

The Crystal Structure of 2,4,6-Tribromoaniline

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The crystal structure of 2,4,6-tribromoaniline has been determined from three-dimensional X-ray data, corrected for secondary extinction effects. The orthorhombic unit cell of dimensions $a = 13.441 \pm 0.004$, $b = 14.623 \pm 0.008$, and $c = 4.263 \pm 0.002$ Å, contains four molecules. The space group symmetry is $P2_12_12_1$. The positions of the atoms in the molecule deviate slightly from a planar configuration owing to intramolecular repulsions between the amino group and the adjacent bromine atoms and, for the same reason, the triangle formed by the three bromine atoms is somewhat distorted from threefold symmetry. The amino group is apparently pyramidal. The compound is isostructural with 1,3,5-tribromobenzene and 1,3,5-trichlorobenzene. Both bromine containing compounds melt at approximately 119°C. Intermolecular distances are of the van der Waals type.

Introduction

Preliminary studies revealed that 2,4,6-tribromoaniline crystallizes with the same space group as that reported for 1,3,5-tribromobenzene (Milledge & Pant, 1960). The unit-cell dimensions were observed to differ only slightly from those of symmetric tribromobenzene. Both compounds melt at approximately 119°C. Thus the crystal structures and lattice energies must be rather similar in the two cases. The entropies of fusion, however, should differ appreciably if the crystal structure of 2,4,6-tribromoaniline is not disordered. 2,4,6-tribromoaniline is an 'overcrowded' compound with the possibility of atoms being displaced from a common plane. The amino group might favour a pyramidal configuration, as is observed for example in aniline (Evans, 1960). Since these factors may be expected to influence further the values of the entropy of fusion, it was of considerable interest to compare the implications of the X-ray diffraction analysis with experimental values for the entropies of fusion. The heats of fusion of these compounds have not been determined hitherto, but it is hoped that results will be available shortly.

Experimental

Aniline reacts readily with bromine in a dilute glacial acetic acid solution to form a precipitate of the slightly soluble 2,4,6-tribromoaniline. The compound was dried and recrystallized from ethanol to yield colourless, needle-shaped single crystals having a melting point of 119°C. Several single crystals of practically square cross section of dimensions 0.06×0.06 mm² were mounted in a thin-walled boron-lithium capillary and used in obtaining intensity measurements at room temperature. Integrated equi-inclination Weissenberg photographs were obtained of the reflexions of the first four layers, with rotation of the specimen through 200° about the needle (*c*) axis, using filtered Cu *K*α radiation. All of the measurable spot intensities of the

five film photographs of each layer were obtained photometrically, while the weakest intensities were estimated visually. The mean intensity data of each layer line (normalized to a common scale) were corrected for effects due to the Lorentz and polarization factors in the normal way. No explicit correction was applied for absorption, although secondary extinction effects were corrected during structure refinement. The total number of reflexions of the four layers is 974 while the number having non-zero intensity is 715. The remaining reflexions (of non-observable intensity) were allocated intensities according to $I = \frac{1}{2}I_{\min}$. The unit-cell dimensions were refined by the use of least-squares techniques based on 15 resolved and indexed lines measured on a powder photograph obtained with a Guinier camera, using KCl as a calibrated standard.

Determination of the structure

The crystals belong to the orthorhombic system. The unit cell of dimensions $a = 13.441$ (0.004) Å, $b = 14.623$ (0.008) Å and $c = 4.263$ (0.002) Å contains four molecules of 2,4,6-tribromoaniline. The numbers in parentheses are estimated standard deviations in cell dimensions. The values correspond closely to those recently reported for this compound by Schlemper & Konnert (1967). The calculated density is 2.614 g.cm⁻³. The non-centrosymmetric space group is $P2_12_12_1$, whose axially projected symmetries are *pgg*. There is one molecule per asymmetric unit.

Approximate values of the *x* and *y* parameters of the three independent bromine atoms were derived from the projection of the Patterson function along the *c* axis (Fig. 1). A permanent set of structure factor signs was then obtained from electron density maps which revealed the approximate positions of the light atoms, except for those of hydrogen. The parameters were further refined by full-matrix least-squares techniques wherein the bromine atoms were given anisotropic temperature factors which were computed accor-

ding to the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Following this procedure the R value fell from 15.5% to 6.6%, excluding some reflexions which were obviously suffering from extinction effects, together with the non-observed reflexions.

The next step was to find approximate values of the z parameters of the bromine atoms. Firstly, relative values of the z parameters were derived by means of a comparison of the molecular dimensions obtained from the projection, with those of an assumed planar model. Structure factors of indices $hk1$, $hk2$ and $hk3$ for different values of z were then computed for the three bromine atoms having the same relative positions. The plot of R value *vs* z (non-observable reflexions excluded) revealed a well-defined minimum approximately equal to 0.25. The corresponding z values of the bromine atoms served as a basis for a further least-squares refinement, wherein reflexions of different layers had to be taken separately in order to include the refinement of individual scale factors. Isotropic temperature factors were used. This process was continued until the R value had dropped to approximately 17%. The z values of the nitrogen atoms and of the carbon atoms were then computed and incorporated in the process of refinement, in which isotropic temperature factors continued to be used. The experimental data were then converted to a common scale of values and employed simultaneously in a further least-squares refinement which involved anisotropic temperature factors of the bromine atoms. An R value of 8.1% was thus obtained.

Inspection of the resulting $F_o - F_c$ table showed that correction of the experimental data for secondary extinction effects was desirable, especially in the determination of the hydrogen parameters. The correction was based on Zachariasen's theory (Zachariasen, 1963). Values of the derivative of the absorption factor (inverse of transmission factor) with respect to the absorption coefficient as a function of the Bragg angle and the equi-inclination angle, were obtained from the appropriate tables given in *International Tables for X-ray Crystallography* Vol. II, p.295 (Buerger, 1960) assuming for simplicity a cylindrical shape for the crystal. The value of the constant C in $F_{\text{corr}} = F_o(1 + C\beta I)$ was determined separately for each layer by minimizing $\Sigma(F_o - F_{\text{corr}})^2$. Corrected values of the observed amplitudes are collected in Table 1. The scale factors and atomic parameters were then adjusted against the corrected data using least-squares techniques. Only small changes in the parameter values were thus obtained.

A three-dimensional partial difference synthesis was then evaluated using these data. The contributions to the structure factors from all atoms except those of hydrogen were subtracted. Electron density maxima representing the hydrogen atoms of the carbon ring appeared in the positions to be expected. The amino-hydrogen positions were difficult to predict and are therefore less trivial. They also appeared as relatively well defined peaks. The maximum electron densities of the hydrogen atoms are from 0.6 to 0.8 $\text{e} \cdot \text{\AA}^{-3}$, which

agrees with results obtained for other hydrogen containing compounds [see for example McDonald (1960); Brown & Marsh (1963)].

