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The Crystal Structure of *cis*-5, 6, 13, 13a-Tetrahydro-3,9-dihydroxy-1, 2, 10-trimethoxy-8*H*-dibenzo[*a,g*]quinolizine Hydrobromide Monohydrate

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The structure of a synthetic tetrahydroprotoberberine type base, $C_{20}H_{23}O_5N$, has been determined by X-ray analysis of the hydrobromide which is monoclinic with four molecules in a unit cell of dimensions, $a=17.43$, $b=13.01$, $c=8.97$ Å and $\beta=93.5^\circ$, space group Ic . The structure was solved by the heavy-atom method and refined by the least-squares method using 1977 observed reflexions. The final R value was 0.115. It has been found that the quinolizidine ring system in this molecule takes a *cis* conformation as that in capaurine hydrobromide does. The dihedral angle between the two benzene rings is 67.2° .

Introduction

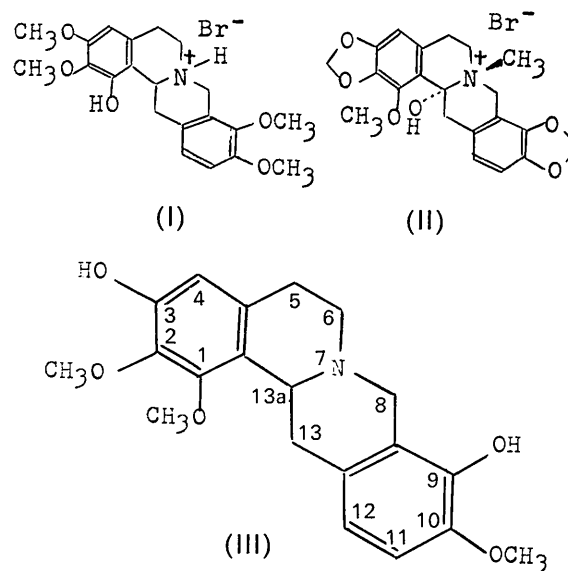
In a previous paper (Shimanouchi, Sasada, Ihara & Kametani, 1969), we reported the crystal structure of capaurine hydrobromide (I) and pointed out that the *BC* ring junction takes a *cis* conformation, which was an unexpected result. Recently, Stermitz, Coomes & Harris (1968) reported that coulteropine hydrobromide (II) has a *trans* form. It appears therefore that the potential barrier between the *cis* and *trans* forms of a 1-substituted dibenzoquinolizidine system may not be so large. The present work was initiated by our general interest in the factors determining the ring conformation of a molecule and the effect of intermolecular interactions on it.

The hydrobromide of (III), which is one of the synthetic bases prepared by Kametani and his co-workers in the course of the study of capaurine and capaurimine, was chosen in order to study the effect of substituents in comparison with (I).

Experimental

The hydrobromide of (III) was prepared by adding aqueous hydrobromic acid to a solution of (III) in methanol. It recrystallizes from the methanol-ether mixture as pale yellow prisms.

The crystallographic and physical data obtained are: $C_{20}H_{23}O_5N \cdot HBr \cdot H_2O$, m.p. $195-197^\circ$ (decomp.), monoclinic, $a=17.43$, $b=13.01$, $c=8.97$ Å, $\beta=93.5^\circ$. Space group, Ic . Four molecules per unit cell. Volume of the unit cell, 2030 Å³. Density (by flotation), 1.475 g.cm⁻³, density (calculated), 1.489 g.cm⁻³. Linear absorption coefficient for Cu $K\alpha$ radiation,



$\mu=33.22$ cm⁻¹. Total number of electrons per unit cell, $F(000)=944$.

Multiple-film equi-inclination Weissenberg photographs were taken at room temperature for the layers 0-7 about the *c* axis and the layers 0-9 about the *b* axis, with Cu $K\alpha$ radiation. Only one crystal was used, of dimensions $0.05 \times 0.05 \times 0.02$ cm.

Intensities were estimated by visual comparison with a standard scale prepared from the same crystal. Relative intensities ranged from 1 to 7500. Reflexions from 2142 planes were recorded out of 2300 possible (*hkl*)'s in the Cu sphere. Of these reflexions, 165 were observed

