

The Crystal Structure of *o*-Phenylenediamine Dihydrobromide

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The crystal structure of *o*-phenylenediamine dihydrobromide has been determined from X-ray single-crystal data and refined by the method of least squares to a final *R*-value of 0.055. The crystals are orthorhombic with two formula units $C_6H_4(NH_2)_2 \cdot 2HBr$ in a unit cell with the dimensions $a = 7.534$, $b = 4.738$, and $c = 12.672$ Å.

The hydrogen atoms of the amino groups have not yet been located. The C-N distance of 1.45 Å found in the structure indicates, however, that the amino groups are protonated. The structure thus consists of cations $C_6H_4(NH_3)_2^{2+}$ and bromide ions. The cations are, with the exception of the amino hydrogens, planar by symmetry and parallel to the *ac*-plane and also linked together *via* hydrogen bonds (N-H...Br).

In aqueous and in alcoholic solutions, *o*-phenylenediamine forms compounds with hydrobromic acid containing one or two bromide ions. This investigation of *o*-phenylenediamine dihydrobromide was started in order to study the packing of *o*-phenylenediamine molecules together with different halide ions. It will be followed by a report on *o*-phenylenediamine hydrochloride, isostructural with *o*-phenylenediamine hydrobromide, $C_6H_4(NH_2)_2 \cdot HBr$.

EXPERIMENTAL

Preparation and analysis. Colourless crystals of *o*-phenylenediamine dihydrobromide in the form of six-edged plates were obtained by dissolving *o*-phenylenediamine in 30 % hydrobromic acid and allowing the solution to evaporate. The crystals were analysed for bromine, nitrogen, carbon, and hydrogen. The results of the analyses were in good agreement with the values calculated for $C_6H_4(NH_2)_2 \cdot 2HBr$. (Found: Br 59.1; N 10.0; C 26.4; H 3.9. Calc.: Br 59.2; N 10.4; C 26.7; H 3.7.)

Single crystal work. Some large crystals were cut to approximate cubes and ground to spheres according to Buerger.¹ An almost spherical crystal with a diameter of 0.25 mm was chosen for the X-ray work. Intensity data were collected for the reflections *h*0*l* - *h*4*l* (433 independent reflections) with an integrating Weissenberg camera using Ni-filtered CuK radiation. The multiple film technique was used, and the relative intensities of the reflections were measured by means of a flying spot integrating microdensitometer. The

intensities were corrected for Lorentz and polarization effects, and an absorption correction was also applied ($\mu R = 1.5$). No correction was made for extinction effects, however.

Cell dimensions and density. The dimensions of the unit cell were determined from powder photographs taken in a Guinier-Hägg focusing camera with $\text{CuK}\alpha_1$ radiation and potassium chloride as an internal standard.

CRYSTAL DATA

$$\begin{array}{ll} a = 7.5341 & (8) \text{ \AA} \\ b = 4.7379 & (6) \text{ \AA} \\ c = 12.6716 & (12) \text{ \AA} \\ V = 452.32 & (8) \text{ \AA}^3 \end{array} \quad \begin{array}{l} D_m = 1.97 \text{ g cm}^{-3} \\ D_x = 1.98 \text{ g cm}^{-3} \\ Z = 2 \end{array}$$

Refinement of the cell parameters was performed with a least-squares program. The density was determined by the flotation method using a bromoform-chloroform solution.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

Space group and atomic positions. The Weissenberg photographs showed systematic extinctions of the reflections $hk0$ with $h+k \neq 2n$, except for one weak reflection, which was probably due to multiple reflection and was therefore deleted from the data. The possible space groups are $Pm2_1n$ (No. 31 with orientation different from that given in the International Tables²) and $Pm\bar{m}n$ (No. 59). The structure determination was started assuming space group $Pm\bar{m}n$ with origin at $\bar{1}$.

