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A Neutron Diffraction Study of 1,2-Diaminobenzene Monohydrochloride

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The structure of $C_6H_4(NH_2)_2.HCl$ has been refined from single-crystal neutron diffraction data. Full-matrix least-squares calculations based on F^2 converged to a final R of 0·039 for the 782 observed reflexions. The crystals are orthorhombic, space group $P2_12_12_1$, with $a=9{\cdot}312$ (2), $b=4{\cdot}920$ (1), $c=16{\cdot}155$ (3) Å, $Z=4$. The structure is composed of $C_6H_4N_2H_5^+$ and Cl^- ions. Three cations are coordinated to one Cl^- ion through hydrogen bonds $N-H\cdots Cl^-$. All H atoms of the NH_3^+ group and one H of the NH_2 group are involved in hydrogen bonds.

The structures of 1,2-diaminobenzene monohydrochloride, dihydrochloride and dihydrobromide have been solved from X-ray data (Stålhandske, 1972*a*, *b*, 1974). Only approximate positions of the H atoms were obtained for the monohydrochloride and dihydrobromide. Neutron diffraction studies were therefore performed in order to determine the H positions and to reveal the hydrogen-bonding systems. The present article deals with the structure of the monohydrochloride.

Experimental

Large colourless crystals were grown, by slow evaporation at room temperature, from an aqueous solution containing equimolar quantities of 1,2-diaminobenzene and HCl.

Crystal data

1,2-Diaminobenzene monohydrochloride, $C_6H_4N_2H_5^+Cl^-$, F.W. 144·60, orthorhombic, $P2_12_12_1$, $a=9{\cdot}312$ (2), $b=4{\cdot}920$ (1), $c=16{\cdot}155$ (3) Å, $V=740{\cdot}13$ Å^3, $Z=4$, $D_x=1{\cdot}30$, $D_m=1{\cdot}31$ g cm^{-3} (flotation). Cell parameters were determined from powder photographs taken in a Guinier–Hägg focusing camera with Cu $K\alpha_1$ radiation and KCl as an internal standard.

A crystal, $3{\cdot}5\times3{\cdot}5\times4{\cdot}0$ mm, packed in thin Al foil, was used for data collection. The crystal was mounted with **b** parallel to the φ axis on an automatic Hilger–Ferranti four-circle diffractometer, located at the DR3 reactor at the Danish Atomic Energy Commission Research Establishment, Risø, Denmark. The wavelength of the monochromatized neutron beam was 1·025 Å and the flux at the specimen $0{\cdot}9\times10^6$ n cm^{-2} s^{-1}. The reflexions were measured by the ω-scan and the step-scan technique.

The total scan range for a reflexion was 3·36° with the peak-scan (2·40°) in steps of 0·04° and background scans (0·48°) in steps of 0·08°. In the range $0{\cdot}07<\sin\theta/\lambda<0{\cdot}618$, 1916 reflexions were recorded in sequence of increasing $\sin\theta/\lambda$. A standard reflexion, 321, was measured after every 15 reflexions. Background corrections were made (Lehmann & Larsen, 1974). The peak is separated from the background in such a way that $\sigma(I)/I$ is minimized, where I is the integrated intensity and $\sigma(I)$ its e.s.d. based on counting statistics. Squared structure amplitudes were obtained as $F_o^2 = I \sin 2\theta$ and were corrected for absorption by Gaussian numerical integration. The crystal shape was described by six boundary planes. The linear absorption coefficient was calculated to be 2·0 cm^{-1}, assuming a value of 34 b for the incoherent scattering cross-section for H and with the values of (μ/ϱ) for Cl, N, C in *International Tables for X-ray Crystallography* (1962). The resulting transmission factors fall in the range 0·50–0·56. After averaging symmetry-related reflexions, 824 independent reflexions remained. Of these, 42 were considered unobserved and deleted in the refinement [these had $F^2 < 2\sigma_c(F^2)$, where $\sigma_c(F^2)$ is based on counting statistics].

