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The Crystal Structure of *p*-Dimethylaminobenzaldehyde Hydrobromide

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p-Dimethylaminobenzaldehyde hydrobromide ($C_9H_{11}NO \cdot HBr$) crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The cell dimensions are $a = 12.65 \pm 0.02$, $b = 10.20 \pm 0.02$, $c = 7.42 \pm 0.03$ Å, $\beta = 90^\circ 30' \pm 20'$. The structure was solved by heavy-atom methods using three-dimensional X-ray data. The positions of hydrogen atoms were located from a difference Fourier synthesis. The structure was refined by three-dimensional full-matrix least squares method leading to a final R value of 10.8%. The intra- and intermolecular features of the structure are discussed in detail. The amino nitrogen atom has been found to assume a tetrahedral configuration. The planar benzene ring is almost coplanar with the aldehyde group. The partial double-bond character of the exocyclic C–C bond has been attributed to a number of resonance forms. The only hydrogen bond (between the amino nitrogen and the bromine atom) is of the type $N^+ - H \cdots Br^-$ with a length of 3.127 ± 0.018 Å. The molecules are held together by van der Waals forces.

Introduction

The determination of the crystal and molecular structure of *p*-dimethylaminobenzaldehyde ($C_9H_{11}NO$) in the form of its hydrohalides has been undertaken by us in an attempt to correlate their structural features and biological functions. This compound plays an important role in differentiating between serum eruptions and true scarlet fever. From the chemical point of view also, *p*-dimethylaminobenzaldehyde is an interesting compound. The three isomers exist with aldehyde and dimethylamino groups in the *p*, *m* and *o* positions with respect to each other. If structural studies of all three isomers, *i.e.* *p*-, *m*-, and *o*-, could be made, they might furnish useful information. Thus, both from structural and functional points of view the study of this compound is indeed significant. The present communication deals with the complete solution of the crystal and molecular structure of *p*-dimethylaminobenzaldehyde hydrobromide. A preliminary account of the structure of this compound has already been published (Dattagupta & Saha, 1970) and was also pre-

sented at the Fourth All India Symposium in Biophysics (Saha & Dattagupta, 1969).

Experimental

The compound was prepared by treating *p*-dimethylaminobenzaldehyde with 30% hydrobromic acid and single crystals were grown by allowing the solution to evaporate at about 35–40°C. The transparent needle shaped crystals thus grown belong to the monoclinic system, *c* being the needle axis. As the crystal was unstable under normal atmospheric conditions, it was sealed in a thin glass capillary tube for taking X-ray photographs. The unit cell dimensions, as determined from rotation, oscillation and Weissenberg photographs are: $a = 12.65 \pm 0.02$, $b = 10.20 \pm 0.02$, $c = 7.42 \pm 0.03$ Å, $\beta = 90^\circ 30' \pm 20'$.

Systematic absences, $0k0$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, indicate that the space group is $P2_1/c$. The density of the crystals, as measured by the method of flotation, has been found to be 1.54 g cm^{-3} , while that calculated for four formula units ($C_9H_{11}NO \cdot HBr$) per unit cell is

1.59 g cm⁻³. Three-dimensional intensity data were collected from multiple-film equi-inclination Weissenberg photographs using Cu K α radiation. Six layers of data by rotation about the *c* axis (the needle axis) were recorded. Practical difficulties existed in cutting the crystals to the correct shape and size for taking photographs along the other axes. Only zero and first layers were therefore recorded about the *b* axis with the idea of putting the intensities on the same relative scale by the cross-layer correlation method. The crystals selected for photographs taken about the *c* and *b* axes were

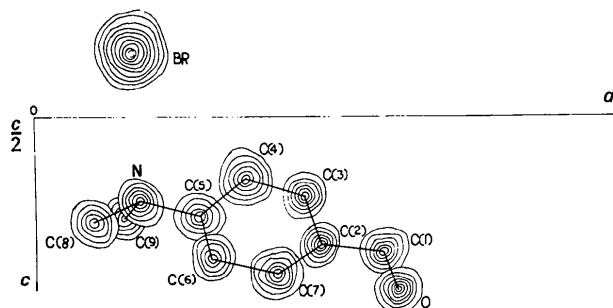


Fig. 1. Final electron density map.