From a two-dimensional Patterson projection $P(upw)$ the four bromine atoms were found to occupy twofold point positions. In space group $Pm\bar{m}n$ the twofold point positions are

$$\begin{array}{l} 2(a): (\frac{1}{2}, \frac{1}{4}, z; \frac{3}{4}, \frac{3}{4}, \bar{z}) \\ 2(b): (\frac{1}{2}, \frac{3}{4}, z; \frac{1}{4}, \frac{1}{4}, \bar{z}) \end{array}$$

A least-squares calculation based on the positions of the bromine atoms was now performed, followed by a two-dimensional electron density difference synthesis. This projection clearly revealed all carbon and nitrogen atoms in the organic groups with the atoms located in the point position

$$4(f): (x, \frac{1}{4}, z; \bar{x}, \frac{3}{4}, \bar{z}; \frac{1}{2} - x, \frac{1}{4}, z; \frac{1}{2} + x, \frac{3}{4}, \bar{z})$$

All non-hydrogen atomic positions were thus found using only the $h0l$ data.

Refinement of the structure. The parameters obtained above were now refined by the method of least squares, and the calculations were based on the three-dimensional intensity data. All atoms were at first assigned individual isotropic temperature factors and refined together with inter-layer scale factors, and convergence was reached at an R -value of 0.068. Anisotropic temperature factors were then introduced for the bromine atoms. The positional and thermal parameters of all non-hydrogen atoms were refined together with an overall scale factor; the resulting R -factor was 0.062. Inspection of the structure factors after this calculation showed that five strong low-angle

reflections had much too small observed values. These reflections were therefore excluded in a further refinement, which gave an R -factor of 0.056.

At this stage of refinement the C–N distance was calculated. The resulting value of 1.45 Å indicated that the $-\text{NH}_2$ groups of $\text{C}_6\text{H}_4(\text{NH}_2)_2$ are protonated to $-\text{NH}_3^+$. In the space group used here ($Pm\bar{m}n$) the carbon hydrogen atoms and one of the hydrogen atoms in the $-\text{NH}_3^+$ group must occupy fourfold positions and the other two hydrogen atoms the general eightfold position, if the $-\text{NH}_3^+$ group is not rotating.

Electron density difference sections and bounded projections around $y = \frac{1}{4}$ were computed using data with $\sin\theta/\lambda < 0.35$. In these maps the carbon hydrogen atoms were found, but the hydrogen atoms of the $-\text{NH}_3^+$ group could not be located.

A least-squares refinement in the non-centrosymmetrical space group $Pm\bar{2}_1n$ followed by bounded projections resulted neither in a significantly lower R -value nor in the location of the hydrogen atoms in the NH_3^+ group. The structure was therefore considered to be centrosymmetric.

A final refinement was performed, including the located hydrogen atoms with fixed parameters, which gave an R -factor of 0.055. The least-squares refinements were based on F -values using Cruickshank's weighting scheme with the values 18, 0.02, and 0.0015 for the constants a , c , and d , respectively. Only observed reflections were included in the calculations. The final atomic parameters with standard deviations are given in Table 1a, and in Table 1b the root-mean-square components of thermal vibration along the principal axes of the ellipsoids of the bromine atoms are listed. The observed and calculated structure factors are presented in Table 2.

Table 1a. Final positional and thermal parameters with standard deviations in brackets.

The temperature factor expression used for the bromine atoms was $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$, where $\beta_{12} = \beta_{13} = \beta_{23} = 0$.

Atom	x	y	z	B or β_{11}	β_{22}	β_{33}
Br(1)	$\frac{1}{4}$	$\frac{3}{4}$	0.5303 (1)	0.0147 (3)	0.0348 (8)	0.0043 (1)
Br(2)	$\frac{1}{4}$	$\frac{1}{4}$	0.2630 (1)	0.0124 (3)	0.0326 (8)	0.0054 (1)
N	0.0519 (11)	$\frac{1}{4}$	0.6694 (6)	3.3 (1)		
C(1)	0.1575 (11)	$\frac{1}{4}$	0.7646 (6)	2.3 (1)		
C(2)	0.0663 (13)	$\frac{1}{4}$	0.8607 (7)	3.0 (1)		
C(3)	0.1589 (13)	$\frac{1}{4}$	0.9550 (7)	3.1 (2)		
H(2)	-0.075	$\frac{1}{4}$	0.855	4.0		
H(3)	0.110	$\frac{1}{4}$	1.025	4.0		

Table 1b. Root-mean-square components, R_i (Å), of thermal displacements along principal axes of the ellipsoids of vibration.

Atom	R_1	R_2	R_3
Br(1)	0.206	0.186	0.199
Br(2)	0.209	0.189	0.193

Table 2. Observed and calculated structure factors for *o*-phenylenediamine dihydrobromide. Reflections marked with an asterisk were excluded in the final refinement.