Structure refinement

The final coordinates for the heavy atoms taken from the X-ray study (Stålhandske, 1972*a*) were used as starting parameters in a least-squares refinement. A subsequent difference synthesis revealed the positions of the nine H atoms in the protonated molecule. Finally all atoms were refined with anisotropic thermal parameters together with a scale factor and a parameter to correct for isotropic secondary extinction (Zachariasen, 1967). The function minimized was $\sum w_i(F_o^2 - |F_c|^2)^2$; weights were $w_i^{-1} = \sigma_c^2(F_o^2) + (0{\cdot}015F_o^2)^2$. The value of $S = [\sum w_i|F_o^2 - |F_c|^2|^2/(m-n)]^{1/2}$, where m is the total number of observations and n the number of parameters varied, was 2·12. The final $R(F^2) = \sum|F_o^2 - |F_c^2||/\sum F_o^2 = 0{\cdot}039$ and $R_w(F^2) = [\sum w|F_o^2 - |F_c|^2|^2/\sum wF_o^4] = 0{\cdot}053$; the extinction parameter $g = 1{\cdot}08\ (5) \times 10^4$.

The coherent scattering amplitudes used, in units of 10^{-12} cm, for Cl, N, C and H were 0·96, 0·94, 0·665 and −0·374 respectively (Bacon, 1972). The final positional parameters are given in Table 1* and the anisotropic thermal parameters with r.m.s. components in Table 2. A short account of the programs used has been given (Stålhandske, 1974).

Table 1. *Atomic fractional coordinates* ($\times 10^5$)

For the numbering of the atoms see Fig. 1.

	x	y	z
Cl	6506 (13)	850 (30)	49802 (9)
N(1)	24812 (17)	51448 (34)	43372 (9)
N(2)	41084 (17)	94754 (37)	36763 (12)
C(1)	24673 (19)	57125 (35)	34501 (11)
C(2)	15853 (23)	41838 (46)	29454 (13)
C(3)	14945 (24)	47630 (56)	21061 (14)
C(4)	23057 (26)	68965 (53)	17892 (14)
C(5)	32033 (24)	84214 (49)	23011 (12)
C(6)	32961 (18)	78578 (38)	31473 (12)
H(2)	9654 (52)	25340 (110)	32127 (33)
H(3)	8269 (65)	35830 (130)	17005 (33)
H(4)	22215 (63)	74190 (130)	11387 (29)
H(5)	38100 (54)	101020 (130)	20476 (30)
H(11)	18990 (52)	33910 (100)	44720 (28)
H(12)	20009 (52)	67430 (100)	46504 (27)
H(13)	35164 (42)	48820 (100)	45680 (22)
H(21)	45770 (53)	85770 (110)	41517 (34)
H(22)	47975 (54)	107210 (120)	33852 (36)

Description and discussion of the structure

The structure is built up of $C_6H_4N_2H_5^+$ and Cl^- ions. The protonated molecule with the atoms numbered according to Table 1 is shown in Fig. 1, and selected bond lengths and angles in Fig. 2.

In the benzene ring the weighted average C–C length is 1·391 (2) and the average C–H distance 1·083 (3) Å. These values are in good agreement with those found in the neutron diffraction work on L-tyrosine [1·393 (1), 1·085 (2)] and L-tyrosine hydrochloride [1·391 (1), 1·086 (3) Å] (Frey, Koetzle, Lehmann & Hamilton,