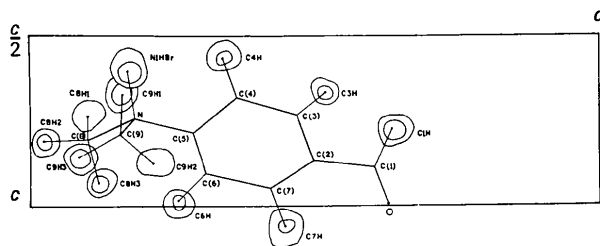


Fig. 2. Difference Fourier map.

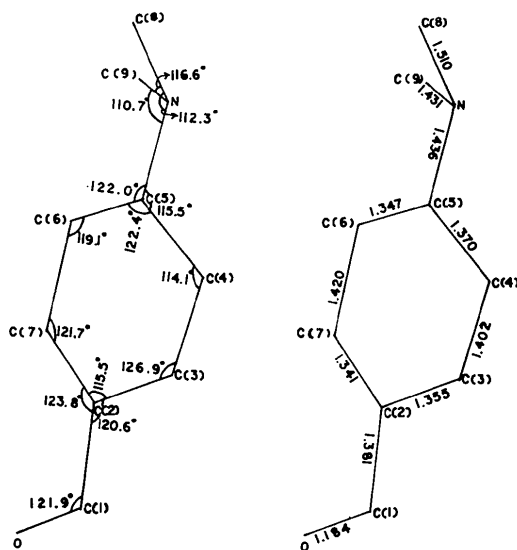


Fig. 3. Intramolecular bond distances and angles.

of square cross-sections of length 0.28 and 0.20 mm respectively. About 900 independent reflexions, out of 1097 accessible in the limiting sphere of Cu K α radiation, were collected and the intensities were estimated visually by comparison with a set of standard intensity strips prepared specially for this purpose. The reflexions with almost unobservable intensities were assigned a value of one-half the minimum measured intensity. The intensities were corrected for spot shape (Philips, 1954, 1956, 1962), and Lorentz and polarization factors. Absorption corrections for intensity were made by assuming the crystals to be cylindrical with radii 0.017 and 0.012 cm about the *c* and *b* axes respectively, the absorption coefficient for *p*-dimethylaminobenzaldehyde hydrobromide crystal being 57.1 cm⁻¹ (Cu K α). The intensity data from different layers were brought to the same scale by cross-layer correlation method and converted to absolute values by Wilson's method. The scale and temperature factors were initially obtained from Wilson plots and later refined by the least-squares method.

Structure determination

An attempt was first of all made to determine the structure from two-dimensional data, namely those of the *h*0*l* and *h**k*0 reflexions. The positions of the bromine atoms were located from the Patterson projections along the *b* and *c* axes. An attempt was then made to derive the structure from the Patterson projections and the minimum function due to Buerger, but it did not provide any meaningful clue. Therefore the two-dimensional bromine-phased Fourier synthesis was computed and an attempt was made to derive the structure from the Fourier map and the minimum function plot. This also did not work as there was considerable overlapping of peaks in the projections.

A three-dimensional Fourier synthesis was then computed using observed structure amplitudes and the phases of the heavy atom. The weight assigned to each term (Woolfson, 1956) is

$$W = 2P_+ - 1$$

where P_+ is the probability that the sign of F is the same as that of F_H and is given by,

$$P_+ = \frac{1}{2} + \frac{1}{2} \tanh \left(\frac{|F| |F_H|}{\sum f_i^2} \right)$$

where $|F|$ is the observed structure amplitude, $|F_H|$ is the calculated structure amplitude due to the heavy atom and $\sum f_i^2$ is the sum of the squares of the scattering factors for the light atoms. Structure factors using G. A. Mair's *SFLS* program and Fourier summation using F. R. Ahmed's three-dimensional Fourier program were computed on IBM 1620. A spoke and bead model was built. This trial structure was satisfactory from stereochemical considerations. The disagreement index R , defined by

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

was found to be 0.28 (that for heavy atoms only being 0.42) at this stage.