H	K	L	F _{obs}	F _{calc}	H	K	L	F _{obs}	F _{calc}	H	K	L	F _{obs}	F _{calc}	H	K	L	F _{obs}	F _{calc}
0	0	2	28.1	21.2	8	0	8	7.3	8.1	7	1	6	21.0	20.0	7	2	3	24.5	24.1
0	0	3	19.9	23.2	9	0	1	9.7	8.8	7	1	7	13.2	12.7	7	2	4	17.2	17.3
0	0	4	77.2	90.7	9	0	3	13.5	14.6	7	1	8	9.3	9.8	7	2	6	6.2	6.8
0	0	5	52.0	53.6	9	0	4	7.8	8.5	7	1	9	10.9	10.7	7	2	7	19.6	19.8
0	0	6	10.0	9.4						8	1	1	24.1	22.2	7	2	8	17.2	16.1
0	0	7	6.8	8.0	0	1	1	10.8	12.0	8	1	2	8.0	6.3	8	2	0	21.1	19.7
0	0	8	29.8	30.1	0	1	2	51.8	45.1	8	1	3	6.8	5.9	8	2	1	13.7	13.0
0	0	10	41.2	40.8	0	1	3	33.6	26.5	8	1	5	16.8	17.5	8	2	3	10.0	6.2
0	0	11	11.1	12.2	0	1	4	40.3	34.9	8	1	6	17.7	16.8	8	2	4	23.5	21.4
0	0	14	21.8	20.2	0	1	5	81.1	63.7	9	1	2	21.7	20.0	8	2	5	8.6	8.5
0	0	15	21.2	21.4	0	1	6	62.0	61.0	9	1	3	12.6	11.6	8	2	6	7.9	7.7
0	0	16	6.9	8.6	0	1	8	12.8	12.7	9	1	4	6.0	5.6	9	2	1	7.9	7.3
1	0	1	17.9	18.1	0	1	9	40.3	37.9										
1	0	3	73.2	86.8	0	1	10	56.4	55.7	0	2	1	33.8	34.6	1	3	0	16.1	18.9
1	0	4	45.9	44.7	0	1	11	15.3	14.4	0	2	2	18.1	13.5	1	3	1	34.6	36.9
1	0	5	7.4	7.1	0	1	12	8.3	7.7	0	2	3	20.7	18.3	1	3	2	63.2	65.6
1	0	6	8.2	11.2	0	1	13	18.9	17.3	0	2	4	70.7	67.7	1	3	3	37.2	37.0
1	0	7	67.1	72.3	0	1	14	15.8	15.4	0	2	5	43.0	40.1	1	3	4	12.4	11.2
1	0	8	54.7	55.6	1	1	0	49.5	45.7	0	2	6	10.8	9.1	1	3	5	6.4	6.5
1	0	9	19.5	17.5	1	1	1	62.7	71.0	0	2	7	7.3	6.4	1	3	6	33.9	34.8
1	0	11	30.6	29.6	1	1	2	82.6	113.9	0	2	8	24.1	24.3	1	3	7	15.4	15.2
1	0	12	34.7	35.0	1	1	3	62.2	65.8	0	2	9	6.6	6.7	1	3	8	16.9	16.3
1	0	14	9.1	10.5	1	1	4	21.4	20.5	0	2	10	35.9	32.9	1	3	9	14.1	14.4
2	0	0	78.5	101.0	1	1	5	14.1	11.2	0	2	11	9.9	10.3	1	3	10	10.4	10.4
2	0	1	47.9	54.9	1	1	6	54.1	54.4	0	2	14	18.7	16.7	1	3	12	14.4	14.4
2	0	2	8.3	5.9	1	1	7	27.0	22.8	0	2	15	16.5	17.7	1	3	13	16.5	16.4
2	0	3	37.1	34.3	1	1	8	26.5	24.3	1	2	1	20.3	18.1	2	3	1	42.0	43.3
2	0	4	90.0	102.5	1	1	9	20.7	20.0	1	2	2	4.5	3.1	2	3	2	19.1	18.9
2	0	5	29.7	32.1	1	1	10	32.1	15.8	1	2	3	63.6	63.6	2	3	3	11.2	10.7
2	0	6	37.2	34.5	1	1	12	21.6	21.1	1	2	4	37.9	34.7	2	3	4	9.9	8.1
2	0	8	27.6	26.6	1	1	13	24.0	24.1	1	2	5	5.5	4.0	2	3	5	34.7	33.9
2	0	9	19.6	18.8	1	1	14	4.9	5.9	1	2	6	9.4	9.3	2	3	6	40.2	39.7
2	0	10	23.9	22.9	1	1	15	5.0	4.2	1	2	7	55.6	57.0	2	3	7	7.1	6.4
2	0	11	27.4	28.2	2	1	1	69.5	77.0	1	2	8	44.5	44.5	2	3	8	9.8	9.4
2	0	14	18.5	18.1	2	1	2	35.9	32.9	1	2	9	14.6	13.9	2	3	9	30.0	30.7
2	0	15	14.3	15.4	2	1	3	16.8	16.1	1	2	11	25.5	24.3	2	3	10	25.0	23.9
3	0	1	57.6	62.3	2	1	4	11.1	12.6	1	2	12	28.7	28.9	2	3	13	11.4	11.2
3	0	2	8.6	9.5	2	1	5	45.3	49.3	1	2	15	5.4	4.1	3	3	0	11.0	11.7
3	0	3	60.3	65.7	2	1	6	61.4	63.5	2	2	0	60.3	76.2	3	3	1	22.8	23.2
3	0	4	46.7	49.3	2	1	7	12.7	11.1	2	2	1	41.7	40.8	3	3	2	46.5	49.3