Table 1. *Final atomic coordinates and temperature factors*

The anisotropic temperature factors are expressed in the form

$$\exp \{ -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl) \} .$$

Br	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
	0.0000	0.0378	0.0000	0.00299	0.00384	0.01124	-0.00002	-0.00471	-0.00552	
	x/a	y/b	z/c	B						
	O(1)	-0.0478	-0.3825	-0.6262	1.98 Å ²					
	O(2)	-0.2045	-0.3785	-0.7283	2.23					
	O(3)	-0.3084	-0.2803	-0.5577	3.24					
	O(4)	0.2227	-0.1874	0.0073	2.12					
	O(5)	0.2846	-0.3484	0.1483	2.68					
	O(W)	0.1085	-0.1148	0.2354	6.21					
	C(1)	-0.1029	-0.3373	-0.5384	1.47					
	C(2)	-0.1803	-0.3362	-0.5966	1.91					
	C(3)	-0.2331	-0.2897	-0.5075	2.14					
	C(4)	-0.2099	-0.2449	-0.3756	2.32					
	C(5)	-0.1130	-0.2013	-0.1696	2.49					
	C(6)	-0.0295	-0.2176	-0.1137	1.04					
	N(7)	0.0181	-0.2071	-0.2469	1.16					
	C(8)	0.1025	-0.1944	-0.2021	1.82					
	C(9)	0.1947	-0.2798	-0.0240	1.57					
	C(10)	0.2242	-0.3692	0.0449	2.14					
	C(11)	0.1961	-0.4656	0.0063	2.58					
	C(12)	0.1360	-0.4751	-0.1020	2.07					
	C(13)	0.0337	-0.3972	-0.2784	1.67					
	C(14)	0.0060	-0.2962	-0.3520	1.21					
	C(15)	-0.0799	-0.2956	-0.4066	1.08					
	C(16)	-0.1332	-0.2509	-0.3169	1.52					
	C(17)	0.1327	-0.2913	-0.1324	1.19					
	C(18)	0.1033	-0.3871	-0.1706	1.56					
	C(19)	-0.0336	-0.3285	-0.7584	3.75					
	C(20)	-0.2076	-0.4920	-0.7289	4.69					
	C(21)	0.3244	-0.4364	0.2171	4.30					

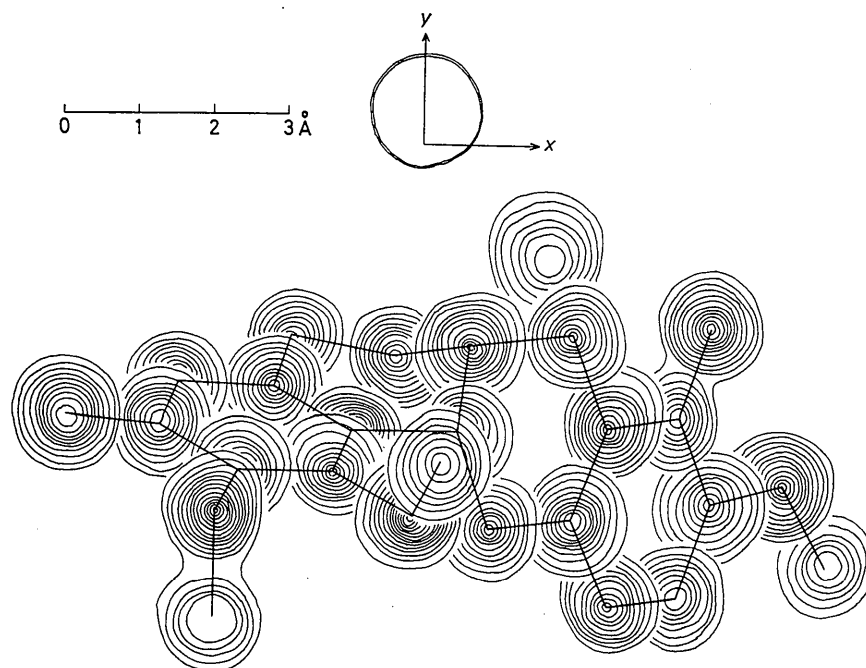


Fig. 1. Composite electron density diagram of sections parallel to (001). The contours are at intervals of $1.0 \text{ e.}\text{\AA}^{-3}$ starting with $1.0 \text{ e.}\text{\AA}^{-3}$. The contours of the bromine atom are omitted.

as zero intensity. The corrections for the Lorentz and polarization factors were made as usual and those for spot-shape in higher layer photographs were made by the method of Phillips (1954). The correction for absorption was neglected.

Structure determination

The structure was solved by the heavy-atom method. The y coordinate of the bromine atom was obtained

from the Patterson function and the x and z coordinates were arbitrarily set as zero. The first three-dimensional Fourier synthesis, based on the bromine atom only, showed a pseudosymmetry of $I2/c$. However, the bond length and angle criteria made it possible to distinguish the correct light atom peaks from the false ones and to construct a plausible molecular model. The second electron-density distribution was computed by taking the contribution of these atoms into account. The resulting map clearly showed peaks

Table 2. *Estimated standard deviations*

[$\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ in Å]									
Br	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
	0.0034	0.0018	0.0034	0.00005	0.00008	0.00020	0.00017	0.00017	0.00031
			$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$			
		O(1)	0.0107	0.0111	0.0107	0.18			
		O(2)	0.0114	0.0117	0.0111	0.19			
		O(3)	0.0132	0.0138	0.0132	0.24			
		O(4)	0.0110	0.0113	0.0111	0.19			
		O(5)	0.0119	0.0125	0.0122	0.21			
		O(W)	0.0211	0.0202	0.0213	0.41			
		C(1)	0.0141	0.0143	0.0142	0.22			
		C(2)	0.0155	0.0159	0.0154	0.25			
		C(3)	0.0158	0.0165	0.0162	0.26			
		C(4)	0.0165	0.0177	0.0169	0.27			
		C(5)	0.0172	0.0179	0.0175	0.28			
		C(6)	0.0126	0.0131	0.0125	0.20			
		N(7)	0.0110	0.0114	0.0111	0.17			
		C(8)	0.0148	0.0157	0.0147	0.25			
		C(9)	0.0144	0.0150	0.0144	0.22			
		C(10)	0.0161	0.0168	0.0163	0.26			
		C(11)	0.0175	0.0184	0.0174	0.28			
		C(12)	0.0160	0.0166	0.0161	0.25			
		C(13)	0.0146	0.0152	0.0147	0.23			
		C(14)	0.0133	0.0137	0.0134	0.20			
		C(15)	0.0129	0.0134	0.0130	0.20			
		C(16)	0.0144	0.0152	0.0143	0.22			
		C(17)	0.0132	0.0139	0.0133	0.20			
		C(18)	0.0143	0.0149	0.0144	0.22			
		C(19)	0.0216	0.0225	0.0218	0.39			
		C(20)	0.0255	0.0263	0.0251	0.48			
		C(21)	0.0241	0.0234	0.0239	0.43			