Refinement of the structure

The three-dimensional refinement of the structure was carried out by the full-matrix least-squares method. To begin with, two cycles of refinement using isotropic temperature factors were made on the CDC 3600 computer using the modified (Srikanta, 1964) version of the *ORFLS* program of Busing, Martin & Levy (1962). The function minimized in the least-squares calculation was $\sum w(|F_o| - |F_c|)^2$, where the summations are over the set of crystallographically independent observed planes and the w 's are the weights for each term. In this case, unit weight was assigned to all the reflexions. The scattering factors for Br⁻, O, N and C atoms were taken from *International Tables for X-ray Crystallography* (1960). The R value at this stage was found to be 0.22. It was observed that the temperature factor for C(9) was considerably higher than that for other carbon atoms. At this stage a difference Fourier map was calculated using J. F. Blount's Pre-Fourier program. It showed a negative region at the assigned position of C(9), whereas the rest of the atomic sites in the map were almost flat. A Fourier summation was then computed using the same program with all non-hydrogen atoms except C(9). A new peak, though weaker in

strength, was assigned to the C(9) atom as it better satisfied the stereochemical requirements. The high electron density of the peak which was earlier assigned to the C(9) atom was probably due to its proximity to the bromine atom. The value of R calculated with the altered coordinates of C(9) was 0.20. After two more cycles of refinement, R came down to 0.16. As the shifts in the atomic parameters were less than their estimated standard deviations, the refinement with isotropic temperature factors was stopped at this stage. The data was then checked for extinction effects and it was found that only one low order reflexion (020) had its $|F_c|$ much higher than the corresponding $|F_o|$ value, [$|F_o| = 86.4$; $|F_c| = 157.1$]. This reflexion was excluded from the refinement. Considering the reliability of visual estimation of intensities, a threshold value Y_{MIN} was fixed at 7% of the maximum observed structure amplitude and all the reflexions with $|F|$ less than the threshold value were excluded of full-matrix refinement and R value calculation. Two more cycles of full-matrix refinement with anisotropic temperature factors for the non-hydrogen atoms were carried out and the R value at this stage was found to be 0.115. A three-dimensional difference Fourier synthesis based on the last cycle of refinement was then computed to locate the hydrogen atom positions. Further refinement included the hydrogen atoms, the temperature factors assigned to the hydrogen atoms being those of the heavier atoms to which they are attached. After one

Table 1. Fractional atomic coordinates of non-hydrogen atoms and their estimated standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>
Br	0.1611 (2)	0.0225 (3)	0.3176 (4)
O	0.6237 (15)	0.2213 (19)	0.9988 (32)
N	0.1727 (11)	0.0211 (17)	0.7386 (25)
C(1)	0.5955 (17)	0.1450 (30)	0.8883 (38)
C(2)	0.4898 (22)	0.1171 (27)	0.8592 (46)
C(3)	0.4597 (17)	0.0316 (29)	0.7288 (39)
C(4)	0.3560 (19)	-0.0045 (26)	0.6824 (38)
C(5)	0.2798 (20)	0.0576 (23)	0.7809 (42)
C(6)	0.3031 (15)	0.1501 (25)	0.9043 (34)
C(7)	0.4107 (20)	0.1762 (28)	0.9469 (38)
C(8)	0.0934 (24)	0.1219 (31)	0.8017 (56)
C(9)	0.1531 (25)	-0.1120 (33)	0.7894 (45)

Table 3. Fractional atomic coordinates of hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)H	0.6310 (195)	0.1550 (287)	0.7720 (364)
C(3)H	0.5090 (206)	0.0030 (289)	0.6560 (378)
C(4)H	0.3350 (211)	-0.0500 (260)	0.5614 (388)
C(6)H	0.2550 (178)	0.1600 (258)	0.9944 (346)
C(7)H	0.4333 (210)	0.2300 (273)	1.0666 (383)
N(1)H Br	0.1640 (169)	0.0231 (219)	0.6000 (484)
C(8)H(1)	0.0920 (280)	0.2150 (321)	0.7320 (623)
C(8)H(2)	0.0170 (277)	0.1040 (330)	0.8090 (585)
C(8)H(3)	0.1136 (284)	0.1601 (327)	0.9323 (616)
C(9)H(1)	0.1580 (247)	-0.1600 (314)	0.6666 (438)
C(9)H(2)	0.2083 (262)	-0.1500 (316)	0.8750 (434)
C(9)H(3)	0.0803 (259)	-0.1201 (314)	0.8587 (447)