Since the geometry of the amino group is of considerable interest, further refinements of the positions of the amino hydrogen atoms were attempted using least-squares techniques. Only those reflexions for which $\sin \theta/\lambda \leq 0.35 \text{ \AA}^{-1}$ were included, and all other parameters were held constant. An isotropic temperature factor of 3 \AA^2 was assigned to the hydrogen atoms of which the two hydrogen atoms of the benzene ring were represented by the calculated values of the space coordinates, assuming a C-H distance of 1.90 \AA . In this way, a small but significant reduction in $\Sigma W(F_o - F_c)^2$ was achieved. As was to be expected, the corresponding R value decreased very little. Values of the positional parameters of the hydrogen atoms and their standard deviations are given in Table 2.

In continuing the process of refinement, the contributions of the hydrogen atoms were included as fixed quantities based on the values in Table 2. Prior to further calculation, the weights of the reflexions, determined from the weighting scheme $W = (k_1 + F_o + k_2 F_o^2)$, were altered slightly in order to reduce the variation of $W(|F_o| - |F_c|)$. In the subsequent refinement, which was based on isotropy of the lighter atoms, the atomic par-

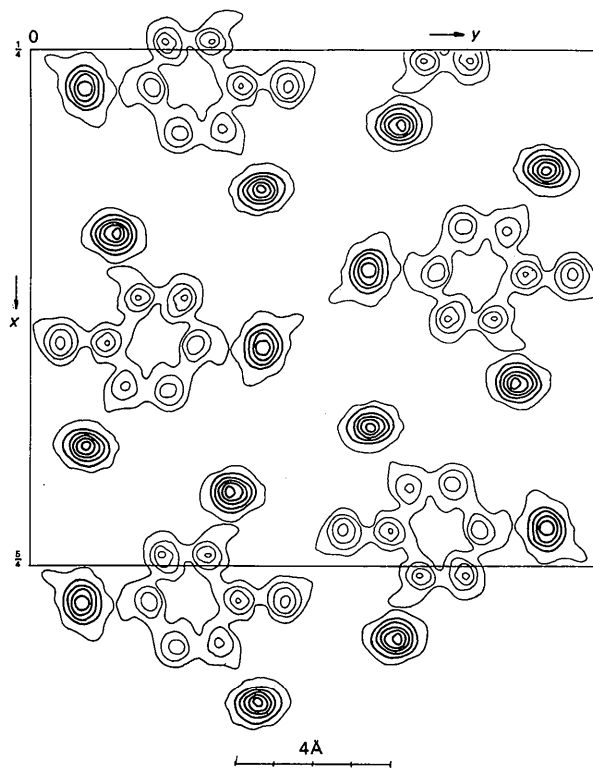


Fig. 1. Electron density projection along the c axis based on corrected values of observed structure factor amplitudes. Contours at intervals of $2 \text{ e} \cdot \text{\AA}^{-2}$ for the light atoms and at intervals of $10 \text{ e} \cdot \text{\AA}^{-2}$ for bromine. The first contour represents $2 \text{ e} \cdot \text{\AA}^{-2}$.

Table 1. *Observed and calculated structure factor amplitudes including calculated phases*

The observed amplitudes are corrected for effects due to secondary extinction.

