The Structure of Ibogaine

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Ibogaine, $C_{20}H_{26}N_2O$, is an alkaloid in which an indole ring system is attached to a seven-membered nitrogen containing ring, two sides of which form part of an adjoining tricyclic *iso*-quinuclidine ring system. Although unknown at the commencement of this analysis, the structure has recently been determined by chemical methods. This analysis confirms the conclusions of the chemical work with the exception of the stereochemistry of a substituent ethyl group.

The X-ray analysis was carried out independently of the chemical evidence on the hydrobromide crystals, which are orthorhombic with $a = 18 \cdot 68$, $b = 10 \cdot 76$, $c = 9 \cdot 95$ Å, $P2_12_12_1$. The heavy-atom method was used with three-dimensional Fourier syntheses and structure factors computed on an IBM 650. Four successive refinements with progressive addition of the light atoms revealed the structure. Subsequent refinement with an anisotropic temperature factor on the bromine ion reduced the R-factor to $0 \cdot 17$.

Introduction

Ibogaine is one of the twelve alkaloids that have been isolated from tabernanthe iboga, a West African shrub, (Henry, 1949; Dickel, Holden, Maxfield, Paszek & Taylor, 1958). Most of these alkaloids, and especially ibogaine, have an effect on the central nervous system, the action being that of a stimulant.

Ibogaine has the composition $C_{20}H_{26}N_2O$ and belongs to the group of the indole alkaloids. The molecule has an indole ring system attached to a seven-membered nitrogen containing ring, two sides of which form part of an adjoining *iso*-quinuclidine ring system, as shown in I.

At the inception of this study, the configuration of the molecule was unknown other than that it contained an indole group. It has recently been determined by chemical methods to be I, (Bartlett, Dickel & Taylor, 1958), with only an ambiguity in the *cis* or *trans*

position of the ethyl group which is substituent to the *iso*-quinuclidine ring.

Our X-ray crystal structure analysis has confirmed the deductions from the chemical evidence by a completely independent physical technique making no use of the chemical information other than the empirical formula; thus it fulfils the confirmatory rôle usually provided by the configurational synthesis in organic chemistry. We have shown that the substituent ethyl group is *cis* with respect to the *iso*-quinuclidine nitrogen; this is contrary to a tentative arrangement as *trans*, inferred from the ease of methiodide formation by Bartlett, Dickel & Taylor (1958). The analysis has also provided more detailed stereochemical information concerning the shape of the molecule and the relative orientation of the various ring systems. Of interest in relation to the hydrobromide and hydrochloride salt formation are observa-
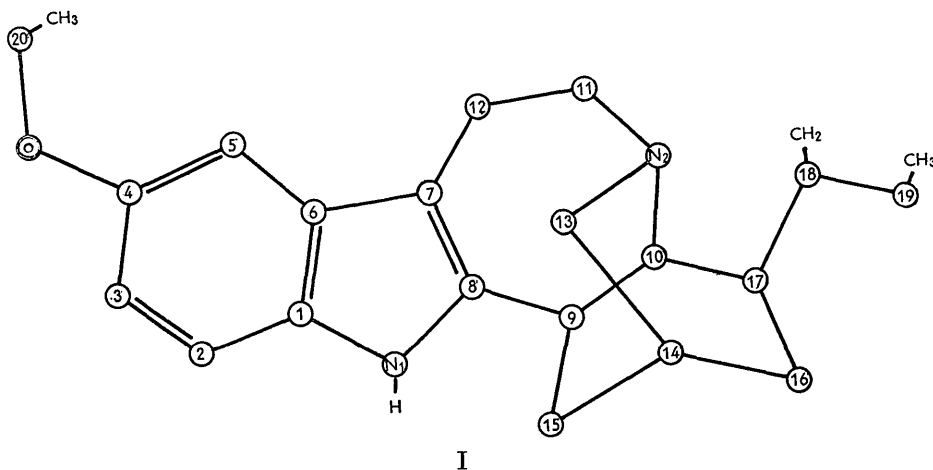

I

Table 1. *The crystal data from ibogaine and the hydrochloride and hydrobromide*

Compound	Space group	a axis	b axis	c axis	U	Z	Dm	Dx
$C_{20}H_{26}N_2O$	$P2_12_12_1$	17·30 Å	10·58 Å	20·01 Å	3663 Å³	8	1·125 g.cm.⁻³	1·142 g.cm.⁻³
$C_{20}H_{27}N_2OCl$	$P2_12_12_1$	18·47	10·74	9·49	1883	4	1·223	1·245
$C_{20}H_{27}N_2OBr$	$P2_12_12_1$	18·68	10·76	9·95	2000	4	1·299	1·333

tions pertaining to the distinction in the nitrogen to halogen binding between the indole $NH_2^+ \cdots Br^-$ and the *iso* quinuclidine $NH^+ \cdots Br^-$, corresponding to the expectation that the later should be much more basic in character.

Crystal data

The crystal data for ibogaine, ibogaine hydrochloride and ibogaine hydrobromide are given in Table 1. The ibogaine itself was unsuitable for crystal structure analysis, not only because of the difficulty of solving the 'phase-problem', but also because there are two sets of crystallographically independent molecules in the unit cell, thereby doubling the number of unknown parameters in the crystal structure over the number required to provide the structural information of chemical interest.

The intensity measurements

In order to have available data for the application of the isomorphous replacement and the heavy-atom interpretation techniques for phase determination, the X-ray intensity measurements were made on both salts. The more complete experimental record was made for the hydrobromide, since it became apparent during the course of the analysis that the heavy atom technique would provide the solution to the crystal structure. The three-dimensional data were obtained by eye-estimation of Weissenberg photographs about the principal axes using the multiple-film method and Cu K radiation.

Nine layers were photographed about the longer axes, a and b, and six about c. No corrections were made for absorption. Excluding absorption and extinction errors, the precision of the measurements of the amplitudes was estimated from self-consistency to be about 5%. Of the 2260 reflections theoretically accessible within the limiting sphere of the reciprocal lattice, 1050 were observed. There was an appreciable fall-off in intensity with sin θ on the photographs and no additional reflections could be observed over the background scattering, even with exposure times up to 120 hr. This was subsequently ascribed to the relatively large thermal motion of the bromine ions in the crystal lattice, which is discussed later.