3	0	5	10.5	8.6	2	1	8	15.9	15.1	2	2	3	26.4	25.4	3	3	3	26.5	26.8
3	0	6	12.2	10.8	2	1	9	44.1	46.0	2	2	4	71.8	75.8	3	3	4	10.9	10.8
3	0	7	52.3	53.3	2	1	10	34.5	35.1	2	2	5	26.4	26.1	3	3	5	7.6	7.4
3	0	8	42.4	44.0	2	1	13	17.6	16.4	2	2	6	25.8	25.8	3	3	6	32.3	33.5
3	0	10	12.6	13.1	2	1	14	19.0	18.0	2	2	8	21.8	21.5	3	3	7	14.5	14.0
3	0	11	31.6	31.9	3	1	0	26.3	25.4	2	2	9	15.3	15.0	3	3	8	13.2	12.5
3	0	12	22.0	21.6	3	1	1	34.7	37.3	2	2	10	19.0	18.9	3	3	9	16.0	15.5
3	0	15	5.7	5.6	3	1	2	68.6	70.1	2	2	11	23.2	23.0	3	3	11	7.0	7.0
4	0	0	63.8	69.4	3	1	3	39.2	40.7	2	2	14	15.7	15.1	3	3	12	12.2	12.1
4	0	1	49.4	52.1	3	1	4	19.4	17.3	3	2	1	44.5	45.3	3	3	13	13.3	15.0
4	0	3	22.4	21.1	3	1	5	11.4	12.5	3	2	2	7.9	7.6	4	3	1	31.8	33.0
4	0	4	52.1	51.2	3	1	6	48.8	52.5	3	2	3	48.7	51.1	4	3	2	9.6	8.8
4	0	5	39.2	36.6	3	1	7	22.0	21.3	3	2	4	38.3	37.8	4	3	3	11.6	11.6
4	0	7	12.0	10.4	3	1	8	18.2	18.8	3	2	5	5.9	5.5	4	3	4	8.0	7.9
4	0	8	19.1	18.2	3	1	9	23.0	23.4	3	2	6	9.1	8.8	4	3	5	39.6	41.2
4	0	9	9.7	9.9	3	1	11	9.7	9.9	3	2	7	40.6	43.3	4	3	6	22.4	22.8
4	0	10	15.1	15.0	3	1	12	18.4	17.6	3	2	8	34.5	36.0	4	3	8	6.0	5.7
4	0	11	23.8	24.7	3	1	13	21.8	21.7	3	2	10	10.8	10.6	4	3	9	26.3	27.1
4	0	14	12.9	12.6	3	1	14	5.2	6.2	3	2	11	26.4	26.2	4	3	10	19.0	19.1
5	0	1	25.7	24.8	3	1	15	5.1	4.5	3	2	12	18.2	17.8	5	3	1	13.4	13.6
5	0	2	13.2	12.4	4	1	1	46.0	51.5	3	2	14	4.7	4.5	5	3	2	37.8	39.9
5	0	3	49.7	50.6	4	1	2	12.5	12.7	4	2	0	50.2	55.7	5	3	3	21.2	20.7
5	0	4	26.5	27.0	4	1	3	16.0	17.4	4	2	1	36.8	39.9	5	3	6	13.1	13.0
5	0	5	24.4	22.8	4	1	4	12.7	12.5	4	2	3	16.1	16.6	5	3	7	16.8	15.6
5	0	6	21.7	21.9	4	1	5	56.4	62.8	4	2	4	40.0	41.5	5	3	8	8.6	9.2
5	0	7	46.7	45.3	4	1	6	32.3	34.3	4	2	5	28.8	29.1	5	3	9	7.8	7.5
5	0	8	34.8	34.1	4	1	8	9.6	8.6	4	2	6	7.5	7.1	6	3	1	20.9	21.3
5	0	11	19.4	19.8	4	1	9	38.2	39.8	4	2	7	9.9	8.6	6	3	2	7.6	7.8
5	0	12	18.8	17.9	4	1	10	29.0	28.3	4	2	8	15.4	14.9	6	3	3	10.9	10.0
6	0	0	50.1	48.7	4	1	13	12.3	11.8	4	2	9	8.9	8.3	6	3	5	31.4	32.5
6	0	1	30.9	29.5	4	1	14	12.6	11.6	4	2	10	12.1	12.3	6	3	6	12.8	12.0
6	0	3	18.3	16.5	5	1	1	18.7	19.8	4	2	11	19.8	20.5	6	3	8	4.1	4.7
6	0	4	28.7	28.2	5	1	2	52.7	61.2	5	2	1	19.9	20.5	6	3	9	15.6	17.8
6	0	5	27.2	25.6	5	1	3	31.4	31.8	5	2	2	9.7	9.4	7	3	1	10.6	9.7
6	0	7	11.4	11.7	5	1	4	7.8	7.6	5	2	3	37.9	41.0	7	3	2	22.4	22.5
6	0	8	16.3	14.4	5	1	6	18.7	19.0	5	2	4	20.5	22.2	7	3	3	11.6	11.0
6	0	9	7.7	6.8	5	1	7	22.8	22.6	5	2	5	20.0	18.3	7	3	6	13.6	13.7
6	0	10	11.0	11.0	5	1	8	13.0	13.3	5	2	6	17.3	17.7	7	3	7	8.4	8.8
6	0	11	16.4	16.2	5	1	9	10.0	10.6	5	2	7	34.1	37.1	8	3	1	14.9	15.4
7	0	1	24.8	24.0	5	1	12	16.8	15.8	5	2	8	26.8	27.8	8	3	2	5.4	4.2
7	0	3	30.9	29.1	5	1	13	16.1	16.5	5	2	11	16.2	16.5	8	3	3	3.1	4.2
7	0	4	22.0	21.1	6	1													