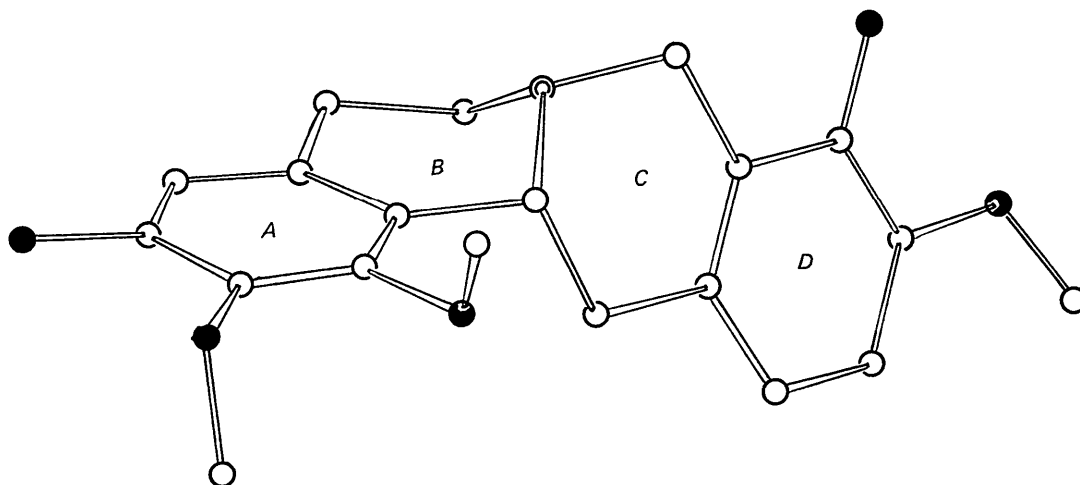


Fig. 2. Conformation of the molecule.

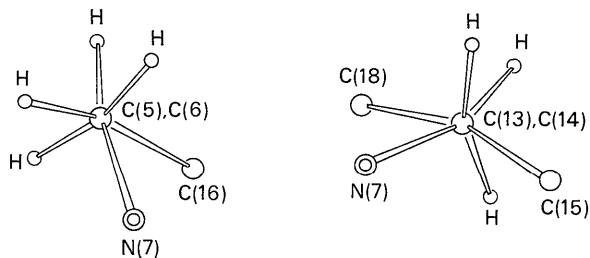


Fig. 4. Conformations about the C-C single bonds of rings *B* and *C*.

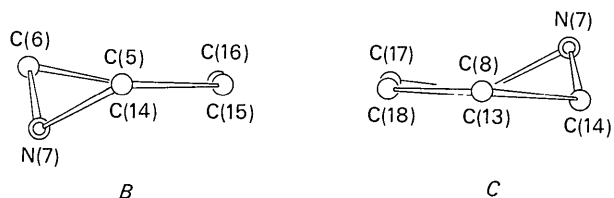


Fig. 5. Rings *B* and *C*, viewed along the lines C(5)⋯C(14) and C(8)⋯C(13) respectively.

temperature factors, of the form $\exp\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)\}$, were applied to the bromine atom, while the thermal motion of the light atoms was assumed to be isotropic. After several cycles of least-squares refinement, the discrepancy index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, was 0.132 for the observed reflexions. At this stage a difference synthesis was computed, and it revealed a significant residual peak which could be assigned as the water oxygen atom. A further three cycles of least-squares including this atom reduced the R value to 0.115. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and temperature factors are given in Table 1 and their standard deviations in Table 2. The rather small values of the temperature factors might be the consequence of neglecting the absorption correction. Observed and calculated structure factors are listed in Table 3. The final three-dimensional electron density distribution, calculated with phases based on these parameters, is shown in Fig. 1.

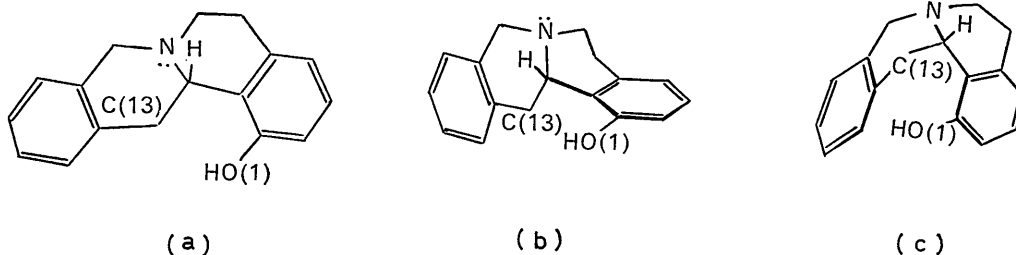


Fig. 6. Three possible conformations of dibenzo[*a,g*]quinolizidine.

