

The Crystal Structure of 1,4-dibromocycl(3,2,2)azine

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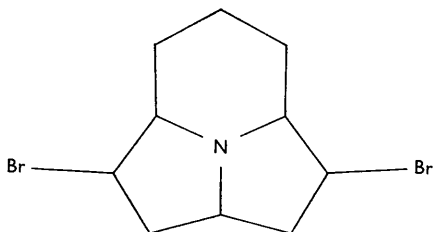
1,4-Dibromocycl(3,2,2)azine is monoclinic, probably $P2_1/n$;

$$a = 16.52, b = 4.01, c = 14.13 \text{ \AA}; \beta = 91.2^\circ, Z = 4.$$

The structure was determined by heavy-atom methods, and refined with the aid of three-dimensional differential syntheses. The molecule is almost exactly planar, and the distance between adjacent parallel molecules is 3.46 Å. The analysis was complicated by the considerable anisotropy of thermal motion of the bromine atoms.

Introduction

Cycl(3,2,2)azine, a stable aromatic compound, has been synthesized by Windgassen, Saunders & Boekelheide (1959). A crystal-structure analysis was begun in this laboratory in an attempt to discover the stereochemistry and packing of the molecules. The analysis proved unexpectedly difficult, however, and it was felt that useful information might be more easily obtained from an analysis of the derivative 1,4-dibromocycl(3,2,2)azine.



Experimental details

The crystals available for examination were fragile yellow lath-like growths. Good specimens were rare, and all but the smallest seemed invariably to be twinned. Unit cell, space group, and most of the three-dimensional intensity data were (with some difficulty) obtained from a twinned crystal of moderate size, using precession and Weissenberg photographs. The analysis was well advanced when this laboratory acquired a General Electric Geiger-counter spectrometer and goniostat. In order to remove some apprehensions as to the magnitude of absorption errors, and some uncertainties due to overlapping of twin reflections, all measurements were repeated with this equipment, using a much smaller, and fortunately single, crystal.

The crystal data are:

Monoclinic, probably $P2_1/n$

$$a = 16.52 \pm 0.01, b = 4.01 \pm 0.01, c = 14.13 \pm 0.01 \text{ \AA}; \\ \beta = 91.2 \pm 0.1^\circ.$$

Frequently twinned on $10\bar{1}$.

$$D_x \text{ (calculated density)} = 2.12 \pm 0.01 \text{ g.cm.}^{-3} (Z = 4).$$

$$D_o \text{ (observed density)} = 2.1 \pm 0.1 \text{ g.cm.}^{-3}$$

(by flotation in aqueous AgNO_3 solution).

$$\mu = 111 \text{ cm.}^{-1} (\text{Cu } K\alpha).$$

The specimen ultimately examined was (approximately) a rectangular solid $0.023 \times 0.050 \times 0.25$ mm., the longest axis coinciding with **b**. It was mounted with the fibre parallel to **b**, and intensity data were collected using the 'moving-crystal-moving-counter' technique (Furnas, 1957). The angular settings for all reflections sought were precomputed. Cu $K\alpha$ radiation and a General Electric SPG 1 (argon-filled) counter tube were used throughout. The combination of a nickel filter and a reverter (a form of pulse-height analyser) provided effectively monochromatic response. For the more intense reflections the X-ray tube current was reduced in order to keep the counting rate well within the region of linear response. The background counting rate was found to be almost entirely a function of θ , and therefore individual background counts were not made. Instead, the required values were obtained from an empirical curve. The net intensity counts ranged from 1 to 12,000, with 1 as the least count of the system. As the corresponding background count was never less than 3, it is clear that the weakest reflections were not very accurately measured.

The only reciprocal-lattice points scanned were those corresponding to reflections observed in the initial survey. These had been recorded on y -axis zero- and upper-level Weissenberg photographs, for $k \leq 3$.