The hydrochloride data could have been extended further had they proved useful in the structure determination. In fact they were restricted to the zero and a few additional layers about each principal axis.

The two-dimensional analysis

Access to a high-speed digital computer was not possible at the beginning of this research, and in consequence

an attempt was made initially to carry through an analysis using two-dimensional Fourier methods. The halogen atom parameters were determined from Patterson projections to be (0·120, 0·432, 0·26); the z coordinate was inaccurate due to the proximity to $\frac{1}{4}z$; subsequently it was found to be 0·234. As a consequence of this, systematic groups of planes had small halogen contributions and their omission from the Fourier synthesis introduced spurious symmetry. The isomorphous replacement method followed by successive Fourier refinement failed to provide a solution to the phase problem. In the ($h0l$) projection, of the 106 signs deduced, 23 proved later to be incorrect, in the ($hk0$) projection the proportion was 16 incorrect in 112, and at no stage in the two-dimensional work was the correct orientation of the molecules deduced. The heavy-atom method applied to the hydrobromide data for the projections also failed, and such deductions as were tentatively made regarding the orientation of the molecules were shown later to be incorrect.
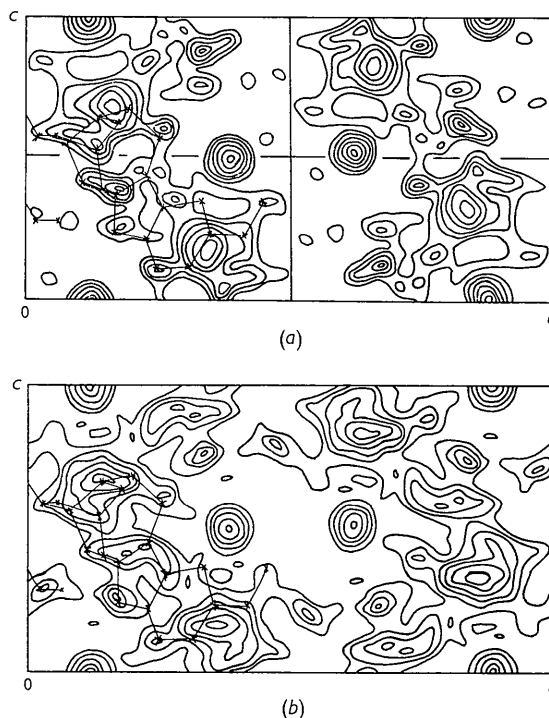

Fig. 1. (*a*) Fourier projection down b axis. Isomorphous replacement method. (*b*) Fourier projection down b axis. Heavy-atom method.

However, in retrospect, it is apparent that the correct general orientation of the molecules might have

been deduced from the Fourier projections. Those which were thought at the time to be the more promising are shown in Fig. 1, with the true atomic positions subsequently deduced from the three-dimensional work superimposed.

The three-dimensional analysis; solution to the phase problem

In view of some uncertainty with regard to the validity of the assumption that the hydrobromide and hydrochloride were isomorphous, the heavy-atom method was used with the three-dimensional data for the hydrobromide.

The bromine parameters were redetermined from a three-dimensional Patterson differential synthesis at a point close to the Br–Br vector. This computation was carried out on an IBM 650 using programs by Shiono (1957). The new bromine parameters were (0·119, 0·435, 0·247). The bromine phase angles were calculated from these coordinates and applied to the corresponding structure amplitudes for the computation of a three-dimensional Fourier map of the electron-density distribution (this was computed in the first stage by hand and thereafter by IBM 650, since the complete three-dimensional program for the machine was not operating satisfactorily at that time). This Fourier synthesis showed a large number of peaks in addition to the large bromine peak. With some imagination a model based on the structure I, which was then considered the most likely, could be fitted so that sixteen of the twenty-three atoms, excluding hydrogen, could be placed either on peaks or on positive areas of the Fourier synthesis. Positions were assigned to all the atoms on the basis of the model and the phases were recalculated using both bromine and all light-atom parameters. An average isotropic temperature factor was deduced from Wilson plot; a value of $B = 3·0$ Å^{-2} was applied to the bromine and all light atoms were given carbon scattering factors with $B = 4·0$ Å^{-2}. A second three-dimensional Fourier synthesis was computed. The electron-density distribution thereby obtained showed no improvement on the previous one, nor was it possible to obtain a better fit for the model. Some warning that this might be the case was given by the poor agreement between the observed and calculated structure amplitudes which was 0·45 for the general (hkl) reflections.

Obviously a more cautious approach was indicated. The bromine coordinates were checked by computing a Fourier differential synthesis using the observed amplitudes and the bromine-only phases. This gave slightly different parameters from those derived from the Patterson synthesis, i.e., (0·1188, 0·4340, 0·2401).

Reexamining the two previous three-dimensional syntheses, eight light-atom peaks were selected on the basis of peak height and shape, and persistence in both syntheses. Some of these were quite isolated from each other, and no consideration whatsoever was given to

the model structure or any possible stereochemical factors, other than that there could not be a light atom closer than 3 Å to the bromine ion.

Using the new bromine parameters and the eight light atoms with isotropic temperature factors and scattering factors as before, a new set of phases was computed. A third three-dimensional synthesis was computed. Comparing this with the first three-dimensional synthesis, it was found that four of the carbon peaks increased in height and became more spherical, two remained unchanged and two decreased. The positions of the two 'atoms' which decreased were omitted and to the remaining six were added eight more peaks which now appeared to be significant. The phases were recalculated with the bromine and fourteen light atoms; a fourth synthesis was computed and the same criterion was applied. At this stage two more of the original peaks were omitted but nineteen of the twenty-three atoms could be assigned. Comparison with the model now indicated the likely positions for the remaining four atoms, and relatively small peaks were found at these positions from which parameters could be obtained. The agreement between observed and calculated structure amplitudes was qualitatively good at this stage, and the R-factor was 0·31 including unobserved reflections.