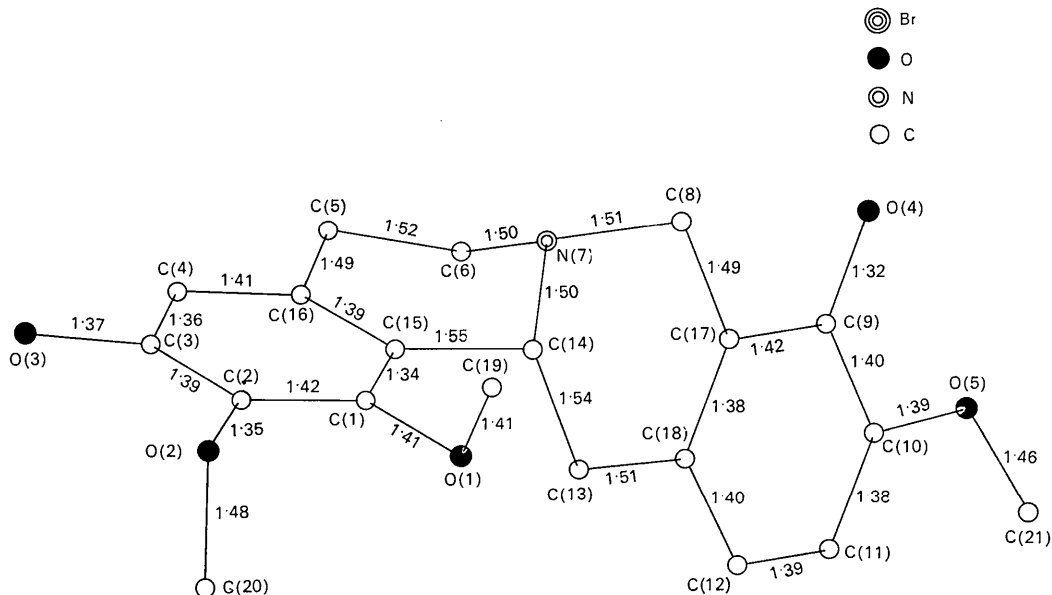


Fig. 7. Bond lengths (Å).

The computations were done on a HITAC 5020E computer in the University of Tokyo with programs written by Dr T. Ashida.

Results and discussion

Conformation

As shown in Fig. 2, it has been established that this compound is *cis*-5,6,13,13a-tetrahydro-3,9-dihydroxy-1,2,10-trimethoxy-8H-dibenzo[*a,g*]quinolizine hydrobromide monohydrate.

A view in Fig. 3 along the bond N(7)–C(14) shows that the *BC* ring fusion is *cis* and the conformation about this bond is almost completely staggered with conformation angles of about 60°. Rings *B* and *C* contain only one bond between tetrahedral carbon atoms. Views along these bonds in Fig. 4 show that both conformations are intermediate between staggered and eclipsed, the rings themselves being neither half-chair nor half-boat, as shown in Fig. 5. They are very close to those in capaurine hydrobromide.* The three C–N–C bond angles range from 110.4 to 112.0°, indicating that as already reported the nitrogen atom is tetrahedrally hybridized as in capaurine hydrobromide (Shimanouchi, Sasada, Ihara & Kametani, 1969). It is worth noticing that these features are very similar to those in capaurine hydrobromide, while the substituents and the crystal structure are quite different from each other.

* In the previous paper (Shimanouchi, Sasada, Ihara & Kametani, 1969), we described the conformations of the corresponding rings in capaurine as half-chair, but strictly speaking, this was not correct; they are neither half-chair nor half-boat.

In the quinolizidine skeleton, three conformations are considered, one *trans* (*a*) and two *cis* forms (*b*) and (*c*) as shown in Fig. 6. The present molecule and capaurine hydrobromide take the form (*b*), which appears to be the most stable. If the molecule took the form (*a*), the O(1)···C(13) distance would be too short (about 2.8 Å). On the other hand, if it took the (*c*) form, the two aromatic rings would be too close to each other. The observed O(1)···C(13) distance is 3.353 Å in the present molecule. The *trans* form of coulteropine hydrobromide (II) (Stermitz, Coomes & Harris, 1968) seems to result from the interaction between the hydroxyl group and the methyl group on the nitrogen atom and that between the hydroxyl and the methoxy group on C(1). Therefore, the *cis* conformation of the present molecule and capaurine hydrobromide does not seem to be characteristic of the crystal state of acid salts, and it may be considered that these free bases also take the *cis* form. In fact, it has been already reported that the stereochemistry of the acid salts of the quinolizidine derivatives is very similar to that of the free base (Moynehan, Schofield, Jones & Katritzky, 1962).

Molecular geometry

Intramolecular bond lengths and angles are shown in Figs. 7 and 8 respectively, and listed in Tables 4 and 5 with their estimated standard deviations. On account of the large standard deviations, the fluctuation of the lengths among the equivalent bonds of a certain type may not be significant. The average bond length of the aromatic C–C bonds is 1.390 Å. The average is 1.510 Å for the C(*sp*²)–C(*sp*³), 1.530 Å for the C(*sp*³)–C(*sp*³), 1.366 Å for the C(*sp*²)–O, 1.450 Å for the C(*sp*³)–O and 1.504 Å for the three C–N bonds.