0 4 0	232.0	238.10	180.0	6 14 0	17.3	14.47	180.0	15 5 0	20.0	17.99	-90.0	6 2 1	87.6	93.55	-166.8
0 6 0	109.0	110.44	-180.0	6 15 0	18.5	17.61	0	15 7 0	11.9	11.62	90.0	6 3 1	35.2	37.00	56.1
0 8 0	39.4	39.19	0	6 16 0	21.9	22.23	180.0	15 8 0	16.1	14.21	90.0	6 4 1	86.3	93.62	-156.8
0 10 0	39.6	39.02	0	6 17 0	10.4	10.31	0	16 0 0	13.1	10.66	180.0	6 5 1	49.1	47.77	-61.7
0 12 0	44.2	42.48	0	7 1 0	148.4	151.25	90.0	16 1 0	9.3	6.80	0	6 6 1	61.4	60.08	49.0
0 16 0	36.9	36.80	180.0	7 2 0	11.0	11.0	0	16 3 0	13.2	15.04	180.0	6 8 1	81.6	79.04	22.6
0 18 0	14.1	14.82	180.0	7 3 0	110.7	108.11	-90.0	16 5 0	16.4	14.81	180.0	6 9 1	15.6	11.67	-177.3
1 1 0	13.6	14.13	90.0	7 4 0	27.5	26.09	90.0	17 1 0	17.2	19.11	90.0	6 10 1	52.1	49.84	-77.8
1 2 0	6.9	3.93	-90.0	7 5 0	98.4	104.53	-90.0	17 2 0	21.6	24.56	-90.0	6 12 1	28.4	29.61	-151.5
1 3 0	52.7	53.55	90.0	7 6 0	11.9	9.76	-90.0	0 2 1	227.6	218.05	180.0	6 14 1	31.4	31.47	148.6
1 4 0	70.4	72.43	90.0	7 8 0	29.2	27.00	-90.0	0 3 1	77.4	74.46	-90.0	6 15 1	18.9	18.44	66.0
1 5 0	75.7	78.78	-90.0	7 9 0	33.1	32.19	90.0	0 4 1	104.0	102.79	180.0	6 17 1	10.8	3.92	131.7
1 6 0	21.4	20.87	90.0	7 10 0	17.4	15.96	-90.0	0 5 1	120.9	114.13	90.0	7 0 1	46.5	47.21	90.0
1 7 0	114.8	115.96	-90.0	7 11 0	38.5	37.23	90.0	0 7 1	33.5	30.42	-90.0	7 1 1	73.8	73.55	-91.4
1 8 0	60.0	62.23	-90.0	7 12 0	18.5	16.81	90.0	0 8 1	106.3	104.27	0	7 2 1	45.3	47.33	12.2
1 9 0	63.4	63.66	90.0	7 13 0	17.4	18.59	90.0	0 9 1	80.3	76.51	-90.0	7 3 1	88.1	90.82	-67.6
1 10 0	16.2	13.45	-90.0	7 15 0	14.8	15.94	-90.0	0 10 1	43.7	41.34	0	7 4 1	49.3	44.44	-154.8
1 11 0	76.0	74.93	90.0	7 17 0	26.1	26.68	-90.0	0 12 1	56.3	55.46	180.0	7 5 1	19.5	20.55	-81.2
1 12 0	40.9	40.89	90.0	8 0 0	24.4	22.59	0	0 13 1	36.9	34.84	90.0	7 6 1	56.1	56.26	-151.3
1 15 0	31.1	28.68	-90.0	8 1 0	21.7	21.21	0	1 0 1	46.4	44.64	180.0	7 7 1	62.4	62.09	44.9
1 16 0	23.3	24.11	-90.0	8 2 0	26.4	27.66	180.0	1 0 2	77.7	84.15	90.0	7 8 1	46.0	44.99	-53.3
1 17 0	15.1	14.39	-90.0	8 3 0	16.3	15.05	-180.0	1 2 1	153.3	151.51	174.1	7 9 1	51.4	51.13	100.1
2 1 0	6.7	6.50	-180.0	8 4 0	27.3	24.09	-180.0	1 3 1	141.5	139.76	-116.8	7 10 1	26.0	25.97	35.5
2 2 0	20.6	18.35	0	8 5 0	42.0	41.15	180.0	1 4 1	52.2	53.17	-89.5	7 12 1	27.9	23.92	158.4
2 3 0	14.8	12.55	0	8 6 0	38.1	36.49	0	1 5 1	36.5	35.43	-82.9	7 13 1	41.7	40.02	-87.9
2 4 0	62.5	61.87	-180.0	8 7 0	25.6	24.22	0	1 6 1	37.8	38.66	-47.7	8 0 1	32.4	31.07	90.0
2 5 0	114.7	117.68	0	8 8 0	28.1	25.22	0	1 7 1	93.1	93.68	36.9	8 1 1	57.4	56.25	-121.5
2 6 0	11.7	8.53	180.0	8 9 0	35.5	33.60	0	1 8 1	17.9	17.30	110.2	8 2 1	25.4	24.02	-60.3
2 7 0	26.8	23.31	-180.0	8 10 0	26.4	23.12	180.0	1 9 1	55.1	53.12	115.1	8 3 1	36.1	36.56	-72.2
2 8 0	36.4	38.79	0	8 11 0	13.3	11.27	180.0	1 10 1	20.7	20.22	94.9	8 4 1	24.7	24.70	-70.0
2 9 0	76.9	79.64	180.0	8 13 0	25.1	24.16	180.0	1 11 1	45.6	42.75	-170.6	8 5 1	44.2	42.99	50.0
2 10 0	11.7	8.69	0	8 15 0	10.2	9.18	0	1 12 1	19.9	17.21	21.2	8 6 1	38.0	38.21	162.1
2 11 0	12.4	9.04	0	9 1 0	43.5	42.58	90.0	1 13 1	32.1	31.02	-61.5	8 7 1	17.5	15.74	55.8
2 13 0	42.5	39.62	0	9 2 0	14.9	13.28	-90.0	1 15 1	23.1	21.51	-47.1	8 8 1	21.3	18.89	113.0
2 17 0	10.8	9.27	-180.0	9 3 0	23.4	22.62	-90.0	1 16 1	19.2	14.23	-160.6	8 9 1	18.4	15.46	175.2
3 1 0	42.2	41.68	-90.0	9 4 0	57.2	54.94	90.0	2 0 1	146.1	162.80	-90.0	8 10 1	33.0	35.23	-90.5
3 2 0	233.6	227.32	90.0	9 5 0	36.1	33.63	90.0	2 1 1	62.1	64.17	-39.5	8 15 1	14.7	17.99	-62.0
3 3 0	86.7	85.60	90.0	9 6 0	25.2	24.85	90.0	2 2 1	56.7	55.97	134.9	9 0 1	43.4	42.05	90.0
3 4 0	84.4	87.83	90.0	9 7 0	12.9	8.53	90.0	2 3 1	51.4	52.52	-121.4	9 1 1	56.6	57.09	-26.5