The interatomic distances were now checked, up to 3·5 Å, using an IBM 650 distance program written by Templeton (1957). Within the molecule-ion, the light-atom interatomic distances lay between 1·3 and 1·75 Å, the Br–N distances were 3·2 and 3·4 Å, and all other intermolecular-ion or bromine to molecule-ion distances were greater than 3·5 Å. This was considered a satisfactory criterion at this stage.
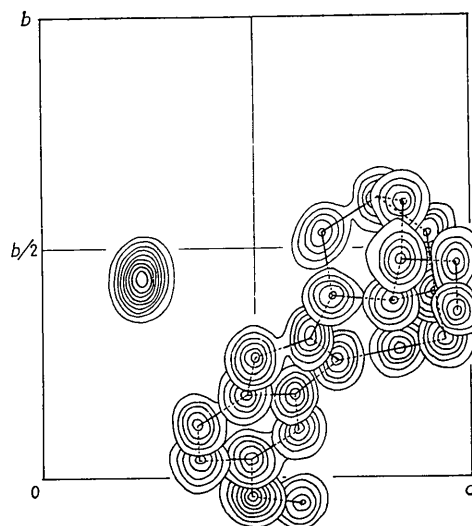

Fig. 2. Three-dimensional Fourier synthesis of ibogaine hydrobromide, represented sectionally with respect to the a axis.

The phases were recomputed and a fifth three-dimensional Fourier was evaluated by means of

Table 2. *Bromine atom parameter refinement*

Br	Initial isotropic	Shifts Isotropic		Anisotropic		Final
x	0·1200	−0·0000	−0·0000	−0·0001	−0·0000	0·1199
y	0·4338	−0·0001	−0·0001	−0·0004	−0·0003	0·4328
z	0·2343	0·0003	0·0000	0·0003	0·0000	0·2350
B_{11}	3·0 Å^{-2}	5·719	2·100	−0·214	0·101	5·89 Å^{-2}
B_{22}	3·0	6·402	3·473	0·361	0·106	7·08
B_{33}	3·0	0·588	−0·009	−0·130	0·024	3·04
B_{23}		0·451	0·552	0·322	0·215	0·72
B_{31}		−0·108	−0·293	−0·184	−0·089	−0·33
B_{12}		0·155	0·268	0·082	0·025	0·25

differential syntheses. The subsequent structure factor agreement was $R = 0·22$ using C, N and O scattering factors with isotropic temperature factors of $B = 3·8$ Å^{-2}, and for the bromine, $B = 3·0$ Å^{-2}. The electron-density map in which all the atoms are clearly indicated at this stage of the analysis is shown in Fig. 2.

It was certain at this point that the phase problem had been solved, so a post-mortem was held on the mechanics of the process.

An examination of the first three-dimensional Fourier synthesis revealed that the electron-density distribution of the ibogaine molecule was contained therein, but was distorted and was made difficult to recognize by spurious peaks often exceeding the true peaks in magnitude.

The four atoms which were the last to be revealed were C_1, C_{13}, C_{18}, and C_{19} with the numbering shown in I and in Figs. 3 and 4. This must be dependent upon the relationship of their phase contribution to the structure factors to that of the bromine atoms, and there is no obvious way of predicting *a priori* which atoms are likely to be ill-defined in the early stages of the analysis. The non-appearance of C_1 does, however, explain the difficulty throughout the early stages which arose through an inability to recognize the chemically most certain feature of the molecule, which was the indole ring. Even in the two-dimensional projection, a low density region was correctly assigned to the benzene ring and a high density region to the isoquinuclidine cage but they were incorrectly oriented with respect to each other. Similarly in the first attempt to interpret the three-dimensional Fourier, the orientation of the molecule was incorrect by about 90° with respect to the a and c axes, due, in part, to an inability to recognize the indole ring system. This would account for the non-refinement of that interpretation despite the fact that the bromine and 13 of the 23 light atomic positions were subsequently found to be quite close to the true positions.

The three-dimensional refinement

This refinement was carried out by means of the isotropic structure factor and differential Fourier synthesis reiterative cycles for the carbon, nitrogen

and oxygen atoms and anisotropic refinement cycles for the bromine atom, using the IBM 650 programs of Shiono (1957, 1958).

The successive parameter shifts for the bromine atom are shown in Table 2. The tendency for the anisotropic thermal parameter shifts to overshoot was corrected by applying $\frac{1}{3}$ of the computed shift at each stage (cf. Jeffrey & Shiono, 1959). An n-shift correction of 1·5 was applied to the positional coordinates.

Despite the large thermal anisotropy of the bromine atom, there was no evidence of significant anisotropic thermal motion for the ibogaine atoms. From the comparison of observed and calculated curvatures of the light atoms, the following isotropic thermal factors were obtained; C1 to C17, $B = 3·70$ Å^{-2}; C18 to C20, $B = 3·80$ Å^{-2}; N, $B = 3·80$ Å^{-2}; O, $B = 3·65$ Å^{-2}.

Table 3. *Fractional atomic coordinates*

Atom	x	y	z	Atom	x	y	z
N_1	0·170	0·258	0·496	C_{10}	0·081	0·383	0·814
N_2	0·145	0·405	0·915	C_{11}	0·197	0·301	0·937
O	0·415	0·963	0·482	C_{12}	0·257	0·278	0·832
C_1	0·230	0·182	0·472	C_{13}	0·183	0·527	0·893
C_2	0·254	0·112	0·364	C_{14}	0·138	0·605	0·790
C_3	0·313	0·039	0·369	C_{15}	0·144	0·532	0·651
C_4	0·355	0·038	0·488	C_{16}	0·061	0·601	0·838
C_5	0·334	0·103	0·609	C_{17}	0·025	0·476	0·837
C_6	0·269	0·180	0·591	C_{18}	0·979	0·473	0·967
C_7	0·230	0·256	0·695	C_{19}	0·938	0·365	0·967
C_8	0·172	0·307	0·626	C_{20}	0·455	0·939	0·604
C_9	0·113	0·389	0·674				

The positional coordinate shifts for the light atoms were initially quite large (1 Å for C_{19}, 0·5 Å for C_{18}, and less than 0·2 Å for other atoms). After four refinement cycles, the coordinate shifts were less than 0·04 Å. The final agreement index was $R = 0·168$, using the Br parameters given in the final column of Table 2, and the final light atom parameters given in Table 3. Table 4 lists the observed and calculated structure amplitudes. Tables 5 and 6 list the intra- and intermolecular distances respectively. Table 7 lists the intramolecular bond angles. The data for Tables 5, 6 and 7 were computed using an interatomic distance program for the IBM 650 prepared by Shiono (1960). The standard deviations, calculated by the method of Cruickshank (1949, 1950, 1954) are given in Table 8.