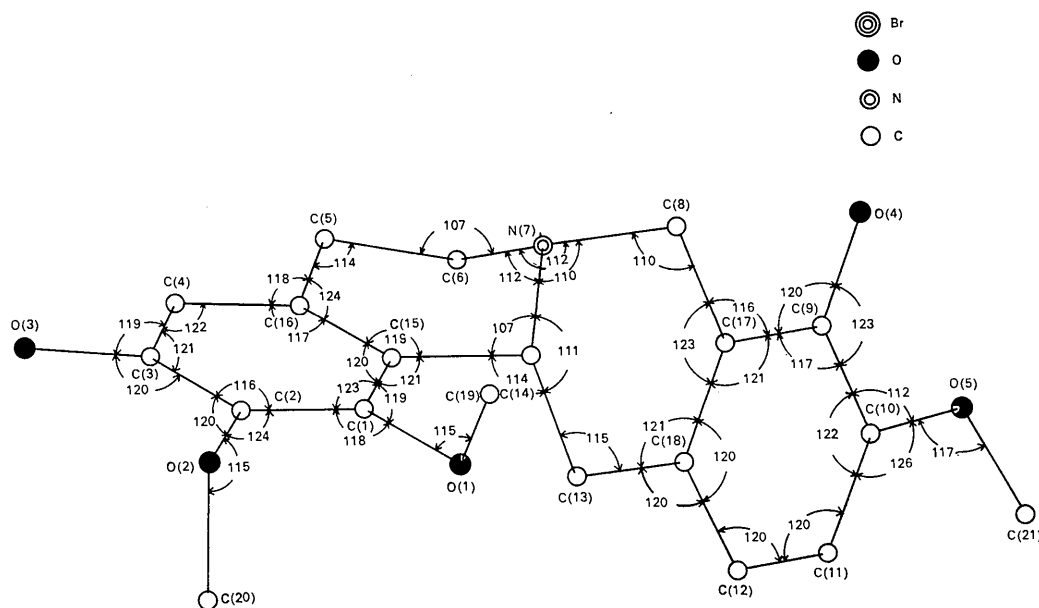


Fig. 8. Bond angles (degrees).

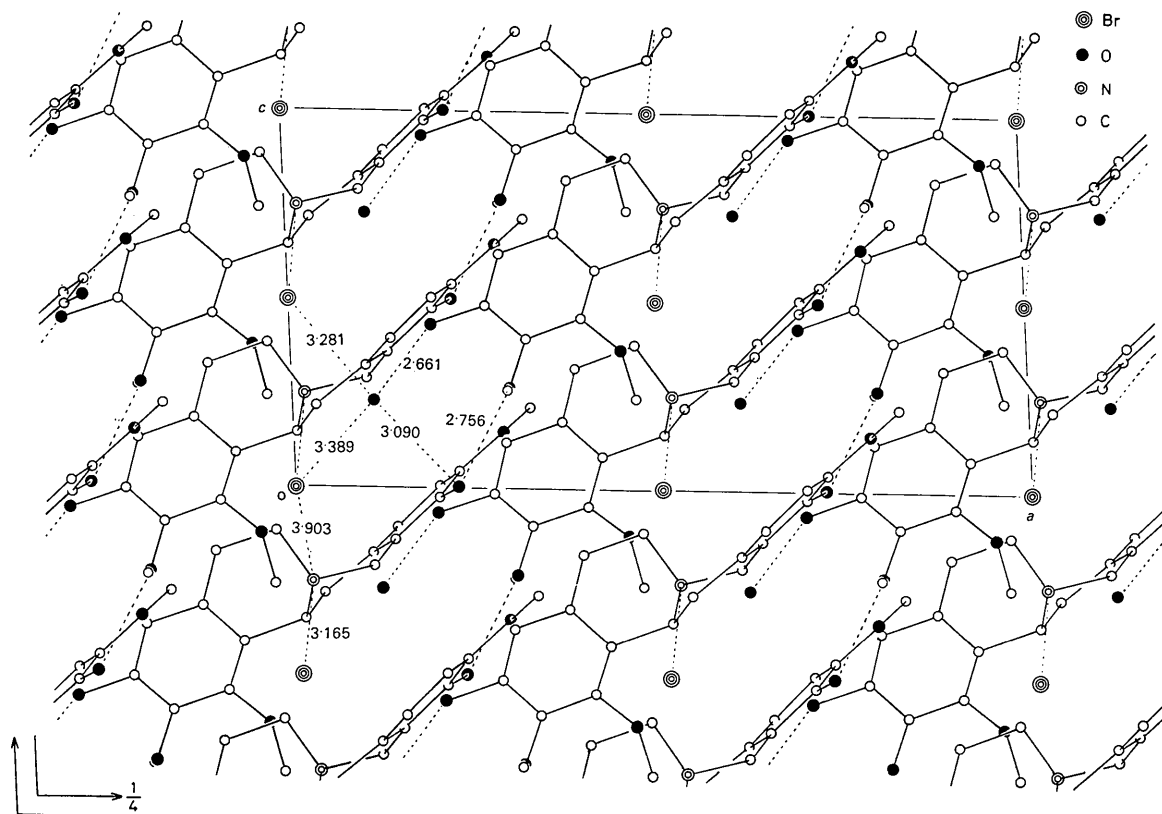


Fig. 9. The crystal structure projected along the b axis and some short intermolecular distances (\AA).