3 5 0	10.7	6.84	-90.0	9 8 0	72.4	71.46	-90.0	2 4 1	98.4	98.57	103.2	9 2 1	45.5	45.38	30.8
3 6 0	84.3	87.44	-90.0	9 9 0	18.0	17.21	90.0	2 5 1	41.3	39.00	163.2	9 3 1	65.6	64.81	-151.1
3 7 0	60.0	62.02	-90.0	9 10 0	25.4	22.90	-90.0	2 6 1	18.7	17.35	-37.3	9 4 1	37.3	38.22	-62.1
3 8 0	111.4	113.34	-90.0	9 12 0	35.1	35.30	90.0	2 7 1	40.3	39.21	194.5	9 5 1	20.6	19.02	140.8
3 9 0	18.5	18.71	90.0	9 14 0	21.0	21.63	90.0	2 8 1	46.3	44.88	-37.6	9 6 1	35.2	35.04	-111.3
3 10 0	32.9	29.71	-90.0	9 15 0	8.4	8.72	-90.0	2 9 1	24.1	21.85	67.9	9 7 1	40.7	40.24	37.3
3 11 0	41.2	38.95	90.0	10 0 0	79.1	77.38	0	2 10 1	23.5	19.46	131.1	9 10 1	19.9	21.61	94.1
3 12 0	47.7	44.35	90.0	10 1 0	88.8	90.95	180.0	2 11 1	22.2	21.62	-9.1	9 11 1	20.8	21.01	-152.4
3 13 0	33.8	32.75	-90.0	10 3 0	92.6	87.93	180.0	2 12 1	20.1	14.24	-120.5	9 12 1	18.1	16.23	86.2
3 14 0	46.7	47.59	90.0	10 4 0	50.5	47.67	180.0	2 13 1	20.2	18.12	-81.4	9 13 1	13.5	14.28	-34.8
3 16 0	14.8	11.66	90.0	10 5 0	12.9	9.39	0	2 14 1	19.8	19.71	-100.7	10 0 1	28.1	26.43	-90.0
3 17 0	12.2	11.49	90.0	10 6 0	13.1	8.58	0	2 15 1	19.9	18.65	-125.6	10 1 1	73.3	70.95	-153.1
3 18 0	20.4	23.95	-90.0	10 7 0	53.3	52.37	0	2 16 1	16.4	16.40	47.3	10 2 1	19.1	16.80	173.5
4 0 0	31.8	30.05	-180.0	10 8 0	18.0	14.25	0	3 0 1	158.6	174.06	90.0	10 3 1	32.1	30.48	-50.2
4 1 0	115.8	117.88	180.0	10 9 0	25.5	21.70	0	3 1 1	28.7	29.21	-52.1	10 4 1	29.7	27.67	104.3
4 2 0	39.5	40.10	0	10 10 0	20.7	21.91	180.0	3 2 1	85.0	87.66	127.8	10 5 1	75.3	74.37	31.4
4 3 0	191.3	192.15	180.0	10 13 0	18.5	19.70	180.0	3 3 1	38.4	38.82	-13.7	10 6 1	21.7	20.88	-83.7
4 4 0	39.6	38.38	0	10 14 0	12.3	13.05	0	3 4 1	106.0	104.09	-67.3	10 7 1	26.1	23.77	-5.4
4 5 0	9.4	8.36	0	10 15 0	9.1	11.04	180.0	3 5 1	12.6	9.04	172.6	10 8 1	16.4	13.77	-57.2
4 6 0	86.1	87.64	180.0	11 2 0	27.4	26.36	-90.0	3 6 1	138.8	137.54	-65.5	10 9 1	38.8	38.29	-132.4
4 7 0	73.9	75.74	0	11 3 0	31.2	29.70	90.0	3 7 1	58.8	57.39	159.8	10 10 1	19.2	17.76	66.0
4 8 0	33.6	31.50	180.0	11 5 0	28.5	26.37	-90.0	3 8 1	57.5	53.82	-177.2	10 11 1	37.2	36.83	172.2
4 9 0	47.2	45.34	0	11 6 0	18.7	16.02	90.0	3 10 1	83.1	79.84	105.0	10 13 1	14.8	15.07	86.9
4 10 0	68.0	68.05	0	11 7 0	46.0	43.54	-90.0	3 11 1	28.7	26.61	-36.8	11 1 1	23.0	24.58	-110.6
4 11 0	17.4	13.39	180.0	11 8 0	17.1	17.18	90.0	3 12 1	55.0	51.50	53.6	11 2 1	36.2	34.06	-148.0
4 12 0	16.0	12.52	0	11 9 0	22.0	20.76	90.0	3 16 1	32.9	32.69	-115.9	11 3 1	37.3	34.15	-103.3
4 13 0	21.9	19.01	180.0	11 11 0	35.1	33.83	90.0	4 0 1	34.5	33.15	-90.0	11 4 1	26.0	25.09	37.3
4 14 0	30.3	28.54	180.0	11 13 0	10.8	9.20	-90.0	4 1 1	102.3	111.08	156.7	11 6 1	23.3	24.83	36.5
4 15 0	26.1	23.66	180.0	11 14 0	9.1	10.09	-90.0	4 2 1	53.6	55.60	166.8	11 7 1	34.9	31.07	48.0
4 17 0	9.8	8.87	0	12 1 0	28.5	26.52	180.0	4 3 1	28.5	28.76	38.4	11 8 1	28.8	30.90	178.3
5 1 0	25.9	24.12	90.0	12 3 0	44.0	41.48	180.0	4 4 1	38.0	37.49	156.8	11 12 1	17.0	21.46	-10.3
5 2 0	98.7	94.60	90.0	12 5 0	37.1	36.85	0	4 5 1	130.9	131.92	-32.8	12 0 1	54.4	51.62	-90.0
5 3 0	16.3	17.26	0	12 6 0	18.4	16.98	180.0	4 6 1	38.9	39.38	-54.6	12 1 1	24.9	23.05	136.6
5 4 0	12.2	10.25	-90.0	12 7 0	22.1	20.62	0	4 7 1	43.5	42.90	-20.2	12 2 1	20.2	15.67	146.4
5 5 0	22.2	20.34	-90.0	12 9 0	13.7	12.28	180.0	4 8 1	46.4	44.49	-44.9	12 4 1	36.7	35.24	98.3
5 6 0	71.4	73.35	-90.0	13 1 0	26.3	24.58	90.0	4 9 1	76.0	72.60	129.3	12 5 1	23.0	21.61	-18.6
5 7 0	29.2	27.24	90.0	13 2 0	22.4	20.31	90.0	4 10 1	47.5	44.77	81.5	12 8 1	19.9	18.45	-77.8
5 8 0	45.8	45.54	90.0	13 4 0	13.5	10.34	-90.0	4 11 1							