Table 4. *Observed and calculated structure amplitudes*

h k l	$|F_o|$	$|F_c|$
0 0 2	44·0	44·3
4	40·8	45·3
6	13·1	12·1
8	27·7	41·2
10	10·7	9·7
12	7·4	10·4
0 1 1	36·6	41·3
2	41·5	40·8
3	11·0	9·4
4	42·3	47·4
5	6·7	5·8
6	18·1	24·7
7	25·9	28·9
8		7·1
9		3·8
10	23·0	31·8
0 2 0	116·6	143·3
1	46·2	42·9
2	55·5	57·4
3	101·1	107·7
4	32·3	30·6
5	51·0	47·0
6	31·1	28·4
7	38·3	45·3
8	25·2	35·2
9	9·1	11·2
10	15·1	13·9
11		8·0
12	4·9	5·7
0 3 1	31·7	43·9
2	28·7	19·1
3	28·6	28·1
4		0·7
5	42·2	41·7
6	20·7	19·5
7	29·7	31·8
8	14·7	6·6
9	27·2	28·3
10		1·9
11	10·7	12·7
0 4 0		3·6
1	78·1	93·7
2	45·8	41·4
3	73·1	73·6
4	18·4	15·1
5	49·8	52·4
6	24·6	19·9
7	26·5	20·4
8	12·9	9·5
9	32·6	26·3
10		0·2
11	10·0	8·8
0 5 1	13·4	16·7
2	10·7	7·6
3	24·9	25·9
4	21·2	11·2
5		6·5
6		10·9
7	17·0	14·0
0 6 0	50·6	63·2
1	19·4	20·8
2	45·9	60·7
3	30·9	31·1
4	28·3	27·6

h k l	$|F_o|$	$|F_c|$
5	17·9	22·1
6	15·3	16·4
7	14·4	13·0
0 7 1	4·1	12·7
2		0·1
3	10·7	11·4
4	15·2	13·5
5	20·2	22·1
6		18·7
7	11·0	6·2
0 8 0	20·7	20·0
1	12·8	0·7
1 0 1	29·3	22·6
2	24·5	23·8
3	81·4	99·6
4	27·6	38·3
5	42·2	56·4
6		10·4
7	45·5	69·2
8	26·6	33·0
9	12·4	9·5
10	10·0	13·2
1 1 0	58·1	82·1
1	22·1	23·6
2	116·2	132·0
3	60·9	62·2
4	41·2	50·1
5	40·1	42·6
6	35·3	39·7
7	32·9	37·0
8	12·5	13·1
9	21·7	23·2
10	12·6	13·9
11		15·3
1 2 0	77·0	110·6
1	53·4	63·2
2	41·3	44·3
3	63·5	60·6
4	34·1	42·1
5	30·7	33·8
6	36·4	35·4
7	38·2	42·9
8	12·9	10·9
9	15·7	14·0
10	9·9	9·5
11	8·6	11·7
12	7·5	12·0
1 3 0		4·3
1	101·4	118·5
2	25·2	17·2
3	57·9	56·7
4	31·4	34·2
5	22·8	24·5
6	27·7	26·3
7	22·8	21·6
8	26·7	25·6
9	19·2	17·0
10	16·3	14·3
1 4 0	32·2	41·9
1	9·2	9·0
2	55·3	60·4

h k l	$|F_o|$	$|F_c|$
3	37·1	31·5
4	47·5	50·6
5	9·9	10·8
6	37·8	28·0
7	12·2	8·0
8	22·3	14·2
9	24·3	21·3
10	13·5	12·4
11	13·0	14·5
1 5 0	15·4	19·3
1	38·9	46·7
2	21·4	21·6
3	20·9	20·2
4	46·9	40·3
5	26·0	25·5
6	15·8	12·8
7	33·7	31·0
8	16·7	20·4
9	15·2	15·3
10		10·5
1 6 0	20·1	9·9
1	24·0	30·2
2	28·1	26·7
3	28·8	16·0
4	27·4	21·4
5	26·9	27·6
6	25·7	20·1
7	16·3	16·0
8		13·2
1 7 0	28·4	42·5
1	19·5	20·9
2	22·0	22·6
3	35·1	8·4
4	19·7	22·7
5		8·3
6	12·6	15·7
7	13·1	13·3
1 8 0	18·2	6·1
1	19·9	33·5
2		8·1
1 9 0	15·1	10·6
1		9·3
2 0 0	107·5	85·5
1	70·8	83·5
2	13·6	12·6
3	41·2	42·8
4	35·8	39·4
5	22·0	16·6
6		7·6
7	43·5	48·3
8		4·9
9	27·4	38·9
10		7·2
11	10·0	15·2
2 1 0	76·7	96·8
1	59·6	76·1
2	52·8	54·4
3	105·7	107·1
4	43·5	41·5
5	74·5	92·0
6	13·6	15·6
7	31·4	28·9
8	20·5	22·2

h k l	$|F_o|$	$|F_c|$
9	32·7	40·1
10		4·9
2 2 0	101·0	120·0
1	75·0	91·6
2	53·6	38·1
3	11·6	4·6
4	44·4	41·4
5	29·9	33·2
6	29·2	35·1
7	8·2	5·9
8	21·4	18·9
9	28·9	33·9
10	18·0	24·0
11	8·6	8·9
12	7·4	10·6
2 3 0	37·2	50·3
1	77·2	67·7
2	97·3	97·5
3	23·7	18·2
4	65·6	59·9
5	32·2	27·9
6	47·0	52·3
7		7·7
8	14·9	13·9
9		8·7
10	18·1	15·7
2 4 0	24·8	23·7
1	23·4	17·6
2	15·7	13·9
3	29·4	31·4
4	25·3	25·0
5	16·0	6·9
6	39·4	39·9
7	18·3	14·0
8	25·3	24·0
9	10·9	6·7
10	19·0	17·1
2 5 0	41·6	59·3
1	20·9	20·4
2	36·1	35·5
3	31·3	22·7
4	58·3	62·3
5	21·0	22·1
6	30·6	31·7
7	17·2	17·6
8	16·1	19·3
9	15·2	14·1
2 6 0		2·4
1	11·8	11·7
2	15·9	10·5
3	23·9	26·1
4		6·7
5	14·4	10·0
6	11·5	14·7
7	16·4	21·8
2 7 0	6·9	3·3
1	26·3	40·2
2	14·6	11·2
3	38·8	44·0
4	12·0	10·8
5	18·9	19·7
6	14·3	14·0
7	13·1	15·7