Table 2. Thermal parameters (anisotropic) and their estimated standard deviations

The temperature factor expression used was $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	0.0048 (2)	0.0101 (4)	0.0109 (8)	-0.0006 (2)	-0.0003 (3)	-0.0005 (4)
O	0.0050 (14)	0.0093 (28)	0.0197 (67)	-0.0029 (15)	0.0025 (24)	-0.0013 (30)
N	0.0006 (9)	0.0016 (19)	0.0077 (50)	0.0005 (12)	0.0004 (16)	-0.0009 (24)
C(1)	0.0019 (14)	0.0130 (42)	0.0066 (77)	0.0006 (19)	-0.0046 (27)	-0.0026 (42)
C(2)	0.0043 (19)	0.0060 (35)	0.0180 (87)	0.0005 (21)	0.0005 (33)	-0.0029 (42)
C(3)	0.0021 (14)	0.0109 (37)	0.0115 (76)	0.0019 (20)	0.0009 (25)	0.0090 (46)
C(4)	0.0050 (19)	0.0072 (35)	0.0084 (71)	-0.0001 (21)	0.0006 (29)	0.0028 (36)
C(5)	0.0038 (17)	0.0043 (32)	0.0163 (80)	-0.0008 (18)	0.0015 (31)	-0.0051 (37)
C(6)	0.0003 (11)	0.0095 (34)	0.0063 (66)	-0.0015 (16)	-0.0004 (21)	-0.0003 (36)
C(7)	0.0051 (19)	0.0090 (35)	0.0061 (70)	0.0003 (23)	-0.0046 (29)	0.0031 (38)
C(8)	0.0094 (32)	0.0089 (44)	0.0507 (151)	-0.0038 (30)	-0.0003 (55)	-0.0119 (63)
C(9)	0.0083 (27)	0.0126 (50)	0.0166 (41)	-0.0044 (29)	0.0020 (38)	0.0089 (49)

Table 4. Intramolecular bond distances, bond angles and their estimated standard deviations

O—C(1)	1.184 (36)	C(9)—N—C(5)	110.7 (2.0) ^o
N—C(5)	1.436 (29)	C(8)—N—C(5)	112.3 (2.0)
N—C(8)	1.510 (36)	C(8)—N—C(9)	116.6 (2.1)
N—C(9)	1.431 (38)	C(6)—C(5)—N	122.0 (2.2)
C(1)—C(2)	1.381 (35)	C(4)—C(5)—N	115.5 (2.2)
C(2)—C(3)	1.355 (42)	C(4)—C(5)—C(6)	122.4 (2.5)
C(2)—C(7)	1.341 (39)	C(7)—C(6)—C(5)	119.1 (2.3)
C(3)—C(4)	1.402 (33)	C(3)—C(4)—C(5)	114.1 (2.4)
C(4)—C(5)	1.370 (37)	C(2)—C(7)—C(6)	121.7 (2.5)
C(5)—C(6)	1.347 (37)	C(2)—C(3)—C(4)	126.9 (2.6)
C(6)—C(7)	1.420 (32)	C(7)—C(2)—C(3)	115.5 (2.7)
		C(1)—C(2)—C(3)	120.6 (2.7)
		C(1)—C(2)—C(7)	123.8 (2.7)
		O—C(1)—C(2)	121.9 (2.6)

cycle of refinement R had decreased to 0.108. The R value for all the reflexions at this stage was 0.129.

The positional and thermal parameters of the atoms together with their estimated standard deviations are given in Tables 1, 2 and 3.* The composite drawings of the final electron density map and the difference Fourier map are shown in Figs. 1 and 2 respectively.