Table 1 (cont.)

16	4	1	13.3	15.70	-32.9	6	1	2	72.5	74.24	15.5	15	0	2	13.3	11.81	0	7	3	3	30.1	29.10	110.4
16	5	1	15.2	18.06	-9.0	6	2	2	45.6	47.43	114.0	15	2	2	19.0	21.62	78.6	7	5	3	20.1	16.42	-119.9
16	6	1	9.5	13.46	112.2	6	3	2	50.2	49.64	0.6	15	6	2	13.2	16.75	-135.0	7	6	3	4.36	39.99	156.9
0	1	2	26.6	29.81	90.0	6	4	2	78.7	78.77	19.0	16	0	2	8.4	8.63	0	7	7	3	20.3	18.21	-103.4
0	2	2	53.3	50.88	180.0	6	5	2	47.7	45.10	-161.8	16	1	2	16.3	21.19	21.6	7	8	3	17.4	14.09	-7.3
0	3	2	30.1	27.93	90.0	6	6	2	35.1	34.38	-13.9	0	1	3	41.7	52.64	-90.0	7	9	3	16.9	11.62	-52.7
0	4	2	24.6	20.71	0	6	7	2	23.9	23.70	-124.5	0	2	3	51.1	50.28	0	7	12	3	15.2	16.41	-166.2
0	5	2	42.3	39.80	-90.0	6	8	2	38.1	36.66	-138.4	0	3	3	53.7	51.00	-90.0	8	0	3	65.3	62.42	90.0
0	6	2	103.7	108.24	0	6	9	2	21.6	18.27	-5.3	0	4	3	23.3	22.84	0	8	1	3	22.4	20.36	-13.4
0	7	2	26.9	27.38	-90.0	6	10	2	21.4	18.38	-149.3	0	5	3	25.1	21.39	90.0	8	2	3	20.1	18.49	15.5
0	8	2	26.3	23.71	0	6	11	2	20.6	16.97	95.6	0	6	3	14.8	12.24	180.0	8	3	3	31.9	28.92	110.5
0	10	2	93.0	92.61	180.0	6	12	2	20.8	18.12	151.4	0	7	3	20.5	18.86	90.0	8	4	3	48.6	44.54	-82.6
0	11	2	25.7	19.66	90.0	7	0	2	27.3	26.87	180.0	0	8	3	26.6	22.22	-180.0	8	5	3	38.9	35.76	114.3
0	12	2	40.5	41.38	180.0	7	1	2	31.2	29.84	-57.9	0	9	3	18.8	17.43	-90.0	8	6	3	22.7	21.51	-133.7
0	13	2	19.4	15.99	90.0	7	2	2	25.2	26.54	-99.7	0	10	3	22.5	23.21	90.0	8	7	3	20.0	17.77	-97.8
0	14	2	31.1	37.24	0	7	3	2	40.8	38.74	-69.4	0	11	3	18.0	17.85	0	8	8	3	25.6	23.54	96.8
0	15	2	17.1	22.12	0	7	4	2	20.1	19.83	-55.1	0	12	3	18.9	22.60	-90.0	8	9	3	39.7	38.38	-85.7
1	0	2	34.7	48.23	180.0	7	5	2	49.5	48.12	96.8	1	0	3	23.9	32.26	-90.0	8	13	3	17.2	21.04	85.5
1	1	2	79.5	87.79	-67.6	7	6	2	24.0	24.17	15.8	1	1	3	70.3	77.20	7.5	9	1	3	10.1	11.31	25.9
1	1	2	128.9	121.82	-104.1	7	7	2	60.7	59.94	95.0	1	2	3	24.6	24.88	-58.8	9	2	3	25.0	23.93	-169.9
1	3	2	82.2	80.72	28.4	7	8	2	18.3	14.90	116.9	1	3	3	55.2	52.06	-178.6	9	3	3	37.1	33.52	132.5
1	4	2	60.8	57.03	11.6	7	9	2	22.9	24.25	-99.5	1	4	3	48.2	46.71	35.4	9	4	3	30.5	26.86	158.5
1	5	2	65.8	62.68	94.1	7	12	2	17.4	16.65	-157.6	1	5	3	66.8	63.40	-176.2	9	6	3	17.1	14.40	15.8
1	6	2	66.5	65.74	62.7	7	13	2	9.6	13.94	68.0	1	6	3	21.5	21.10	59.0	9	7	3	35.8	32.39	-14.0
1	7	2	45.9	44.13	-160.5	7	15	2	24.0	24.66	95.9	1	7	3	25.2	23.88	-43.7	9	8	3	26.1	23.76	6.3
1	8	2	13.7	12.20	-20.0	8	0	2	19.6	20.38	0	1	8	3	55.8	54.31	170.1	9	9	3	19.3	19.33	-120.7
1	9	2	30.0	30.19	-153.8	8	1	2	56.7	55.06	-33.4	1	9	3	20.1	17.40	-6.9	9	11	3	18.1	22.34	175.4
1	10	2	34.3	33.40	-166.1	8	2	2	26.2	25.82	106.3	1	10	3	27.6	28.01	-145.3	10	0	3	17.4	15.10	-90.0
1	11	2	16.0	12.59	34.3	8	3	2	49.8	47.90	-4.7	1	11	3	14.2	12.61	56.5	10	1	3	34.0	31.15	-43.3
1	12	2	27.2	24.82	161.7	8	4	2	42.7	40.16	138.7	1	12	3	25.3	26.47	-24.9	10	3	3	21.1	17.46	-121.3
1	13	2	21.3	20.92	-36.5	8	5	2	50.7	47.88	143.8	1	14	3	19.9	21.51	11.9	10	5	3	32.5	29.99	130.6
1	14	2	14.4	14.31	-33.8	8	6	2	26.7	26.23	-43.6	2	0	3	10.1	8.20	-90.0	10	10	3	13.5	11.25	110.9
1	16	2	8.9	11.35	115.4	8	7	2	32.4	33.23	111.0	2	1	3	23.6	25.75	82.3	11	1	3	23.6	22.35	12.4
2	0	2	24.6	26.94	-180.0	8	8	2	28.8	28.75	-50.4	2	2	3	53.4	54.23	49.3	11	2	3	48.5	46.23	-174.7
2	1	2	78.1	87.84	-135.7	8	9	2	13.9	12.68	-37.8	2	2	3	56.1	55.20	91.1	11	3	3	21.1	20.68	144.1
2	2	2	56.7	58.43	120.6	8	10	2	19.8	15.90	-167.6	2	3	3	27.7	22.26	32.0	11	5	3	17.9	14.74	162.1
2	3	2	56.9	55.13	-172.0	8	11	2	22.1	24.30	-94.2	2	4	3	35.9	36.32	113.0	11	6	3	25.9	25.54	-7.6
2	4	2	53.2	52.58	65.7	8	12	2	12.7	14.29	80.1	2	5	3	70.9	69.86	-105.0	11	7	3	11.3	12.06	-92.5
2	5	2	113.9	109.82	42.9	8	15	2	13.0	14.76	52.1	2	7	3	49.6	50.47	-86.0	12	1	3	16.5	14.01	6.3
2	6	2	28.4	29.12	-6.2	9	0	2	38.4	40.60	0	2	8	3	34.6	35.54	-126.2	12	2	3	19.5	16.14	108.1
2	7	2	29.8	29.04	75.2	9	1	2	22.3	19.16	-118.9	2	9	3	31.3	31.87	-78.3	12	3	3	17.6	19.31	-155.1
2	8	2	45.1	42.17	-80.0	9	2	2	75.7	75.33	-79.0	2	10	3	51.0	51.46	97.4	12	4	3	33.5	35.23	-83.3
2	9	2	37.2	35.10	-151.2	9	3	2	16.9	16.26	151.7	2	12	3	25.3	24.09	70.9	13	1	3	22.0	23.81	140.9
2	10	2	32.8	31.07	-137.2	9	4	2	38.0	34.92	-176.1	2	13	3	23.2	25.73	82.0	13	2	3	14.9	15.19	168.4
2	11	2	35.3	35.94	-62.3	9	5	2	22.6	19.58	87.9	2	14	3	20.3	24.40	-66.4	13	3	3	24.4	25.69	30.6
2	12	2	19.8	16.44	92.0	9	6	2	46.7	45.22	120.9	3	0	3	48.8	50.00	-90.0	13	7	3	7.9	16.93	-126.6
2	14	2	21.7	22.94	65.4	9	7	2	46.7	45.22	120.9	3	1	3	30.9	32.09	166.7	14	3	3	12.1	13.75	66.7
2	15	2	18.5	24.77	145.6	9	8	2	19.7	18.21	-52.5	3	2	3	81.0	78.78	-179.1	14	0	3	10.5	11.06	90.0
3	0	2	38.1	40.99	0	9	10	2	19.2	15.25	-14.8	3	3	3	22.6	21.14	21.5	14	1	3	13.8	16.00	74.1
3	1	2	54.4	58.16	-107.9	9	11	2	17.3	15.77	-91.5	3	4	3	37.7	37.48	66.8	14	2	3	17.0	15.19	168.4
3	2	2	56.6	60.76	-87.3	10	0	2	16.1	14.71	50.0	3	5	3	42.8	41.40	35.5	14	3	3	24.4	25.69	30.6
3	3	2	72.8	72.57	120.2	10	1	2	36.3	34.21	0	3	6	3	42.8	41.40	35.5	14	4	3	12.1	13.75	66.7
3	4	2	98.7	95.24	-104.9	10	2	2	11.3	13.03	13.1	3	7	3	23.5	19.36	-117.5	14	5	3	10.5	11.06	90.0
3	5	2	29.7	31.49	91.4	10	3	2	35.2	33.70	4.6	3	8	3	19.9	18.02	-111.7	14	6	3	12.1	13.75	66.7
3	6	2	22.3	20.58	133.6	10	4	2	26.8	25.11	-152.5	3	10	3	24.9	24.11	-106.9	14	7	3	10.5	11.06	90.0
3	7	2	49.8	49.96	-61.9	10	5	2	20.6	20.45	3.9	3	12	3	13.2	12.28	-8.8	14	8	3	12.1	13.75	66.7
3	8	2	74.2	75.81	89.4	10	6	2	21.8	19.03	.8	3	13	3	17.1	19.61	163.7	14	9	3	10.5	11.06	90.0
3	9	2	18.4	15.89	-13.9	10	7	2	35.1	35.67	-167.5	4	0	3	53.2	51.81	-90.0	14	10	3	12.1	13.75	66.7
3	10	2	26.1	23.77	58.4	10	8	2	20.9	19.86	3.1	4	1	3	63.1	61.61	74.7	14	11	3	10.5	11.06	90.0
3	11	2	20.3	18.70	61.2	10	9	2	33.8	32.44	-177.2	4	2	3	60.5	60.08	88.6	14	12	3	12.1	13.75	66.7
3	12	2	41.2	41.55	-77.0	10	10	2	20.8	22.32	160.3	4	3	3	23.1	22.64	-51.6	14	13	3	10.5	11.06	90.0
3	14	2	20.4	20.72	-100.4	10	13	2	22.4	25.05	4.7	4	4	3	42.0	41.52	55.2	14	14	3	10.5	11.06	90.0
3	15	2	17.4	18.57	-151.0	11	0	2	24.2	24.14	0	4	5	3	48.0	47.71	-105.0	14	15	3	10.5	11.06	90.0
4	0	2	114.7	123.24	180.0	11	1	2	46.8	44.87	-83.7	4	6	3	21.1	19.13	110.7	14	16	3	10.5	11.06	