Table 1. Continued.

H	K	L	FOBS	FCALC	H	K	L	FOBS	FCALC	H	K	L	FOBS	FCALC	H	K	L	FOBS	FCALC
0	3	14	9.3	10.8	1	4	8	25.4	24.4	3	4	3	28.2	27.4	5	4	1	12.8	12.1
0	4	1	15.0	19.2	1	4	9	7.7	7.7	3	4	4	21.0	19.7	5	4	3	23.3	23.2
0	4	2	6.3	6.5	1	4	11	13.6	13.6	3	4	6	4.8	4.7	5	4	4	12.2	12.5
0	4	3	14.2	10.5	1	4	12	13.8	16.8	3	4	7	23.8	24.2	5	4	5	10.1	10.7
0	4	4	39.3	35.7	2	4	0	41.3	40.8	3	4	8	20.6	20.3	5	4	6	9.7	10.0
0	4	5	21.5	20.5	2	4	1	20.5	21.1	3	4	10	4.5	5.8	5	4	7	20.2	21.0
0	4	6	8.6	6.6	2	4	3	12.7	12.5	3	4	11	12.5	14.9	5	4	8	15.2	15.4
0	4	7	4.2	3.5	2	4	4	38.5	39.0	4	4	0	30.1	30.5	6	4	0	23.1	21.8
0	4	8	13.6	13.8	2	4	5	15.5	14.5	4	4	1	20.9	20.9	6	4	1	13.3	13.4
0	4	10	18.2	18.6	2	4	6	13.6	13.4	4	4	3	8.7	8.8	6	4	3	6.8	7.4
0	4	11	6.3	5.5	2	4	7	4.3	2.3	4	4	4	23.5	22.9	6	4	4	13.0	12.8
1	4	1	11.0	11.4	2	4	8	11.9	12.0	4	4	5	16.0	16.0	6	4	5	10.4	12.1
1	4	3	34.8	32.6	2	4	9	7.9	6.3	4	4	6	4.2	4.0	7	4	1	10.7	11.6
1	4	4	21.0	18.7	2	4	10	16.9	10.8	4	4	7	5.8	5.2	7	4	3	12.8	13.9
1	4	6	6.2	4.8	2	4	11	13.0	13.0	4	4	8	7.5	8.4					
1	4	7	30.9	30.7	3	4	1	23.0	23.1	4	4	9	4.6	4.9					
					3	4	2	4.7	4.5	4	4	10	5.7	6.9					