Table 4. Bond lengths and their *e.s.d.*'s

	Distance	<i>e.s.d.</i>
C(1)—C(2)	1.416 \AA	0.021 \AA
C(2)—C(3)	1.394	0.023
C(3)—C(4)	1.358	0.024
C(4)—C(16)	1.409	0.023
C(15)—C(16)	1.392	0.020
C(1)—C(15)	1.339	0.020
C(5)—C(16)	1.494	0.023
C(5)—C(6)	1.524	0.022
C(6)—N(7)	1.502	0.017
N(7)—C(14)	1.501	0.018
C(14)—C(15)	1.548	0.019
N(7)—C(8)	1.509	0.019
C(8)—C(17)	1.489	0.021
C(13)—C(18)	1.510	0.021
C(13)—C(14)	1.535	0.020
C(9)—C(17)	1.418	0.020
C(9)—C(10)	1.399	0.022
C(10)—C(11)	1.383	0.025
C(11)—C(12)	1.390	0.025
C(12)—C(18)	1.404	0.022
C(1)—O(1)	1.408	0.018
O(1)—C(19)	1.413	0.025
C(2)—O(2)	1.347	0.020
O(2)—C(20)	1.479	0.029
C(3)—O(3)	1.367	0.022
C(9)—O(4)	1.321	0.019
C(10)—O(5)	1.386	0.021
O(5)—C(21)	1.457	0.027

The equations of the least-squares planes of the six carbon atoms in the benzene rings A and D are $0.191x' + 0.874y' - 0.447z' + 1.967 = 0$ and $-0.699x' + 0.073y' + 0.712z' - 2.790 = 0$ respectively, where $x' = x + z \cos \beta$, $y' = y$ and $z' = z \sin \beta$. Each ring is planar within the errors. The dihedral angle between these planes is 67.2° , comparable with 70.7° in capaurine hydrobromide.

Crystal structure

The packing arrangements of the molecules viewed along the b and c axes are shown in Figs. 9 and 10 respectively. Some interesting features are observed in them. The bromide ions, by virtue of their small y parameter, are piled up to form columns along the c axis, the separation between successive bromide ions being 4.59\AA . As shown in Fig. 10, there appears to be a forbidden region around the organic molecule. The structure may therefore be considered to be of the tunnel type, which may be of wider interest since it would appear to be feasible to exchange other halide ions through such tunnels. A similar type of tunnel structure has been found in thelepegine methiodide (Fridrichsons & Mathieson, 1963).