Table 4 (cont.)

h k l	$|F_o|$	$|F_c|$	h k l	$|F_o|$	$|F_c|$	h k l	$|F_o|$	$|F_c|$	h k l	$|F_o|$	$|F_c|$
2 8 0		5·1	10	9·9	9·7	7	29·1	25·6	6		2·9
1	15·4	20·0	11	9·7	10·5	8	18·2	20·3	7	45·7	46·1
2	14·5	14·1				9	25·1	27·6	8		9·3
			3 5 0	61·3	68·6	10	8·5	7·3	9	24·5	20·5
2 9 0	18·0	22·8	1	58·9	61·7	11		3·3	10	10·4	10·0
1	22·4	34·2	2	43·9	44·4	12	6·0	9·5	11	7·1	11·8
			3	51·9	47·7				12	6·9	14·8
3 0 1	11·3	9·9	4	16·1	13·4	4 3 0	93·1	94·6			
2	45·5	34·5	5	25·2	19·7	1	26·1	17·6	5 1 0	94·0	122·3
3	88·2	89·3	6		12·6	2	31·2	22·6	1	32·1	37·9
4		3·5	7	12·9	15·1	3	29·1	32·4	2	26·8	24·7
5	48·0	54·0	8	13·2	8·4	4	16·0	6·4	3	63·5	74·4
6	14·0	11·1	9	17·2	12·2	5	16·6	13·4	4	40·1	32·6
7	21·1	9·7				6	18·9	16·8	5	16·1	11·4
8		10·3	3 6 0	19·4	20·3	7	19·6	16·5	6	43·3	42·9
9	16·5	20·7	1	20·0	22·4	8	14·4	15·4	7	28·2	26·7
10	18·4	24·2	2	17·5	10·8	9	20·9	18·0	8	20·6	19·3
11		8·8	3	28·4	26·6	10		14·5	9	23·1	22·3
12	11·8	16·3	4	28·5	26·4	11	14·9	17·7			
			5	12·6	9·5				5 2 0	50·1	41·6
3 1 0	83·5	116·5	6	14·4	14·0	4 4 0	39·8	41·4	1	61·7	61·2
1	69·2	79·2	7	12·3	15·7	1	78·0	90·4	2	77·1	67·0
2	130·3	148·1				2	45·5	41·1	3	44·4	35·3
3	26·3	23·1	3 7 0	14·1	19·4	3	58·8	55·9	4	65·4	56·4
4	50·8	44·3	1	12·3	11·8	4	12·0	7·0	5	23·6	22·8
5	24·9	22·6	2	22·4	23·9	5	39·0	39·4	6	28·9	24·4
6	33·5	31·1	3		5·4	6		2·9	7	34·4	27·3
7	40·4	49·0	4	25·7	31·7	7	41·9	38·3	8	18·1	11·3
8	18·8	14·3	5		7·2	8	20·8	19·4	9	23·2	19·5
9	21·5	22·5	6	22·1	22·2	9	20·2	10·5	10	9·6	8·0
10	16·3	20·3	7	14·8	18·3	10	9·7	7·8	11	6·0	8·7
						11	9·4	7·5	12	4·2	10·0
3 2 0	94·1	107·0	3 8 0	19·0	28·7						
1	73·7	75·8	1		13·7	4 5 0	31·9	38·3	5 3 0	9·0	10·2
2	37·6	30·9	2		6·8	1	21·2	21·2	1	27·6	35·0
3	64·2	53·5	3	25·7	32·8	2	40·3	35·7	2	35·5	34·6
4	27·2	19·0				3	33·7	27·3	3	70·1	68·2
5	36·6	34·5	4 0 0	164·0	125·0	4	16·2	13·6	4	46·4	41·4
6	33·8	33·9	1	12·9	4·5	5	21·3	17·0	5	39·6	34·4
7	31·4	27·7	2	88·6	98·6	6	20·5	16·6	6	24·5	21·7
8	25·6	33·7	3	33·6	21·4	7	22·8	22·4	7	21·9	17·5
9	18·8	18·9	4	79·7	92·9	8	13·2	14·4	8	21·4	18·0
10	11·3	11·1	5	36·8	46·3	9	12·7	12·4	9	16·8	14·1
11	8·4	12·0	6	48·3	48·5				10	11·9	12·2
12	5·5	9·6	7	18·7	17·8	4 6 0	45·2	5·91			
			8	31·2	37·1	1	34·9	44·6	5 4 0	56·5	51·3
3 3 0	50·0	28·7	9		0·0	2	36·1	22·4	1	69·3	74·3
1	36·7	33·4	10		8·8	3	23·6	19·7	2	49·8	59·4
2	50·3	43·6	11		2·7	4	31·3	33·3	3	20·3	16·2
3	70·0	61·4	12	5·4	9·5	5	19·1	17·2	4	34·2	29·2
4	27·4	22·0				6	25·0	26·4	5	21·2	13·0
5	64·8	56·0	4 1 0	29·8	32·9				6	42·4	45·2
6	40·0	39·2	1	12·0	12·4	4 7 0	20·9	24·6	7		7·8
7	37·1	34·6	2	60·6	57·4	1	10·6	6·3	8	24·5	13·4
8	13·0	8·7	3	25·4	22·2	2	15·9	14·8	9	18·8	16·8
9	22·1	23·8	4	36·1	34·0	3	22·2	6·9	10	11·3	8·3
10	17·9	20·7	5	34·8	40·8	4	17·2	13·9	11	7·8	5·7
			6	28·6	34·9	5		5·0			
3 4 0	37·9	41·2	7	26·1	21·6	6	14·5	12·6	5 5 0	18·7	14·7
1	28·6	17·5	8	13·4	7·8	7	11·0	2·3	1	57·9	56·8
2	34·8	38·5	9	13·8	13·9				2	37·1	30·1
3	21·4	16·0	10	16·0	19·9	4 8 0	17·2	19·6	3	31·1	21·8
4	44·5	37·8				1		5·3	4	22·8	18·5
5	16·1	14·3	4 2 0	120·4	129·5	2	26·5	29·5	5	19·4	17·9
6	27·7	27·0	1	88·6	91·0				6	20·4	18·0
7	25·0	26·6	2	75·9	63·1	5 0 1	83·5	79·9	7	15·4	13·1
8	20·8	19·0	3	72·2	63·5	2	35·3	33·1	8		8·4
9	12·8	11·2	4	53·7	50·8	3	67·3	54·7	9	14·8	18·0
			5	48·0	40·9	4	68·1	69·9			
			6	27·6	29·3	5	46·2	42·6	5 6 0	11·6	16·3