Computer programs. Most calculations were performed on the computers CDC 3600 in Uppsala and UNIVAC 1108 in Lund, using programs briefly described by Liminga.³

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of *o*-phenylenediamine dihydrobromide consists of cations $C_6H_4(NH_3)_2^{2+}$ and bromide ions. The cations are planar by symmetry and parallel to the *ac*-plane, with the exception of the amino hydrogens. The non-hydrogen atoms in one unit cell are shown in Fig. 1. A projection of the structure along [010] is given in Fig. 2.

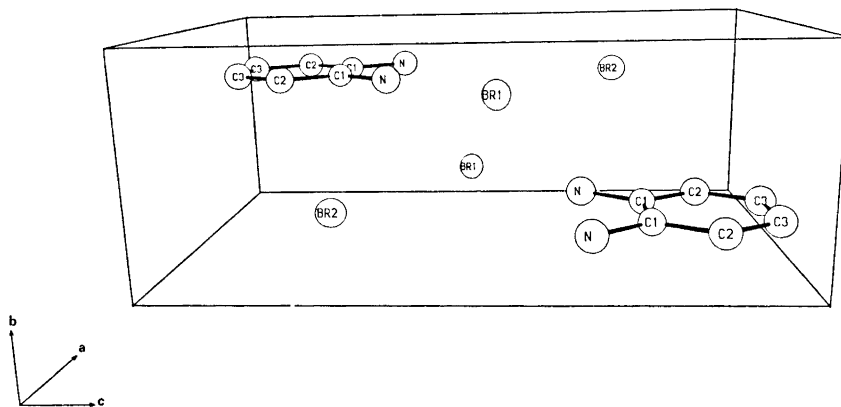


Fig. 1. The non-hydrogen atoms in the unit cell.

The distances and angles in the aromatic molecules (Fig. 3 and Table 3) are normal, even if the C_1-C_1-N angle of 123.4° is somewhat greater than expected. The $C-NH_3^+$ distance of 1.445 Å (Table 3) is significantly longer than the expected value of 1.37 Å for an aromatic $C-NH_2$ bond, but nearly equal to that found in related compounds of aromatic amines (1.455 Å in *m*-tolidine dihydrochloride,⁴ 1.474 Å in *o*-aminophenol hydrochloride,⁵ 1.49 Å

Table 3. Distances(Å) and angles(°) with estimated standard deviations in *o*-phenylenediamine dihydrobromide.

Distances and angles found within the aromatic molecule.

N - C(1)	1.445(11)	N - C(1) - C(1)	123.4(5)
C(1) - C(1)	1.393(17)	C(1) - C(1) - C(2)	119.4(5)
C(1) - C(2)	1.399(12)	C(1) - C(2) - C(3)	120.3(9)
C(2) - C(3)	1.383(13)	C(2) - C(3) - C(3)	120.3(6)
C(3) - C(3)	1.372(19)		
C(2) - H(2)	1.07	C(1) - C(2) - H(2)	116
C(3) - H(3)	0.96	C(2) - C(3) - H(3)	127

Bromine to nitrogen distances and corresponding angles.