Table 2. *Positional parameters of the hydrogen atoms of molecule A (Fig. 3)*

E.s.d. in parentheses. The numbering is that of Fig. 2.

	x	y	z
H(1)	0.765 (0.006)	0.949 (0.006)	1.153 (0.03)
H(2)	0.615 (0.006)	0.963 (0.006)	1.095 (0.03)
H(3)	0.835 (calc)	0.693 (calc)	0.655 (calc)
H(4)	0.524 (calc)	0.732 (calc)	0.467 (calc)

ameter values of Table 3 were derived. The corresponding R value is 5.52% and the calculated structure factors are listed in Table 1. In view of the relatively large values of the standard deviations for the resulting isotropic temperature factors of the light atoms, anisotropic temperature coefficients for these atoms were included in the least-squares refinement. In these calculations, the positional parameters were held constant and the non-observable reflexions excluded. It transpired that a somewhat better result was obtained when only the reflexions of higher indices were employed ($\sin \theta/\lambda \leq 0.35 \text{ \AA}^{-1}$), as had been noted previously (Cruickshank, 1958). The final values of the anisotropic temperature factors thus obtained are given in Table 3 together with estimated values of standard deviations. Those of the bromine atoms changed very little, and differ by less than the estimated errors from the previous values. The R value was little altered by this procedure. It was found that the β_{ij} matrices for the carbon atoms C(1), C(4) and C(5) are not positive definite and

therefore do not have physical significance. This is probably caused mainly by the coupling between the β_{33} values and the calculated individual scale factor values which could not be refined simultaneously.

The rigid body motion analysis was based on a standard treatment (Cruickshank, 1956) although it has recently been shown that the method is not strictly correct in the case of non-centrosymmetric molecules (Schomaker & Trueblood, 1966). Parameters, excluding the position of the origin, which was determined by trial and error (Pawley, 1963), were refined using least-squares techniques. The light atoms were excluded from the calculations, since some of them have larger values of observed vibration amplitudes than the other atoms which are more distant from the libration centre.

Results and discussion

Values of intramolecular distances and angles are given in Table 4, where errors due to uncertainties in the cell dimensions have been disregarded, and the numbering is the same as in Fig. 2. The libration correction of intramolecular distances (Cruickshank, 1961) was found to be significant only for the Br(2)–C(4) distance. (For the others, the corrections amount to about $\frac{1}{2}$ the standard deviation.) The mean value of the carbon–carbon bond length is 1.38₃ Å. Structural details of the benzene ring as revealed by the deviations of the individual C–C bond lengths from the average value, *etc.* are lost owing

Table 3. *Thermal and positional parameters of atoms of molecule A (Fig. 3)*

The numbering refers to Fig. 2. E.s.d.'s in parenthesis.

	x	y	z			
Br(1)	0.8916 (0.0001)	0.8572 (0.0001)	1.0039 (0.0005)			
Br(2)	0.6781 (0.0001)	0.5914 (0.0001)	0.3292 (0.0005)			
Br(3)	0.4781 (0.0001)	0.9024 (0.0001)	0.7879 (0.0005)			
N	0.6865 (0.0009)	0.9499 (0.0008)	1.0485 (0.0037)			
C(1)	0.6839 (0.0010)	0.8656 (0.0009)	0.8804 (0.0039)			
C(2)	0.7700 (0.0011)	0.8151 (0.0010)	0.8367 (0.0048)			
C(3)	0.7687 (0.0011)	0.7334 (0.0011)	0.6754 (0.0050)			
C(4)	0.6791 (0.0011)	0.7029 (0.0010)	0.5425 (0.0047)			
C(5)	0.5945 (0.0011)	0.7532 (0.0010)	0.5729 (0.0040)			
C(6)	0.5978 (0.0012)	0.8349 (0.0011)	0.7478 (0.0045)			
Br(1)	0.00393 (0.00008)	0.00531 (0.00009)	0.03554 (0.00134)	0.00022 (0.00017)	−0.00649 (0.00074)	0.00104 (0.00070)
Br(2)	0.00884 (0.00015)	0.00366 (0.00008)	0.03825 (0.00144)	−0.00187 (0.00020)	0.00536 (0.00081)	−0.00556 (0.00070)
Br(3)	0.00393 (0.00009)	0.00557 (0.00011)	0.05099 (0.00149)	0.00122 (0.00018)	0.00027 (0.00068)	−0.00425 (0.00075)
N	0.00514 (0.00081)	0.00233 (0.00053)	0.02831 (0.01118)	0.00086 (0.00116)	0.00262 (0.00613)	0.00128 (0.00420)
C(1)	0.00329 (0.00066)	0.00441 (0.00075)	0.00421 (0.01162)	−0.00040 (0.00127)	0.00435 (0.00410)	0.00877 (0.00437)
C(2)	0.00485 (0.00085)	0.00452 (0.00085)	0.00352 (0.01162)	0.00131 (0.00148)	−0.00584 (0.00520)	0.00271 (0.00624)
C(3)	0.00341 (0.00073)	0.00489 (0.00091)	0.01734 (0.01218)	0.00137 (0.00139)	0.00357 (0.00529)	0.00937 (0.00645)
C(4)	0.00335 (0.00133)	0.00376 (0.00074)	−0.00575 (0.01139)	−0.00180 (0.00173)	0.00770 (0.00726)	0.00870 (0.00437)
C(5)	0.00513 (0.00102)	0.00487 (0.00088)	−0.00901 (0.01243)	−0.00036 (0.00154)	−0.00430 (0.00463)	0.00489 (0.00465)
C(6)	0.00673 (0.00116)	0.00399 (0.00084)	0.02541 (0.01553)	−0.00376 (0.00175)	−0.00119 (0.00703)	0.00017 (0.00504)

to inaccuracy in the bond length values. It should, however, be possible to predict values of bond lengths within the benzene ring on a different, semi-empirical basis. (See *e.g.* Sakurai, Sundralingam & Jeffrey, 1963). It appears from Table 4 that the C-C-C bond angles having apices at the halogen bonded carbon atoms have been observed to be larger than 120° , whereas the corresponding bond angle centred at the carbon atom linked to the amino group has been found to be less than 120° . Similar results have been obtained for 2-chloro-4-nitroaniline (McPhail & Sim, 1965), *p*-chloroaniline (Palm, 1966) and 2,5-dichloroaniline (Sakurai *et al.*, 1963). In other aniline derivatives, such as 4-nitroaniline (Trueblood, Goldish & Donohue, 1961) 2,3,4,6-tetranitroaniline (Dickinson & Stewart, 1966) and 1,3,5-trinitro-2,4,6-triaminobenzene (Cady & Larsson, 1965), the C-C-C bond angles at the carbon atoms adjacent to the amino groups have all been observed to be significantly less than 120° . Conversely, in pure halogenbenzenes, the C-C-C bond angles centred at the halogenated carbon atoms seem in general to exceed 120° (see *e.g.* Sutton, 1965).