Table 4 (cont.)

h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h k l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
1	22·3	18·3	6 4 0	34·7	39·6	7 2 0	50·5	42·2	2	93·2	101·8
2	24·9	29·8	1	13·1	9·8	1	25·1	26·6	3	25·6	26·0
3	27·2	31·3	2	23·4	22·5	2	25·9	24·3	4	60·1	60·2
4	21·8	15·6	3	23·3	15·9	3		26·5	5		10·2
5	28·6	29·2	4	33·2	26·4	4	40·5	35·6	6	40·8	29·3
6	18·0	23·2	5	24·9	20·4	5	26·8	19·5	7		4·1
			6	26·9	22·8	6	16·0	12·9	8	16·6	12·6
5 7 0	20·5	19·2	7	15·5	15·0	7	20·7	19·9	9		3·2
1	15·4	16·9	8	24·8	22·9	8	17·2	17·0	10	10·8	14·3
2	16·3	17·7	9	10·5	12·4	9	21·1	18·0			
3	22·0	21·6	10	17·8	19·0	10	8·1	9·4	8 1 0	25·1	19·3
4	16·5	11·9				11	7·4	11·9	1	39·7	44·2
5		11·1	6 5 0	25·8	26·6	12	5·8	10·3	2	36·2	40·4
6	19·0	20·9	1	34·1	27·3				3	10·6	15·7
7	13·1	10·3	2	50·1	46·5	7 3 0	33·0	28·0	4	35·2	30·9
			3	49·8	38·0	1	57·8	59·2	5		3·8
5 8 0	14·2	12·7	4	39·8	35·9	2	19·3	14·5	6	25·1	16·8
1	23·7	27·3	5	12·4	6·3	3	65·3	62·6	7	21·5	18·7
			6	39·3	34·7	4	41·6	32·1	8	18·1	16·2
5 9 0	17·6	15·7	7	18·4	14·8	5	37·3	32·3	9	16·4	11·7
			8	18·7	20·1	6	36·6	39·8			
6 0 0	12·0	10·1	9	14·5	14·2	7	28·6	24·4	8 2 0	43·7	38·7
1	10·6	4·6				8	19·6	15·9	1	44·9	45·7
2	48·1	43·6	6 6 0	11·4	8·4	9	10·7	11·2	2	34·8	30·0
3	31·7	37·4	1	19·9	20·9	10	11·4	14·0	3	49·9	46·4
4	32·6	32·2	2	32·4	29·8				4	53·2	51·6
5	60·7	61·4	3	16·5	20·3	7 4 0	63·2	62·7	5	46·8	49·3
6	16·3	10·9	4		8·7	1	20·1	14·1	6	35·8	21·6
7	38·2	36·0	5		11·6	2	15·2	16·5	7	28·6	23·1
8		10·7	6		5·1	3		6·0	8	20·8	14·5
9	29·1	31·2	7	19·1	20·2	4	27·0	26·0	9	8·8	9·3
10		7·3				5	16·2	13·4	10	8·8	12·2
11	11·1	19·4	6 7 0	12·5	6·0	6	31·0	24·9			
			1	22·8	34·3	7	24·0	26·9	8 3 0	42·3	46·2
6 1 0	28·1	30·5	2	21·3	12·5	8	13·0	8·7	1	23·7	20·0
1	63·3	77·5	3	22·8	20·6	9	12·2	14·6	2	12·5	4·3
2	41·0	39·5	4	10·0	11·3	10		2·4	3	18·6	20·9
3	58·0	60·8	5	24·0	26·2	11	6·9	10·8	4	28·7	26·3
4	23·8	21·8	6	15·8	16·1				5		1·0
5	57·8	49·3	7	11·0	13·4	7 5 0	49·8	53·0	6		11·5
6	28·8	19·1				1	29·6	19·6	7	36·8	26·4
7	43·1	39·1	6 8 0		0·9	2	25·2	24·0	8	20·8	21·2
8	16·6	12·9	1	16·1	9·0	3	51·1	46·3	9	14·1	13·8
9	21·6	18·6				4	17·3	11·0			
			6 9 0		9·3	5	29·1	24·9	8 4 0	21·6	10·8
6 2 0	28·3	27·9	1	16·8	24·0	6	22·1	16·9	1	47·0	50·8
1	14·1	11·6				7	22·1	18·2	2	13·4	12·7
2	26·8	16·0	7 0 1	33·3	37·3	8	13·0	10·6	3	62·3	65·3
3	34·7	31·5	2	18·3	9·7				4		2·9
4	58·1	52·1	3	47·5	49·0	7 6 0	21·9	31·7	5	32·2	26·6
5	26·7	24·3	4	28·5	33·6	1	25·1	24·1	6		11·1
6	28·6	19·7	5	24·3	25·7	2		4·6	7	23·9	21·9
7	39·6	30·3	6	26·8	21·6	3	16·7	15·2	8		8·1
8	23·1	27·2	7	15·3	8·6	4	30·4	34·8	9	13·6	14·2
9	17·3	14·8	8	25·5	26·2	5		3·4			
10	14·3	13·6	9	16·8	10·3	6	17·4	21·0	8 5 0	22·0	17·6
11	9·0	12·1	10		4·6				1	23·7	25·0
						7 7 0	25·3	27·0	2	22·4	25·4
6 3 0	92·7	99·3	7 1 0	55·2	65·4	1		8·2	3	22·5	20·1
1	28·2	24·9	1	13·8	13·6	2	24·3	32·8	4	28·8	27·1
2	63·6	58·1	2	63·8	67·0	3	22·6	20·6	5	23·5	24·7
3	38·2	32·5	3	15·8	12·8	4	21·3	18·3	6		3·5
4	52·9	48·7	4	48·9	49·6	5		6·6	7	16·0	11·7
5	20·2	11·8	5	28·8	23·6	6		14·1			
6	42·9	33·0	6	43·7	41·0	7	10·8	13·2	8 6 0	29·9	32·4
7	20·5	19·1	7	37·9	32·6				1	31·2	29·9
8	18·0	15·8	8	20·5	18·0	7 8 0	16·4	1·2	2	32·0	37·3
9		11·8	9	21·0	21·1				3	16·7	13·3
10	9·9	14·4	10	10·4	12·5	8 0 0	87·0	65·3	4	15·4	18·9
						1	12·9	4·6	5	14·0	12·4
									6	17·0	18·2