Br(1) - 4 N	3.308(6)		
- 2 N	3.402(8)		
Br(2) - 4 N	3.394(6)		
N - 2 Br(1)	3.308(6)	C(1) - N - Br(1)	101.3(4)
- Br(2)	3.394(6)	C(1) - N - Br(2)	99.1(4)
- 2 Br(1)	3.402(8)	C(1) - N - Br(1)	171.5(6)

Possible bromine to hydrogen distances and corresponding angles.

Br(1) - 4 H(12)	2.30	Br(1) - H(12) - N	160
- 2 H(11)	3.05	Br(1) - H(11) - N	100
Br(2) - 4 H(11)	2.75	Br(2) - H(11) - N	120

in *p*-phenylenediamine dihydrochloride,⁶ and 1.47 Å in *p*-phenylenediamine dihydrobromide⁷). The crystal structure of anthranilic acid⁸ contains both neutral molecules with C-NH₂ distances of 1.370 Å and zwitterions with C-NH₃⁺ distances of 1.501 Å.

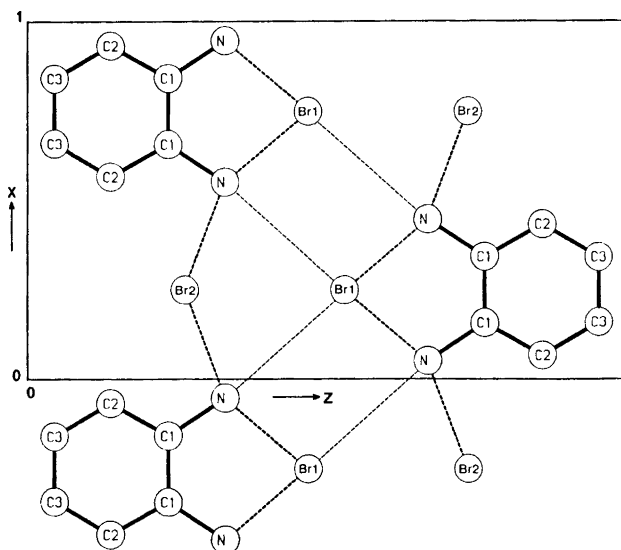


Fig. 2. A projection of the structure along [010]. Covalent bonds are filled. N - Br distances less than 4.0 Å are drawn with dotted lines. The heavier dotted lines indicate two equal N - Br distances.

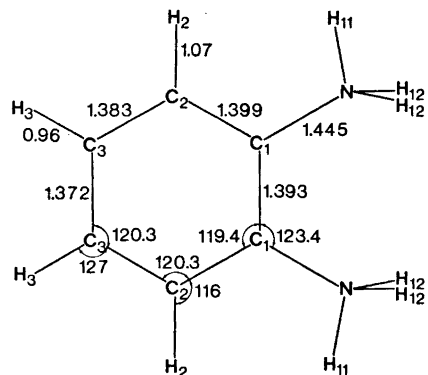


Fig. 3. Bond lengths (Å) and angles (°) in the aromatic molecule with tentative hydrogen atom positions.

The two non-equivalent bromide ions Br(1) and Br(2) in the present structure (Fig. 2) have the point symmetry mm . Their environments are, however, quite different, although both have four neighbouring *o*-phenylenediamine cations. The ion Br(1) is surrounded by four cations $C_6H_4(NH_3)_2^{2+}$ in a tetrahedral arrangement resulting in six short Br–N distances (Fig. 4).

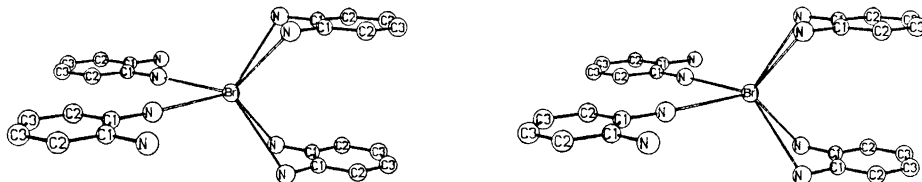


Fig. 4. Stereoscopic view of the environment of the atom Br(1).

Two of the cations have together four equal N–Br(1) distances (3.31 Å), and the other two have each one N–Br(1) distance of 3.40 Å. The ion Br(2) has only one short Br–N contact of 3.39 Å to each of the four surrounding cations (Fig. 5).