The mean value of the C-Br bond distance is $1.891 (0.009) \text{ \AA}$, which compares well with the C-Br bond lengths of $1.896 \pm 0.018 \text{ \AA}$ and $1.897 (0.04) \text{ \AA}$ observed in solid 1,2,4,5-tetrabromobenzene (Gafner & Herbstein, 1960) and solid 3,5-dibromo-*p*-aminobenzoic acid (Pant, 1965) respectively. In symmetric tribromobenzene the mean observed C-Br distance has been stated to be 1.857 \AA (Milledge & Pant, 1960), but no estimate of accuracy is given. In gaseous bromobenzene (Rosenthal, 1964) and *o*-dibromobenzene and hexabromobenzene (Strand, 1966) the observed C-Br distances are $1.869 (0.0002) \text{ \AA}$, $1.88 (0.008) \text{ \AA}$ and $1.879 (0.007) \text{ \AA}$, respectively. The C-Br bond lengths in bromo-substituted methanes are, on the other hand, significantly larger, *viz.* $1.93\text{--}1.94 \text{ \AA}$ (Sutton 1958,

1965). According to theoretical and experimental results (Bersohn, 1954) there appears to be only a small transfer of charge from the lone pair orbitals of the halogen substituent to the benzene nucleus. In bromobenzene, for example, the C-Br double bond character (see *e.g.* Das & Hahn, 1958) has been estimated from observed nuclear quadrupole constant data to be only 0.025 electron (Rosenthal, 1964), whereas in solid

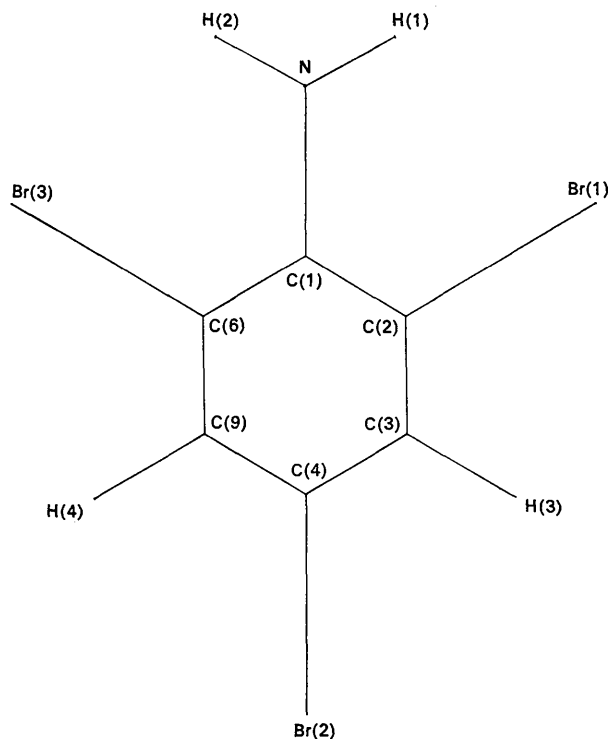


Fig. 2. The 2,4,6-tribromoaniline molecule.

Table 4. Intramolecular distances and angles

E.s.d.s in parentheses. The numbering refers to Fig. 2.

	Distance (Å)		Distance (Å)
Br(1)-C(2)	1.886 (0.016)	C(1)-C(2)	1.386 (0.021)
Br(2)-C(4)	1.891 (0.016) (corr.)	C(2)-C(3)	1.378 (0.023)
Br(3)-C(6)	1.896 (0.016)	C(3)-C(4)	1.403 (0.022)
N—C(1)	1.426 (0.020)	C(4)-C(5)	1.360 (0.021)
		C(5)-C(6)	1.407 (0.023)
N—H(1)	0.99 (0.09)	C(6)-C(1)	1.365 (0.022)
N—H(2)	1.03 (0.09)		
	Angle (°)		Angle (°)
∠C(2)-C(1)-C(6)	118.5 (1.4)	∠Br(1)-C(2)-C(1)	119.9 (1.2)
∠C(3)-C(2)-C(1)	121.2 (1.4)	∠Br(1)-C(2)-C(3)	118.8 (1.1)
∠C(4)-C(3)-C(2)	119.2 (1.4)	∠Br(2)-C(4)-C(3)	118.7 (1.1)
∠C(5)-C(4)-C(3)	120.5 (1.5)	∠Br(2)-C(4)-C(5)	120.8 (0.9)
∠C(6)-C(5)-C(4)	118.8 (1.4)	∠Br(3)-C(6)-C(5)	117.6 (1.2)
∠C(1)-C(6)-C(5)	121.7 (1.4)	∠Br(3)-C(6)-C(1)	120.7 (1.2)
∠N—C(1)-C(2)	120.5 (1.3)		
∠N—C(1)-C(6)	120.9 (1.3)		
∠H(1)-N—C(1)	103.1 (5.4)		
∠H(2)-N—C(1)	104.0 (5.7)		
∠H(1)-N—H(2)	141.7 (9.8)		

1,3,5-tribromobenzene (Bucci, Cecchi, Colligiani & Landucci, 1965) the double bond characters of the three independent Br–C bonds are found to be 0.03, 0.03 and 0.04₅ electrons. In 2,4,6-tribromoaniline the corresponding figures based on the experimental data of Bucci, Cecchi, Colligiani & Mischia (1965) are 0.03₅, 0.02 and 0.03₆ electrons, respectively. Bersohn (1954) found that the trigonal hybridization of the carbon atom was probably the factor mainly responsible for shortening of carbon–halogen bond lengths in benzene derivatives containing halogen substituents.

The N–C bond length has been found to be 1.426 (0.020) Å, in good agreement with the N–C bond length of 1.410 (0.016) Å observed in solid 2,5-dichloroaniline (Sakurai *et al.*, 1963) as is, perhaps, to be expected. In *p*-chloroaniline the N–C bond length has recently been observed to be 1.40 (0.01) Å (Palm, 1966). These values are probably significantly less than the quoted tetrahedral N–C bond distance of 1.47 (0.01) Å (Lide, 1962). Since the carbon atom is assumed to be trigonally hybridized, the shortening may result from the hybridization (see *e.g.* Lide, 1962) as well as from the delocalization of the lone-pair electrons of the donor group which, according to both theoretical and experimental investigations (see *e.g.* Fischer-Hjalmars, 1962; Kwiatkowsky, 1967; and Schaefer & Schneider, 1963), plays a relatively important role in aniline.