Table 4 (cont.)

h k l	$|F_o|$	$|F_c|$	h k l	$|F_o|$	$|F_c|$	h k l	$|F_o|$	$|F_c|$	h k l	$|F_o|$	$|F_c|$
8 7 0		4·6	4	25·2	22·2	9		4·9	5	12·8	16·5
1	12·7	11·5	5	22·0	25·0	10	9·2	13·2	6		4·6
2	23·6	28·4	6	27·0	25·4				7	14·5	11·7
3	23·2	23·1	7	15·6	15·9	10 5 0	29·4	26·8			
4	12·4	19·4				1	19·8	20·3	11 5 0	13·4	20·8
5		4·4	9 6 0	14·9	15·9	2	44·7	56·0	1	30·3	28·6
6	13·1	11·8	1	12·1	14·3	3	22·5	25·5	2	20·8	15·5
			2	12·6	11·5	4	12·4	5·1	3	27·7	19·9
9 0 1	74·0	65·7	3	24·8	31·2	5	15·3	18·7	4		6·6
2	23·2	20·6	4	13·7	16·1	6	29·5	27·7	5	15·6	22·0
3	37·7	32·8	5	16·3	25·0				6		15·8
4	20·8	2·3	6	15·6	22·4	10 6 0		9·7	7	12·7	14·1
5	36·1	40·1				1	10·8	11·0			
6	14·7	13·1	9 7 0	16·0	13·1				11 6 0	14·7	7·3
7	24·7	24·6	1		11·3	10 7 0		2·7	1		6·9
8		10·3	2	26·2	28·0	1	21·3	22·8	2	15·6	18·7
9	15·8	22·6	3	16·1	5·9	2	12·3	12·8	3	14·2	19·5
10	8·1	10·0	4	10·8	9·9	3		26·9	4	14·4	20·7
						4	11·0	9·0			
9 1 0	50·2	39·0	10 0 0	19·6	31·0				11 7 0	13·2	10·0
1	22·4	17·3	1	8·7	10·5	11 0 1	31·0	25·3	1		5·0
2	34·7	38·5	2	19·5	18·2	2	15·1	12·6	2	18·9	24·5
3	13·3	11·5	3		3·3	3		5·9	3	11·0	4·3
4	26·6	28·8	4	24·0	27·8	4	18·4	25·7	4	13·1	20·7
5	22·6	17·6	5	7·9	23·5	5	12·2	15·6			
6	17·3	18·8	6	13·5	16·4	6	13·3	24·9	12 0 0	27·3	13·9
7	12·8	13·2	7	13·5	21·3	7	9·6	15·2	1		0·0
8	11·4	10·0	8		2·0	8		7·4	2	52·4	52·2
9	14·3	21·9	9	15·4	22·2	9		7·7	3	9·8	9·6
			10		7·0	10		10·1	4	25·9	32·4
9 2 0	53·0	38·0				11	5·5	1·2	5		5·3
1	41·9	44·0	10 1 0	21·3	15·5				6	17·8	35·4
2	52·7	62·7	1	49·5	45·6	11 1 0	58·4	54·1			
3	41·3	43·8	2	32·2	33·1	1	25·9	22·6	12 1 0	18·2	24·2
4	30·4	20·8	3	32·7	43·2	2	41·0	34·8	1	26·1	31·0
5	28·1	21·3	4	19·6	15·4	3	14·2	17·6	2	15·5	6·1
6	20·6	18·6	5	36·2	32·8	4	31·5	40·5	3		8·5
7	17·0	14·4	6	12·5	13·4	5	12·3	17·7	4	12·1	18·8
8	9·0	7·2	7	23·7	27·9	6	21·3	23·3	5	18·1	12·8
9	9·7	10·4				7	13·0	16·9	6	9·6	13·0
10	9·8	14·6	10 2 0	19·5	12·8	8	11·2	18·6	7		9·5
			1	16·5	25·3				8	10·9	15·4
9 3 0	34·3	32·1	2	20·7	12·7	11 2 0		0·0	9	8·2	13·4
1	41·6	42·6	3	23·0	23·9	1	19·0	14·1			
2	15·8	14·3	4	24·8	26·1	2	8·5	6·0	12 2 0	40·2	36·8
3	41·6	35·9	5	27·2	25·0	3	15·6	14·9	1	39·6	35·6
4	12·7	6·7	6	25·2	27·1	4	9·3	18·1	2	36·7	31·5
5	13·6	13·5	7	21·7	23·7	5	21·8	17·6	3	30·8	39·9
6		13·7	8	10·1	15·9	6	18·6	22·6	4	16·2	14·7
7	11·0	5·1	9	7·0	8·9	7	11·9	14·7	5	21·9	17·3
8	17·0	16·3				8	9·9	11·2	6	7·7	10·2
9		8·0	10 3 0	58·2	62·0	9	6·8	8·5	7	10·2	10·2
10	8·8	14·6	1	10·2	8·3				8	8·5	13·0
			2	36·7	34·1	11 3 0	19·4	7·3	9	6·4	9·5
9 4 0	59·8	61·5	3	12·5	10·5	1	34·0	26·1			
1	22·6	16·2	4	26·1	14·8	2	19·4	21·7	12 3 0	19·5	22·8
2	41·3	41·7	5	26·5	35·3	3	28·3	25·2	1		3·5
3	9·0	7·4	6	28·9	26·1	4	12·2	11·3	2	31·8	27·5
4	36·8	34·5	7		6·8	5	36·0	41·7	3	15·9	22·0
5	20·0	16·4	8	18·8	22·0	6		9·6	4	16·4	19·4
6	16·7	14·1				7	22·7	26·0	5		6·6
7	13·0	10·1	10 4 0	10·2	13·9	8	10·6	9·6	6		7·8
8	20·3	17·7	1	13·6	10·0	9		7·0	7	10·9	12·2
9		5·5	2	12·1	13·6	10	9·1	9·5			
10	9·7	13·1	3		4·7				12 4 0		8·3
			4	22·4	22·4	11 4 0	26·4	23·2	1	31·8	25·0
9 5 0	20·5	12·6	5	25·8	23·5	1	18·2	10·6	2	17·4	15·5
1	17·8	11·9	6	18·8	15·6	2	16·6	16·5	3	38·7	49·5
2	12·7	9·5	7	16·9	16·2	3	19·4	19·1	4	14·3	20·3
3	24·4	10·1	8	12·3	14·6	4	23·2	33·3	5	28·9	25·1