Table 2. *Thermal parameters*

The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$. The β values have been multiplied by 10^4 and the r.m.s. components (R_i) by 10^3.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Cl	93 (2)	318 (6)	38 (1)	−15 (3)	20 (1)	7 (2)	168 (3)	202 (2)	248 (2)
N(1)	75 (2)	270 (6)	30 (1)	−8 (3)	1 (1)	21 (2)	164 (3)	183 (3)	214 (3)
N(2)	91 (2)	341 (7)	47 (1)	−52 (4)	−6 (1)	29 (2)	167 (3)	213 (3)	264 (3)
C(1)	59 (2)	228 (7)	28 (1)	6 (4)	−1 (1)	10 (2)	157 (3)	167 (4)	197 (3)
C(2)	89 (3)	302 (10)	37 (1)	5 (4)	−9 (1)	−5 (2)	189 (3)	192 (3)	229 (3)
C(3)	132 (3)	431 (1)	35 (1)	45 (6)	−18 (1)	−20 (3)	194 (3)	213 (4)	273 (4)
C(4)	131 (3)	502 (11)	28 (1)	89 (5)	−1 (1)	4 (3)	190 (4)	198 (4)	283 (4)
C(5)	99 (3)	412 (11)	32 (1)	44 (5)	15 (1)	36 (3)	173 (4)	191 (3)	264 (4)
C(6)	63 (2)	274 (8)	31 (1)	10 (4)	5 (1)	23 (2)	164 (3)	165 (3)	219 (3)
H(2)	146 (6)	499 (25)	64 (3)	−93 (12)	−12 (4)	1 (7)	200 (7)	280 (7)	303 (7)
H(3)	216 (9)	729 (33)	56 (2)	−19 (15)	−41 (4)	−34 (8)	218 (8)	305 (8)	343 (7)
H(4)	249 (10)	913 (36)	33 (3)	106 (18)	−4 (4)	20 (7)	204 (6)	296 (8)	368 (8)
H(5)	175 (7)	688 (31)	54 (2)	2 (16)	23 (3)	83 (8)	197 (8)	279 (7)	340 (7)
H(11)	130 (6)	417 (20)	46 (2)	−46 (10)	3 (3)	35 (6)	191 (7)	246 (6)	270 (6)
H(12)	134 (7)	424 (20)	36 (2)	16 (10)	10 (3)	13 (5)	206 (6)	225 (6)	256 (6)
H(13)	110 (5)	508 (22)	37 (2)	3 (10)	−8 (2)	33 (6)	195 (6)	226 (6)	266 (6)
H(21)	153 (7)	551 (27)	57 (2)	−95 (12)	−26 (4)	30 (7)	209 (7)	245 (7)	326 (7)
H(22)	152 (7)	572 (27)	77 (3)	−125 (14)	−3 (4)	51 (8)	192 (9)	291 (7)	342 (7)

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* A list of neutron structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31834 (5pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

1973). The corresponding C–C values for 1,2-diaminobenzene (Stålhandske, 1976) and 1,2-diaminobenzene dihydrochloride (Stålhandske, 1974) are 1·391 (1) and 1·383 (1) Å respectively. Three least-squares planes (Table 3) show that both N atoms deviate from the plane through the benzene ring.

Table 3. *Deviations from least-squares planes through the molecule* (Å × 10^3)

The following atoms were used to define the planes: Plane I C(1) → C(6); Plane II C(1) → C(6), H(2) → H(5); Plane III N(1), N(2), C(1) → C(6), H(2) → H(5).

	Plane I	Plane II	Plane III
N(1)	−72	−82	−34
N(2)	−88	−82	−33
C(1)	−2	−5	25
C(2)	2	−4	10
C(3)	1	2	3
C(4)	−3	6	2
C(5)	3	15	27
C(6)	−1	4	35
H(2)	4	−9	5
H(3)	17	17	−1
H(4)	−37	−22	−40
H(5)	−21	−3	9
H(11)	27	10	57
H(12)	−997	−1008	−952
H(13)	669	659	717
H(21)	383	386	445
H(22)	92	104	151

The C–NH_3^+ length, 1·460 (3), is in good agreement with values found in the following related compounds: 1·457 (2) in 1,2-diaminobenzene dihydrochloride, 1·474 (9) in *o*-aminophenol hydrochloride (Cesur & Richards, 1965) and 1·461 (4) Å in 3-aminobenzoic acid hydrochloride (Arora, Sundaralingam, Dancz, Stanford & Marsh, 1973). These reported C–NH_3^+ lengths are, however, shorter than the value 1·487 given by Marsh & Donohue (1967) as the average value in zwitterionic amino acids and the value 1·501 Å found in the zwitterionic molecule of anthranilic acid (Brown, 1968).

The C–NH_2 distance of 1·391 (3) can be compared with 1·384 (4) found in 3-aminopyridine (Chao, Schempp & Rosenstein, 1975), 1·407 (2) found in 1,2-diaminobenzene, and 1·370 Å found in the neutral anthranilic acid molecule (Brown, 1968).