* A list of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30072. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. Intramolecular bond distances involving hydrogen atoms, and their standard deviations

C(1)—C(1)H	0.982 (267)
C(3)—C(3)H	0.879 (274)
C(4)—C(4)H	1.043 (259)
C(6)—C(6)H	0.914 (245)
C(7)—C(7)H	1.081 (281)
N—H(HBr)	1.034 (358)
C(8)—C(8)H(1)	1.082 (359)
C(8)—C(8)H(2)	0.992 (351)
C(8)—C(8)H(3)	1.071 (438)
C(9)—C(9)H(1)	1.037 (324)
C(9)—C(9)H(2)	1.017 (325)
C(9)—C(9)H(3)	1.062 (331)

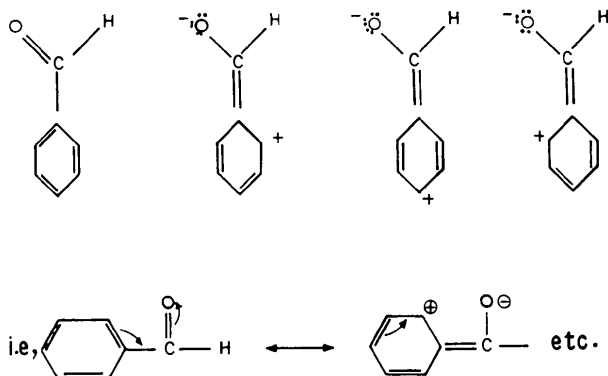


Fig. 4. Resonance structures for the benzaldehyde ion.

Discussion

The intramolecular bond distances and bond angles are given in Table 4 and shown diagrammatically in Fig. 3. Intramolecular bond distances involving hydrogen atoms are given in Table 5.

The lengths of the C—C bonds in the benzene ring of the present compound range from 1.341 to 1.420 Å, the average value being 1.375 Å. This average distance is not significantly different from those reported by other workers for benzene: 1.380 (Palenik, Donohue & Trueblood, 1968), 1.392 (Cox, Cruickshank & Smith, 1958) and 1.397 Å (Stoicheff, 1954). Though the average value of the bond angles in the benzene ring as obtained by us (119.9^o) agrees well with the standard value (120^o), the individual values vary over a wide range of 114.1 to 126.9^o. This variation may be due primarily to the presence of the two groups attached to the benzene ring in the *para* positions. The fact that the heavy atom bromine is attached to the amino nitrogen atom may also have some effect. The equation of the least-squares plane passing through the carbon atoms of the benzene ring is:

$$0.0123x' - 0.7278y' + 0.6858z' = 3.5640$$

where x' , y' , z' (in Å) are referred to a set of orthogonal axes given by $x' = x + z \cos \beta$, $y' = y$ and $z' = z \sin \beta$. The deviations of the individual atoms from the plane are shown as follows:

Atoms	Deviations (Å)
C(2)	-0.015
C(3)	+0.018
C(4)	+0.002
C(5)	-0.026
C(6)	+0.026
C(7)	-0.011

The sum of the three angles around the C(5) atom, *i.e.* C(4)—C(5)—N = 115.5^o, C(6)—C(5)—N = 122.0^o and C(4)—C(5)—C(6) = 122.4^o, is 359.9^o. This indicates the planarity of the four atoms, C(4), C(5), C(6) and N.

The two N—C bonds between the methyl carbon and amino nitrogen atoms in this compound, *i.e.* N—C(8)

and N–C(9), have been found to be 1.510 ± 0.036 and 1.431 ± 0.038 Å respectively. The values of the corresponding C–N bonds in some allied compounds are: 1.531 and 1.464 Å in *N,N*-dimethyl-*p*-nitroaniline (Mak & Trotter, 1965), and 1.450 Å each in *N,N*-dimethyl-*p*-phenylenediamine bromide (Tanaka & Sakabe, 1968). However, the significance test (Cruickshank & Robertson, 1953) indicates that the difference between these two bond lengths is not significant ($t=1.52$ and $P=0.1286$). The average of the three C–N bond lengths (1.460 Å) compares well with the standard C–N bond length (1.47 Å). The protonated amino nitrogen is tetrahedrally bonded to C(5), C(8), C(9) and bromine atom. The angles around N are: C(9)–N–C(5) = 110.7° , C(8)–N–C(5) = 112.3° , C(8)–N–C(9) = 116.6° , Br–N–C(5) = 104.7° , Br–N–C(8) = 106.4° and Br–N–C(9) = 105.1° .