Lorentz-polarization factors for equatorial reflections were applied. Corrections for absorption were

Table 1. Comparison of peak heights and curvatures from F_o and F_c differential syntheses

Quantities from F_c differential synthesis are in italics

Atom	ρ e.Å ⁻³	ρ_{xx} e.Å ⁻⁵	ρ_{yy} e.Å ⁻⁵	ρ_{zz} e.Å ⁻⁵	ρ_{xy} e.Å ⁻⁵	ρ_{yz} e.Å ⁻⁵	ρ_{zx} e.Å ⁻⁵
C ₁	7.4	-77.6	-48.9	-63.6	-4.6	-0.7	16.2
	<i>7.5</i>	<i>-78.5</i>	<i>-50.4</i>	<i>-65.3</i>	<i>-4.0</i>	<i>1.1</i>	<i>14.6</i>
C ₂	6.4	-51.7	-41.8	-46.5	-3.6	2.0	9.1
	<i>6.7</i>	<i>-55.9</i>	<i>-47.1</i>	<i>-49.1</i>	<i>-0.8</i>	<i>3.4</i>	<i>4.3</i>
C _{2a}	6.6	-46.8	-40.8	-56.6	10.4	-1.4	1.1
	<i>6.5</i>	<i>-49.2</i>	<i>-39.9</i>	<i>-51.3</i>	<i>9.4</i>	<i>-2.9</i>	<i>2.9</i>
C ₃	6.6	-49.0	-42.4	-58.1	-2.2	2.1	5.6
	<i>7.0</i>	<i>-53.5</i>	<i>-47.2</i>	<i>-61.1</i>	<i>-1.8</i>	<i>6.1</i>	<i>5.2</i>
C ₄	6.8	-60.5	-45.0	-67.7	-4.9	-0.8	14.7
	<i>7.2</i>	<i>-64.1</i>	<i>-47.8</i>	<i>-70.1</i>	<i>-2.6</i>	<i>0.5</i>	<i>12.5</i>
C _{4a}	7.2	-57.2	-48.2	-71.0	-0.5	-2.1	8.6
	<i>7.3</i>	<i>-63.3</i>	<i>-47.9</i>	<i>-69.7</i>	<i>0.8</i>	<i>-0.6</i>	<i>8.2</i>
C ₅	5.9	-32.4	-41.4	-58.9	2.3	1.4	4.9
	<i>6.3</i>	<i>-41.5</i>	<i>-44.0</i>	<i>-59.2</i>	<i>3.2</i>	<i>4.9</i>	<i>3.7</i>
C ₆	5.7	-31.8	-39.8	-43.2	-5.3	-1.5	2.1
	<i>6.1</i>	<i>-43.3</i>	<i>-43.0</i>	<i>-48.1</i>	<i>-5.9</i>	<i>1.4</i>	<i>1.6</i>
C ₇	6.1	-47.2	-37.4	-47.5	6.3	1.6	12.2
	<i>6.5</i>	<i>-54.8</i>	<i>-42.0</i>	<i>-51.0</i>	<i>5.4</i>	<i>2.4</i>	<i>11.4</i>
C _{7a}	7.3	-73.9	-47.1	-60.4	-2.5	-0.5	15.1
	<i>7.4</i>	<i>-74.9</i>	<i>-47.6</i>	<i>-61.2</i>	<i>-3.9</i>	<i>1.1</i>	<i>5.9</i>
N	8.1	-59.5	-51.9	-56.2	0.2	-9.3	1.3
	<i>7.9</i>	<i>-59.4</i>	<i>-49.8</i>	<i>-51.6</i>	<i>-0.6</i>	<i>-6.4</i>	<i>-1.1</i>
Br ₁	53.6	-444	-330	-453	-6.0	-2.6	107.0
	<i>53.2</i>	<i>-438</i>	<i>-328</i>	<i>-443</i>	<i>-4.2</i>	<i>-3.2</i>	<i>93.0</i>
Br ₄	48.2	-360	-293	-416	-37.8	16.0	107.0
	<i>50.0</i>	<i>-377</i>	<i>-305</i>	<i>-425</i>	<i>-28.6</i>	<i>10.4</i>	<i>97.2</i>

considered to be unnecessary, and were not made. About 2080 reflections were accessible to the spectrogoniometer, and about 1800 of these have $k \leq 3$. Of this number, 930 were observed. The range of observed structure amplitudes was about 1 to 66.