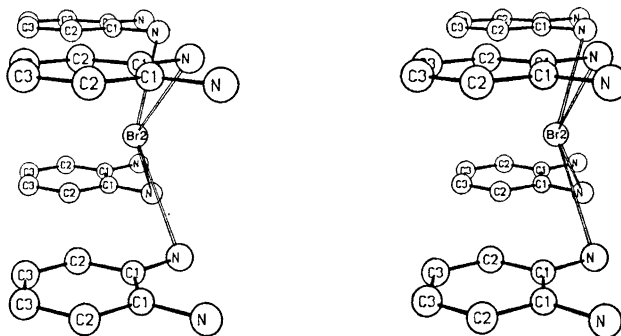


Fig. 5. Stereoscopic view of the environment of the atom Br(2).

The $-\text{NH}_3^+$ groups will thus each have five Br^- ions as close neighbours with the following distances: $\text{N}-2\text{Br}(1)$ 3.31 Å, $\text{N}-\text{Br}(1)$ 3.40 Å, $\text{N}-2\text{Br}(2)$ 3.39 Å (Fig. 2). The corresponding $\text{C}-\text{N}-\text{Br}$ angles are 101° , 171° , and 99° , respectively (Table 3).

The angle of 171° , associated with the $\text{N}-\text{Br}(1)$ distance of 3.40 Å, indicates a short contact rather than a hydrogen bond. Short nitrogen-chloride contacts with an $\text{X}-\text{N}\cdots\text{Cl}$ ($\text{X}=\text{C}, \text{N}$) angle of about 180° are not unusual and are found, *e.g.* in hydrazinium dichloride,⁹ geranylamine hydrochloride,¹⁰ and *m*-tolidine dihydrochloride.⁴

The four remaining Br^- ions may engage in hydrogen bonding to the $-\text{NH}_3^+$ group. In order to discuss the character of the bromine-nitrogen bonds, possible positions of the hydrogen atoms of the $-\text{NH}_3^+$ group were calculated from space group and geometrical considerations. This was performed assuming an $\text{N}-\text{H}$ bond length of 1.05 Å and a tetrahedral distribution of hydrogens at the nitrogen atoms. The protonated *o*-phenylenediamine molecules are situated in symmetry planes at $y=\frac{1}{4}$ and $y=\frac{3}{4}$ and moreover the molecules are symmetrical around $x=\frac{1}{4}$ and $x=\frac{3}{4}$. As mentioned earlier one of the hydrogen atoms in the $-\text{NH}_3^+$ group must occupy a fourfold position and the other two the general eightfold position (p. 3031). Of the fourfold positions in space group *Pmnm*, space considerations exclude all but $4(f)$, and furthermore, of the two possible positions in $4(f)$, one resulted in a very short hydrogen-hydrogen distance (1.8 Å). The positions of the hydrogen atoms in the NH_3^+ group could thus be fixed. The calculated $\text{H}-\text{Br}$ distances and $\text{N}-\text{H}-\text{Br}$ angles (Table 3) suggest that the two $\text{N}-\text{Br}(1)$ distances of 3.31 Å are hydrogen bonds and the two $\text{N}-\text{Br}(2)$ distances are short contacts or perhaps a bifurcated hydrogen bond. If the hydrogen positions discussed are correct, the structure is not held together solely by hydrogen bonds.

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REFERENCES

1. Buerger, M. J. *Crystal Structure Analysis*, Wiley, New York 1960, p. 75.
2. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1965, Vol. I.
3. Liminga, R. *Acta Chem. Scand.* **21** (1967) 1206.
4. Fowweather, F. and Hargreaves, A. *Acta Cryst.* **3** (1950) 81.
5. Cesur, A. F. and Richards, J. P. G. *Z. Krist.* **129** (1965) 283.
6. Chandrasekaran, R. *Acta Cryst.* **B 25** (1969) 369.
7. Won Choi, Q., Chung Hoe Koo, Joon Suk Oh and Chung Soo Yoo. *Daehan Hwahak Hwoejee* **9** (1965) 174.
8. Brown, C. J. *Proc. Roy. Soc. A* **302** (1968) 185.
9. Donohue, J. and Lipscomb, W. N. *J. Chem. Phys.* **15** (1947) 115.
10. Jeffrey, G. A. *Proc. Roy. Soc. A* **183** (1945) 388.

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