The length of the C=O bond in the aldehyde group attached at the *para* position of the benzene ring has been found to be 1.184 ± 0.036 Å; the corresponding values are 1.18 Å in 9-anthraldehyde (Ehrenberg, 1968), 1.20 Å in *o*-nitrobenzaldehyde (Coppens & Schmidt, 1964) and 1.20 Å in glyoxal (LuValle & Schomaker, 1939). The plane containing the aldehyde group and C(2) has been found to make an angle of $1^\circ 39'$ with the plane of the benzene ring; as the hydrogen atom position was not very reliable, it was not included in the plane calculation. The aldehyde group thus is almost coplanar with the benzene ring. As expected, the sum of the three angles around C(2) atom *i.e.* C(7)–C(2)–C(3) = 115.5° , C(1)–C(2)–C(3) = 120.6° and C(1)–C(2)–C(7) = 123.8° , is 359.9° . The length (1.381 ± 0.035 Å) of the exocyclic carbon–carbon bond, C(2)–C(1) in this compound is in good agreement with 1.37 Å in salicylic aldehyde (Wyckoff, 1969), but is shorter than the theoretically calculated (sp^2) single bond lengths between trigonally linked carbon atoms, 1.479 Å (Dewar & Schmeising, 1959) and 1.477 Å (Cruickshank & Sparks, 1960). The partial double-bond character (58%) (Pauling, 1960, p. 236) of the exocyclic C(2)–C(1) bond may be attributed to the resonance of a number of structures in which the molecules can exist (Fig. 4).

In order to have resonance of this type, the benzene ring and the groups attached to it must, according to Pauling (1960, p. 297), approximate to a planar configuration. It may be noted that in the present compound the attached aldehyde group is coplanar with the benzene ring. Incidentally, the resonance is restricted to this part of the molecule only.

The bromine atom is linked to the amino nitrogen $N^+ \cdots H \cdots Br^-$, the length being 3.127 ± 0.018 Å. The distance $H \cdots Br$ is 2.096 Å and the bond angles involving the hydrogen atom are N–H–Br = 174.6° and H–N–Br = 3.7° .

The molecular packing viewed along the *b* and *c* axes is shown in Figs. 5 and 6 respectively. There are a number of close intermolecular contacts, some involving hydrogen atoms attached to carbon atoms. The interatomic distances less than 4 Å are shown in Table 6.

The molecules are held together in three-dimensional space by van der Waals forces. The molecules are arranged in such a way (Figs. 5 and 6) that one molecule is displaced relative to the other along the *a* axis and the aldehyde group of one molecule is situated above the benzene ring of the other, but slightly displaced

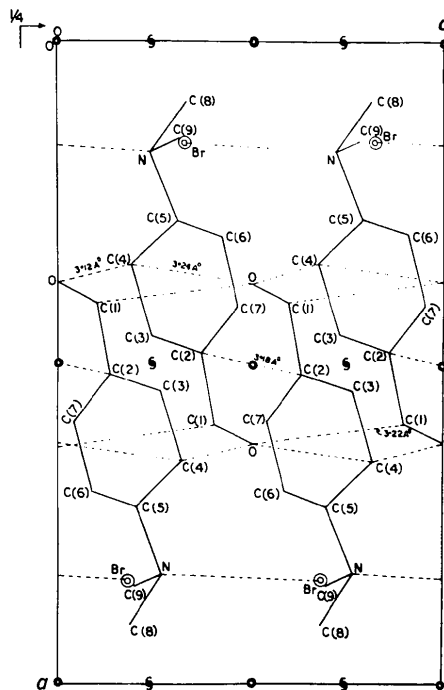


Fig. 5. Molecular packing viewed along the *b* axis.