The Cl^- ion is the only hydrogen-bond acceptor. All three H atoms of the NH_3^+ group are donated to Cl^- ions. The H···Cl distances vary between 2·12 and 2·16 Å (Table 4). The mean of the N–H distances in the NH_3^+ group, 1·040 Å, is close to the values found in amino acids with N–H···Cl hydrogen bonds (Lehmann, 1974). In the NH_2 group only one of the H atoms is involved in a hydrogen bond, a very weak one with a H···Cl distance of 2·49 Å. As the sum of the angles about the amino N is 342·4°, this atom is closer to sp^3 than sp^2 hybridized. The mean N–H distance, 0·996, can be compared with the mean of 1·000 Å found in L-arginine dihydrate (Lehmann, Verbist, Hamilton & Koetzle, 1973), where the N atom of the amino group is sp^3 hybridized and both the amino H atoms are free from hydrogen bonds. The orientations of the H atoms in the NH_2 and NH_3^+ groups are shown in Fig. 3. The angle between the benzene ring and the plane determined by the amino group with its attached C atom is 13°.

Table 4. *Distances* (Å) *and angles* (°) *in hydrogen bonds*

N–H···Cl	N–H	H···Cl	N···Cl	∠N–H···Cl
N(1)–H(11)···Cl	1·042 (5)	2·161 (5)	3·191 (2)	169·3 (4)
N(1)–H(12)···Cl	1·037 (5)	2·137 (5)	3·145 (2)	163·6 (4)
N(1)–H(13)···Cl	1·042 (4)	2·117 (4)	3·153 (2)	172·4 (5)
N(2)–H(21)···Cl	0·988 (6)	2·492 (6)	3·436 (2)	159·8 (5)

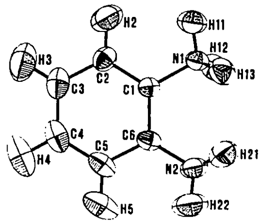

Fig. 1. The cation $C_6H_4N_2H_5^+$ viewed perpendicular to the ring plane. Thermal ellipsoids are drawn to enclose 50% probability.

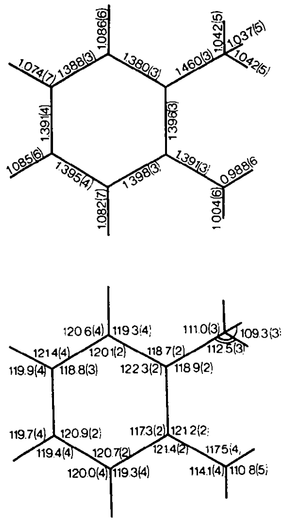

Fig. 2. Distances (Å) and angles (°) in the cation $C_6H_4N_2H_5^+$. Estimated standard deviations are given in parentheses.

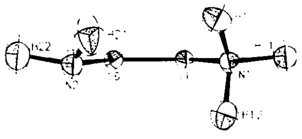

Fig. 3. A perspective drawing of a part of the protonated molecule viewed along the benzene plane, showing the orientations of the hydrogens of the –NH_2 and –NH_3 groups. Thermal ellipsoids are at the 50% probability level.

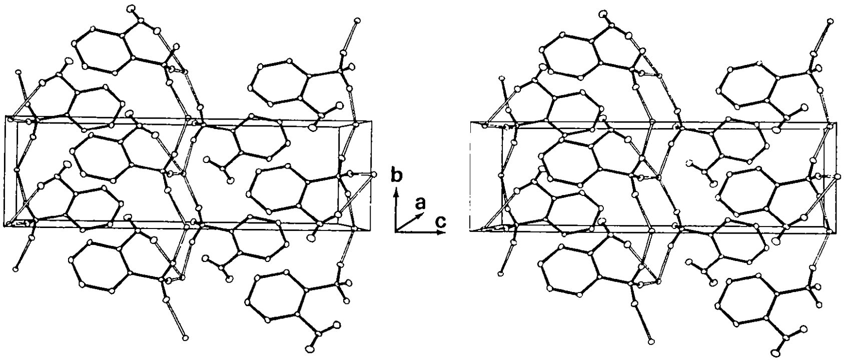

Fig. 4. Stereoscopic illustration of the molecular packing and hydrogen bonding. All carbon hydrogen atoms have been omitted. Covalent bonds are drawn with heavy lines and hydrogen bonds are open.

The hydrogen-bonding network and the molecular packing are shown in Fig. 4. Each Cl^- ion coordinates three cations: two with the NH_3^+ group only and one with a weak bond to the NH_2 group also. The structure is built up of networks of formula ($C_6H_4N_2H_5^+Cl^-$) connected by forces of van der Waals type.

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