In connexion with the above result, it is interesting

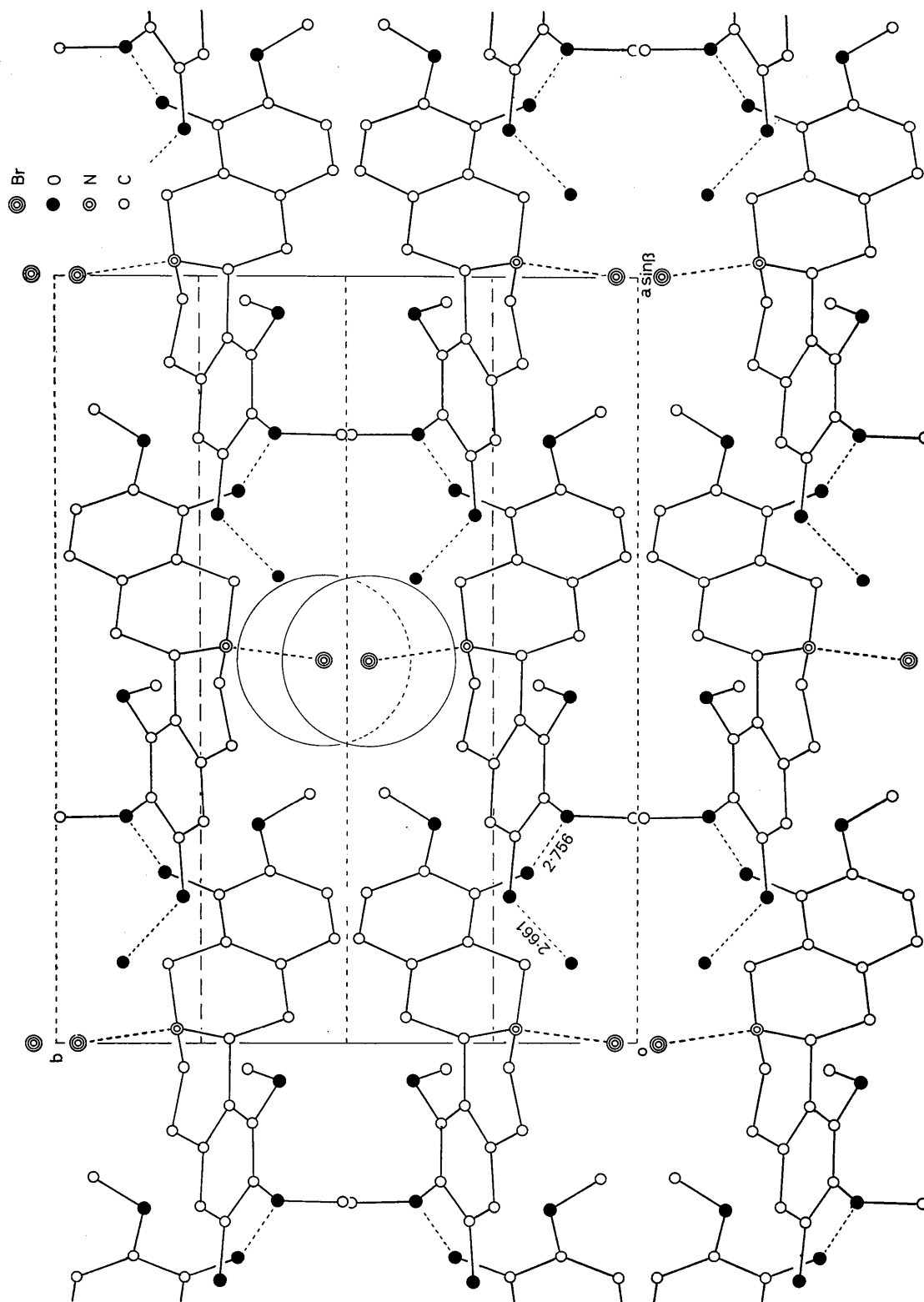


Fig. 10. The crystal structure projected along the *c* axis and some short intermolecular distances (Å).

to compare the approach of the bromide ions to the nitrogen atom with that in capaurine hydrobromide. This is clearly demonstrated in Fig. 11(a) and (b), the projection on the basal plane of the trigonal pyramid,

formed by C(6), C(8), C(14) and N(7). In the present molecule (b) there are two short $N^+ \cdots Br^-$ distances for which some interactions are suggested. No bromide ion is located above N(7), an apex of the trigonal pyramid,

Table 5. Bond angles and their e.s.d.'s

	Angle	e.s.d.		Angle	e.s.d.
C(15)—C(1)—C(2)	123.2°	1.4°	N(7)—C(14)—C(13)	111.3°	1.1°
C(15)—C(1)—O(1)	119.1	1.3	C(13)—C(14)—C(15)	114.4	1.1
C(2)—C(1)—O(1)	117.7	1.3	C(14)—C(13)—C(18)	114.9	1.2
C(1)—C(2)—C(3)	116.1	1.4	N(7)—C(8)—C(17)	109.5	1.2
C(1)—C(2)—O(2)	124.0	1.4	C(18)—C(17)—C(8)	122.9	1.3
C(3)—C(2)—O(2)	119.8	1.4	C(8)—C(17)—C(9)	115.7	1.3
C(2)—C(3)—C(4)	121.0	1.6	C(9)—C(17)—C(18)	121.3	1.3
C(2)—C(3)—O(3)	120.3	1.5	C(17)—C(18)—C(13)	120.5	1.3
O(3)—C(3)—C(4)	118.5	1.5	C(17)—C(18)—C(12)	119.5	1.4
C(3)—C(4)—C(16)	121.7	1.6	C(12)—C(18)—C(13)	119.9	1.4
C(4)—C(16)—C(15)	117.3	1.4	C(17)—C(9)—O(4)	119.9	1.3
C(4)—C(16)—C(5)	118.3	1.4	C(17)—C(9)—C(10)	117.3	1.4
C(5)—C(16)—C(15)	124.2	1.4	O(4)—C(9)—C(10)	122.8	1.4
C(16)—C(15)—C(1)	120.4	1.3	C(9)—C(10)—C(11)	121.9	1.6
C(16)—C(15)—C(14)	119.1	1.2	O(5)—C(10)—C(9)	112.1	1.4
C(1)—C(15)—C(14)	120.6	1.2	O(5)—C(10)—C(11)	125.9	1.5
C(16)—C(5)—C(6)	113.5	1.4	C(10)—C(11)—C(12)	119.7	1.6
C(5)—C(6)—N(7)	106.8	1.1	C(11)—C(12)—C(18)	120.2	1.5
C(6)—N(7)—C(14)	111.5	1.0	C(1)—O(1)—C(19)	115.0	1.3
C(6)—N(7)—C(8)	112.0	1.1	C(2)—O(2)—C(20)	114.9	1.5
C(8)—N(7)—C(14)	110.4	1.1	C(10)—O(5)—C(21)	116.9	1.5
N(7)—C(14)—C(15)	106.9	1.1			