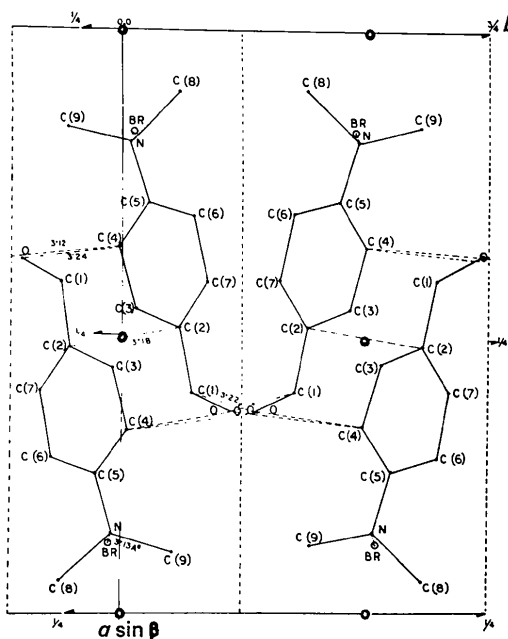


Fig. 6. Molecular packing viewed along the *c* axis.

Table 6. *Intermolecular distances less than 4 Å (excluding hydrogen atoms)*

Symmetry code			
None	$x, y, z;$	vi	$1-x, -y, 1-z$
i	$x, y, 1+z;$	vii	$1-x, 1-y, 1-z$
ii	$-x, -y, 1-z;$	viii	$1-x, -y, 2-z$
iii	$x, \frac{1}{2}-y, \frac{1}{2}+z;$	ix	$1-x, 1-y, 2-z$
iv	$x, \frac{1}{2}-y, z-\frac{1}{2};$	x	$1-x, \frac{1}{2}+y, \frac{3}{2}-z$
v	$x, 1+y, z;$	xi	$1-x, y-\frac{1}{2}, \frac{3}{2}-z$
	C(6)···Br ⁱ		3·798 Å
	C(1)···Br ^{vi}		3·849
	C(8)···Br ^{vii}		3·648
	C(4)···O ^{viii}		3·247
	C(9)···O ^{viii}		3·407
	C(2)···O ^{viii}		3·888
	C(3)···O ^{viii}		3·448
	C(5)···O ^{viii}		3·496
	C(6)···O ^{viii}		3·964
	C(4)···C(1 ^{viii})		3·542
	C(9)···C(1 ^{viii})		3·977
	C(2)···C(1 ^{viii})		3·444
	C(3)···C(1 ^{viii})		3·441
	C(5)···C(1 ^{viii})		3·566
	C(6)···C(1 ^{viii})		3·611
	C(7)···C(1 ^{viii})		3·498
	C(2)···C(2 ^{viii})		3·183
	C(3)···C(2 ^{viii})		3·468
	C(7)···C(2 ^{viii})		3·546
	C(4)···C(3 ^{viii})		3·867
	C(3)···C(3 ^{vi})		3·613
	C(7)···C(3 ^{viii})		3·592
	C(4)···O ^{xi}		3·115
	C(9)···O ^{xi}		3·943
	C(3)···O ^{xi}		3·735
	C(4)···C(1 ^z)		3·666
	C(6)···Br ⁱⁱⁱ		3·844
	C(8)···Br ⁱⁱⁱ		3·727
	O···O ^{iv}		3·757
	C(1)···O ^{iv}		3·219
	C(2)···O ^{iv}		3·580
	C(3)···O ^{iv}		3·692
	O···O ⁱⁱⁱ		3·757
	C(7)···C(2 ⁱⁱⁱ)		3·842
	C(7)···C(3 ⁱⁱⁱ)		3·691
	C(7)···C(4 ⁱⁱⁱ)		3·843

along the c axis. In addition to $N^+-H\cdots Br^-$ type hydrogen bonds, there seem to be close approaches of about 4·2, 4·3 and 4·7 Å between N^+ and Br^- . They are presumably very weak ionic bonds. These bonds un-

doubtedly play a part in the general formation of the structure, which shows very markedly the common situation of layers of inorganic regions separated by the organic portion of the structure.

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