Structure determination

The structure was determined by heavy-atom methods, the contributions of the bromine atoms being sufficient to fix the signs of nearly all the structure factors. Refinement was accomplished with three cycles of structure-factor calculation and differential synthesis, using the procedures of Ahmed & Barnes (1958). The scattering-factor curves used were those of McWeeny (1951) for carbon and nitrogen, and that of Thomas & Umeda (1957) for bromine. Early in the analysis it became obvious that the thermal motion of the bromine atoms was strongly anisotropic; this situation was met by substituting for each bromine atom four atoms of one quarter weight at the corners of an appropriate rectangle (Kartha & Ahmed, 1960). The intention was to match the observed and assumed shapes of these atoms, as revealed by F_o and F_c differential syntheses. The final peak heights and curvatures are compared in Table 1. For the F_c results, the light atoms were assumed to have isotropic

thermal motion, with $B=3.64 \text{ \AA}^2$; for the bromine atoms the effective temperature factors were assumed to range from 3.64 to 7.00 \AA^2 , and the lengths of the sides of the rectangles adopted ranged from 0.29 to 0.39 \AA .

The final atomic positions (including those of the fractional bromine atoms) are given in Table 2. These positions include finite summation corrections (which are simply the differences between assumed and actual peak positions in the F_c differential synthesis). For the light atoms, corrections as great as 0.055 \AA were indicated. Moreover, the magnitudes of the corrections were found to be critically dependent on the assumptions pertaining to thermal anisotropy; in the final stages of refinement a comparatively trivial change in these assumptions caused changes in the corrections of as much as 0.022 \AA . It is considered that residual finite summation errors may seriously limit the accuracy of the analysis.

Assessment of the analysis

The agreement between observed and calculated structure amplitudes is such that there can be little doubt of the essential correctness of the structure. The final agreement residual ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) is 0.093, for observed reflections only. The list of F_o and F_c

Table 2. *Atomic positions*

Coordinates in braces are those of the fractional bromine atoms

Atom	x	y	z
C_1	0.3262	0.5527	-0.1140
C_2	0.2453	0.6185	-0.1352
C_{2a}	0.2030	0.4849	-0.0621
C_3	0.1269	0.4217	-0.0188
C_4	0.1437	0.2447	0.0615
C_{4a}	0.2270	0.1951	0.0744
C_5	0.2866	0.0573	0.1362
C_6	0.3675	0.0848	0.1113
C_7	0.3932	0.2361	0.0210
C_{7a}	0.3348	0.3810	-0.0334
N	0.2580	0.3474	-0.0042
Br ₁	0.4130	0.6914	-0.1948
Br ₂	0.4217	0.6694	-0.1852
	0.4098	0.6410	-0.1987
	0.4162	0.7418	-0.1909
	0.4043	0.7133	-0.2044
Br ₄	0.0664	0.1076	0.1504
	0.0781	0.1106	0.1614
	0.0707	0.0483	0.1508
	0.0620	0.1669	0.1501
Br ₃	0.0546	0.1047	0.1395
	0.0781	0.1106	0.1614
	0.0707	0.0483	0.1508
	0.0620	0.1669	0.1501

is not included here, although it is available from the author on request. Instead a summary of the detailed agreement is given in Table 3. Values of F_o range from 4 to 262, and $F_c(000) = 568$.