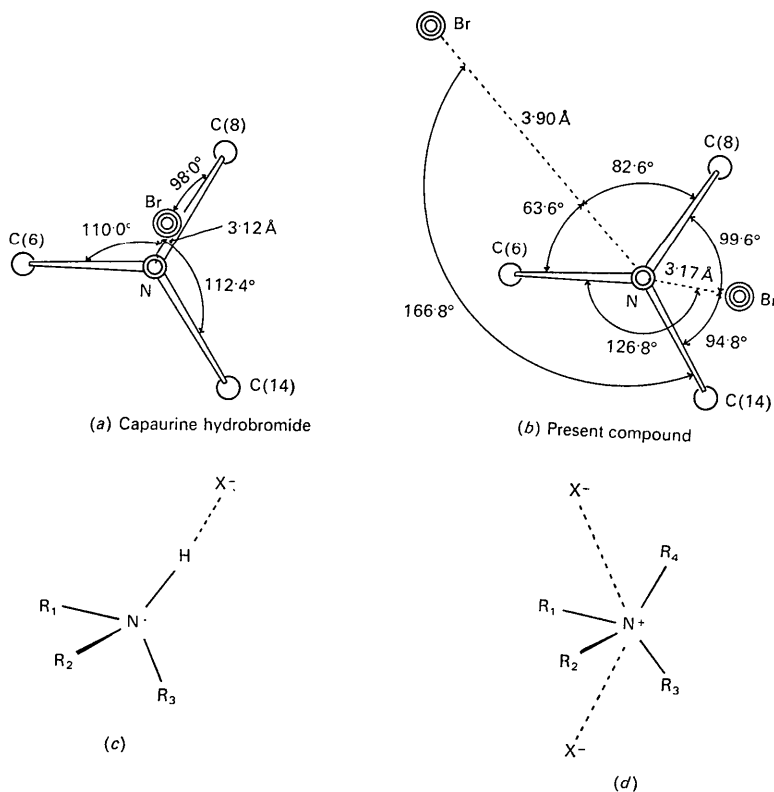


Fig. 11. Comparison of the spatial relationships of the halide anion to the nitrogen atom in capaurine hydrobromide (a) and the present compound (b).

pyramid. The shortest $N^+ \cdots Br^-$ distance is 3.17 Å, slightly longer than that in capaurine hydrobromide as shown in Fig. 11(a) in which the bromide ion occupies a site on the line $N^+-H \cdots Br^-$ as (c). The second nearest approach is 3.90 Å. The spatial relationship of the halide anion to the nitrogen in the present crystal is rather similar to that observed in tetravalent $(R)_4N^+$ ions (d) (Fridrichsons & Mathieson, 1963).

Fairly strong hydrogen bonds, $O-H \cdots O$, are observed, as indicated by dashed lines in Fig. 9, with the $O \cdots O$ distances of 2.76 and 2.66 Å, the angles $C-O \cdots O$ being 127.6 and 130.9° respectively. The distances between $O(W)$ and Br^- were found to be 3.28 and 3.39 Å, and that between $O(W)$ and $O(4)$, 3.09 Å. These distances are reasonable for the forma-

tion of a hydrogen bond. The presence of the molecules of water appears to be essential for stability.

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Structure of $MgAlB_{14}$ and a Brief Critique of Structural Relationships in Higher Borides

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A new boride of approximate composition of $MgAlB_{14}$ has been prepared and the structure determined. The unit cell is orthorhombic $a = 10.313$, $b = 8.115$, $c = 5.848$ Å, space group = *Imam*. Four icosahedral B_{12} groups centered at 000 , $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}00$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ are present. The icosahedra are oriented in such a way that two of the apical atoms lie along the a axis and a mirror plane of the icosahedra lies in the ab plane. The aluminum atoms occupy a fourfold position at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and magnesium occupies a fourfold position at $\frac{1}{2}y0$ ($y = 0.359$). Partial occupancy is indicated for both metal atoms. The extra icosahedral boron atoms occupy the eightfold position at $xy0$ ($x = 0.152$ and $y = 0.622$). Forty boron atoms have six boron and two metal neighbors. Eight boron atoms have six boron neighbors, and eight (extra icosahedral) boron atoms have four boron and three metal neighbors. Aluminum has twelve and magnesium has fourteen neighbors. The B_{12} icosahedral units in $MgAlB_{14}$ are arranged in somewhat distorted closest packed layers which are stacked directly one above the other. This new arrangement of B_{12} units (which is denoted as 4HPo) conforms with the concept of packing models which can be derived by stacking of closest packed layers. It is shown how analysis of unit-cell dimensions and symmetry based on this concept greatly simplified the structure determination. The predictive nature of directional external icosahedral bonding is discussed in light of the tendency of B_{12} borides to form closest packed arrangements. It is shown that flexibility of bonding and presence of interstitial atoms permits a great variety of relative orientations of icosahedra. This observation justifies the use of a quasi-spherical B_{12} model where the three-dimensional framework is built by stacking of closest packed layers of B_{12} units.

Introduction

From the time that the icosahedral boron groups were first established in boron carbide by Zhdanov & Sevastyanov (1941) a number of refractory borides have been found to contain B_{12} polyhedral units in various arrangements. Among these are tetragonal boron (Hoard, Hughes & Sands, 1958), simple rhombohedral boron (Decker & Kasper, 1959), rhombohedral boron phosphides and silicides (Matkovich, 1960, 1961a), rhombohedral boron oxide and arsenide (La Placa & Post, 1961), C_4AlB_{24} (Matkovich, Economy & Giese, 1964), AlB_{10} (Will, 1967), BeB_{12} (Becker, 1960), $B_{12}C_2Al$ (Economy, Matkovich & Giese, 1965), com-

plex rhombohedral boron (Hughes, Kennard, Sul-lenger, Weaklien, Sands & Hoard, 1963) and YB_{70} (Richards & Kasper, 1965). Derivative similarities between various higher borides were first reported by Matkovich (1961b) who noted that compounds of different stoichiometries may be derived from the same icosahedral framework and that differences are due to substitution or degree of occupancy of extra-icosahedral atoms in interstitial holes. A few isotopic series that can be explained in this manner are frequently referred to as derivatives of known boron modifications (Giese, Economy & Matkovich, 1965; Economy, Matkovich & Giese, 1965). A more general observation as to arrangement of icosahedra in the B_{12}