds.

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