The distance from the nitrogen atom to either of the adjacent bromine atoms is approximately 0.35 (0.013) Å less than the sum of the corresponding van der Waals radii (Pauling, 1960), whereas the mean distance between an amine-hydrogen atom and its nearest bromine neighbour is approximately 0.70 Å less than the corresponding van der Waals distance. Furthermore, the Br(1)–Br(3) distance appears to be slightly but significantly longer (0.053 (0.002) Å] than the other two inter-bromine distances, indicating the presence of an overall repulsion between the amino group and the adjacent bromine atoms.

Since the positions of the bromine atoms have been determined to a relatively high degree of accuracy, it may be appropriate to consider the deviations of the atomic positions from the plane containing the bromine atoms, *viz*:

Atom	H(1)	H(2)	N	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
Distance (Å)	–0.32	0.25	–0.054	–0.047	–0.015	–0.011	0.017	0.036	–0.012

The estimated standard deviations in the distances of atoms from the given plane are:

$$\sigma(\text{C})=0.017 \text{ \AA}, \quad \sigma(\text{N})=0.015 \text{ \AA} \quad \text{and} \quad \sigma(\text{H})=0.117 \text{ \AA}.$$

The standard deviations in the positions of the bromine atoms are $\sigma(x)=0.0013 \text{ \AA}$, $\sigma(y)=0.0015 \text{ \AA}$ and $\sigma(z)=0.0021 \text{ \AA}$. The direction of the normal to the plane referred to the three crystallographic axes x , y and z , are 0.1987, 0.4839 and -0.8522 , respectively.

These data show that the position of the nitrogen atom (and probably also that of the C(1) atom) deviate slightly, but nevertheless, significantly, from the plane containing the three bromine atoms. This is a further consequence of the repulsive interaction between the amino group and the adjacent bromine atoms. However, the benzene ring seems to be planar. The results show, in addition, that the amino group is probably pyramidal, with both hydrogen atoms situated on one side of the benzene plane, as is also indicated by spectroscopic measurements on solutions (Krueger, 1962; Hambly & O'Grady, 1962). According to the previously mentioned three-dimensional difference map, the vibration of the hydrogen atoms about their mean positions is, as expected, very pronounced.

Intermolecular interactions appear to be of the usual van der Waals type. It appears from Fig. 3 that intermolecular van der Waals contact distances are found between bromine atoms and between bromine and benzene hydrogen atoms, whose positions were computed from the observed positions of the carbon atoms and a postulated C–H bond length of 1.09 Å, on the assumption of coplanarity and equality of the H–C–C bond angles. The distances from the apparently strongly vibrating amino group to neighbouring molecules seem also to be normal van der Waals contact distances. Thus the present compound is isostructural (isomorphous) with 1,3,5-trichlorobenzene and 1,3,5-tribromobenzene (Milledge & Pant, 1960); the melting point of the latter (119°C) is also that of the present compound. It appears from Table 5 that the introduction of the amino group in symmetric tribromobenzene leads to considerable elongations of the b and c axes, while the a axis becomes slightly shortened. Since the C–N bonds are found to be nearly perpendicular to the direction of the a axis, the observed elongation of the other axes, especially the b axis, seems reasonable in view of Fig. 3.

Compared with 1,3,5-tribromobenzene, 2,4,6-tribromoaniline may be expected to have the higher value of entropy of fusion owing to its lower molecular symmetry. Neglecting additional factors, the entropy increment is given by: $\Delta^2S = R \ln 6$ or $R \ln 3$, depending on whether the present molecule is planar (as is the

case in symmetric tribromobenzene) or not. 2,4,6-Tribromoaniline and symmetric tribromobenzene may be expected to form solid solutions. 2,4,6-Trichloroaniline has recently been reported to be monoclinic (Schlemper & Konnert, 1967) and is therefore not isostructural with the compounds mentioned above. It may be mentioned that the density of 2,4,6-trichloroaniline is 2.5% higher than that of 1,3,5-trichlorobenzene, whereas the density of 2,4,6-tribromoaniline is 1.3%

Table 5. Unit-cell dimensions of some isostructural derivatives of benzene at room temperature

	E.s.d. in parentheses.			Authors
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	
2,4,6-Tribromoaniline	13.462 (0.008)	14.692 (0.014)	4.266 (0.005)	Schlemper & Konnert (1967)
2,4,6-Tribromoaniline	13.441 (0.004)	14.623 (0.08)	4.263 (0.002)	Present
1,3,5-Tribromobenzene	13.55	14.23	4.08	Milledge & Pant (1960)
1,3,5-Trichlorobenzene	13.19	13.93	3.91	Milledge & Pant (1960)

less than that of 1,3,5-tribromobenzene at room temperature.

The full-matrix least-squares computer program used is a somewhat revised version of that written by Gantzel, Sparks & Trueblood (I.U.C. World List No. 384). The Fourier program was written by Gantzel & Hope, Department of Chemistry, University of California, Los Angeles, California, U.S.A. The program used for correcting the structure factor amplitudes for effects due to secondary extinction was written by A. T. Christensen.

The *T-ω* program used is a somewhat revised version of that written by Gantzel, Coulter & Trueblood (ACA Computer Program No. 232 for IBM 709 or 7090).

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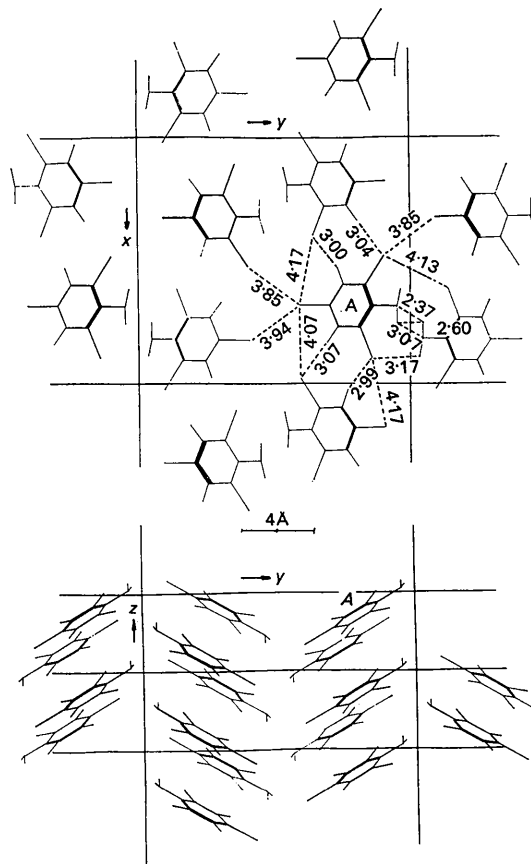


Fig. 3. The lattice structure as seen along the *c* and *a* axes.