Table 3. *Agreement summary*

(a) Observed reflections		
Category	Number of reflections	Largest F_o in category
1 ($\Delta F \leq F_L$ or $\Delta F \leq 0.2F_o$)	862	262
2 ($\Delta F \leq 2F_L$ or $\Delta F \leq 0.4F_o$)	66	63
3 ($\Delta F \leq 3F_L$ or $\Delta F \leq 0.6F_o$)	2	19
(b) Unobserved reflections (accessible on Weissenberg films)		
Category	Number of reflections	Largest F_c in category
1 ($F_c \leq F_T$)	754	13
2 ($F_c \leq 2F_T$)	84	23
3 ($F_c \leq 3F_T$)	2	18

$$\Delta F = ||F_o| - |F_c||.$$

F_L = Structure amplitude corresponding to least count of spectrogoniometer system (maximum value 6).

F_T = Structure amplitude corresponding to threshold intensity on Weissenberg films (maximum value 13).

Each category includes all reflections which meet the specified conditions and which have not been previously included. For example, a reflection in category 2(a) satisfies either (or both) of the conditions $\Delta F \leq 2F_L$ and $\Delta F \leq 0.4F_o$, but does not satisfy either of the corresponding conditions for category 1(a).

The accuracy of the analysis is less satisfactory, as might be expected for a structure in which the aggregate scattering power of the bromine atoms

exceeds that of the lighter atoms. The standard deviations of atomic coordinates have been estimated by the method of Cruickshank, for observed reflections only (Lipson & Cochran, 1953). For bromine atoms the mean value is 0.0015 Å; for the lighter atoms, whose curvatures are appreciably modified by finite summation effects, individual standard deviations range from 0.010 to 0.019 Å, and no useful mean value can be given.

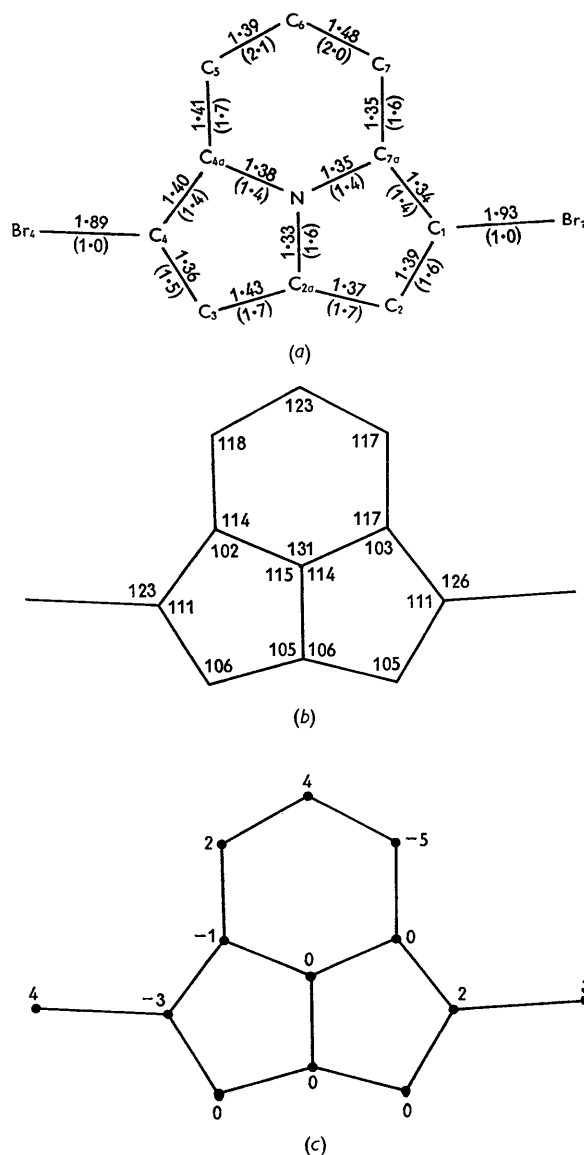


Fig. 1. (a) Bond lengths and their standard deviations. The latter have been multiplied by 100, and are shown in parentheses. The numbering system corresponds to that of Windgassen *et al.* (1959). (b) Bond angles. (c) Distances of atomic positions from mean plane (multiplied by 100).

The bond lengths with their respective standard deviations are shown in Fig. 1(a). It will be seen that there are rather large differences between certain

chemically equivalent bonds. For example, $l_{6,7}$ is 0.09 Å greater than $l_{5,6}$, and for this pair of bonds $\sigma = (\sigma_{5,6}^2 + \sigma_{6,7}^2)^{\frac{1}{2}} = 0.03$ Å. Thus $\Delta l = 3\sigma$. Is this difference significant? Probably not, in spite of the statistical inference. The problem of residual finite summation errors has already been discussed, and it seems likely that the estimated standard deviations give a false impression of the accuracy actually achieved.

Discussion of the structure

In Fig. 1(c) the distances of the atoms from the reference plane $1.188x + 3.460y + 7.064z = 1.513$ are shown. The molecule is very nearly planar, and in particular there is no significant departure from planarity of the group consisting of the nitrogen atom and its three bonded carbon atoms. The estimated standard deviation of the nitrogen position is 0.010 Å, and even allowing for residual finite summation errors it is not considered that this position could be in error by as much as 0.07 Å. The question of the nitrogen configuration is a crucial one, however, and it would be well to consider ways in which a pyramidal configuration might appear to be planar. This could occur, for example, if the structure were disordered or if the nitrogen atom were alternating between equilibrium positions on opposite sides of the mean plane. In both cases the average molecule might be planar, but the nitrogen atom would then be elongated in the direction of the normal. A comparison of the peak heights and curvatures for this atom (Table 1) reveals no such effect, although it is difficult to specify the smallest detectable elongation. It is believed that if the distance between effective equilibrium positions of the nitrogen atom were as much as 0.14 Å, some elongation would most probably be apparent. It is concluded therefore that the nitrogen configuration is probably planar, and that if it is not, the nitrogen atom must be less than 0.07 Å from the mean plane of the molecule.

The bromine atoms are in thermal motion which is such that they appear to be oblate spheroids, with their short, unique axes directed approximately along the bonds. Their shapes, somewhat idealized, are illustrated in Fig. 2. It seems that the thermal motion of these atoms is constrained chiefly by their relatively inextensible bonds.

The distance between the planes of molecules related by the **b** translation is 3.46 Å. Other short intermolecular distances are indicated in Fig. 2.

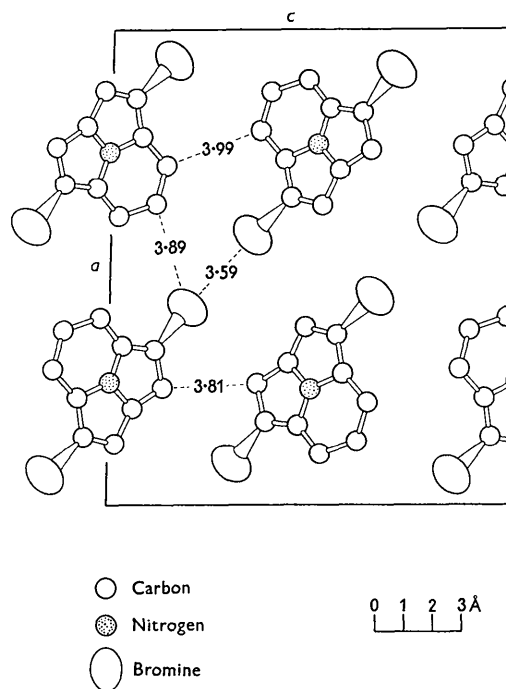


Fig. 2. The structure, viewed along **b**.

All computations for this project were carried out by Dr F. R. Ahmed of this laboratory on an IBM 650 computer made available by the Commanding Officer and staff of No. 1 Army Pay Ledger Unit. Crystalline samples were supplied by Prof. Boekelheide. It is a pleasure to record my indebtedness to all these people, and to Dr W. H. Barnes of this laboratory for valued advice and encouragement.

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