Table 4 (cont.)

h k l	$|F_o|$	$|F_c|$	h k l	$|F_o|$	$|F_c|$	h k l	$|F_o|$	$|F_c|$	h k l	$|F_o|$	$|F_c|$
6	11·0	11·9	2	31·8	35·5	14 5 0	16·0	10·9	3	11·5	19·2
7	12·6	11·4	3		9·2	1		5·3	4	11·4	15·3
			4	22·3	21·6	2	17·6	22·0			
12 5 0		0·1	5	11·0	10·4	3		6·0	16 2 0	10·2	9·5
1	16·3	14·5	6	10·7	11·4	4	15·6	17·4	1	16·1	16·8
2	14·8	11·1	7		5·7				2	19·8	23·7
3		10·0	8	10·9	11·8	15 0 1		2·8	3	11·9	19·1
4	13·0	13·5				2		2·4	4	9·0	5·7
			13 5 0	16·8	22·9	3	11·6	22·3	5	7·4	9·7
12 6 0	15·8	13·5	1	18·4	17·5				6	8·4	12·0
1	15·9	13·4	2		11·7	15 1 0	28·0	24·6			
2		19·1	3	13·0	10·7	1	11·1	16·3	16 3 0		4·4
3	14·4	13·9				2	12·7	10·0	1		11·9
			13 6 0	16·4	21·9	3		10·1	2	11·1	14·5
13 0 1	42·4	37·7	1	21·0	30·3	4	21·6	35·0			
2		8·1				5	11·4	7·8	16 4 0		9·3
3	29·9	43·3	14 0 0	19·8	19·6	6	11·1	10·7	1	22·5	20·0
4	14·5	11·5	1		9·4	7	8·8	11·9	2		4·8
5	24·2	26·0	2	16·5	17·7	8	9·2	11·3	3	10·9	12·8
6		1·7	3		10·2				4		10·6
7	10·8	13·3	4		7·2	15 2 0		0·1	5	13·7	12·4
			5	11·1	13·3	1		7·5			
13 1 0	28·2	26·7				2		7·4	17 0 1	24·1	24·0
1	19·6	21·8	14 1 0		3·2	3		1·4	2		24·3
2	11·7	15·7	1	28·5	31·1	4	7·7	15·7	3	19·4	11·3
3		5·9	2		12·5	5	11·8	12·8	4		3·4
4	9·3	8·7	3	24·8	24·3	6	9·9	13·2	5	13·8	22·3
5	11·3	12·4	4		9·9						
6		6·8	5	11·5	14·1	15 3 0	13·9	9·3	17 1 0	11·5	9·8
7		6·2	6		19·0	1	31·7	37·1	1		7·0
8		7·4	7	14·3	17·3	2	11·0	10·4	2	9·7	14·8
9	7·8	12·1				3	14·8	11·1			
			14 2 0		0·1	4	14·9	20·7	17 2 0	9·1	16·0
13 2 0	26·5	22·7	1	7·2	10·0	5	10·9	11·5	1	16·2	16·7
1	27·0	22·9	2	12·7	13·4	6		7·3	2	13·3	14·1
2	31·6	28·9	3		9·5	7	11·4	14·2	3	10·2	15·3
3	16·2	15·2	4	20·1	22·3				4	8·8	10·6
4	22·6	28·3	5	14·5	21·4	15 4 0		1·9	5	7·1	8·3
5	23·7	24·9	6	13·1	19·2	1	10·9	8·9	6	7·8	10·2
6	7·7	7·5	7	11·2	11·9	2	13·0	12·2			
7	11·6	9·0							17 3 0		3·4
8	6·9	8·7	14 3 0	28·0	22·7	15 5 0		6·5			
9	7·0	9·9	1	12·6	8·9	1	15·7	18·8	17 4 0	10·9	11·8
10	6·1	11·5	2	29·2	27·3				1		0·1
			3	17·0	19·8	16 0 0	20·4	24·4	2	14·4	15·9
13 3 0	10·0	10·1	4	22·7	19·4	1		15·2	3		5·0
1	22·1	20·1	5		10·7	2	21·1	27·1	4	12·0	16·1
2	22·8	29·3	6	10·8	15·4	3		4·5			
3	20·2	14·0				4	11·1	7·0	18 0 0		0·1
4	16·9	15·2	14 4 0	12·6	10·1						
5	11·0	19·6	1	14·3	14·5	16 1 0		9·4	18 1 0		3·0
6	11·0	10·8	2	12·8	13·3	1		14·2	1	11·3	19·6
			3		7·3	2		9·7			
13 4 0	26·9	23·9	4	11·0	9·5				18 2 1	7·5	11·7
1	10·2	7·0	5	10·9	10·7				2	10·0	16·0

The corresponding standard deviations (σ) for the bond lengths and valence angles are included in Tables 5, 6, and 7. These values are of the order of magnitude generally found in the analysis of a non-centric structure of comparable complexity using the bromine heavy-atom method (cf. the structure of annotinine bromohydrin by Przybylska & Ahmed, 1958). While adequate for solving problems of configuration and general stereochemistry, the accuracy is insufficient for a detailed discussion of bond lengths in terms of valence theory.

Discussion of the structure

The general stereochemistry of the molecule is illustrated in Fig. 3, which gives the atomic positions with reference to molecular axes and the plane of the indole rings.

The equation of the plane of the indole rings referred to the crystallographic axes is

$$0.226x + 0.327y - 0.128z = 1 .$$

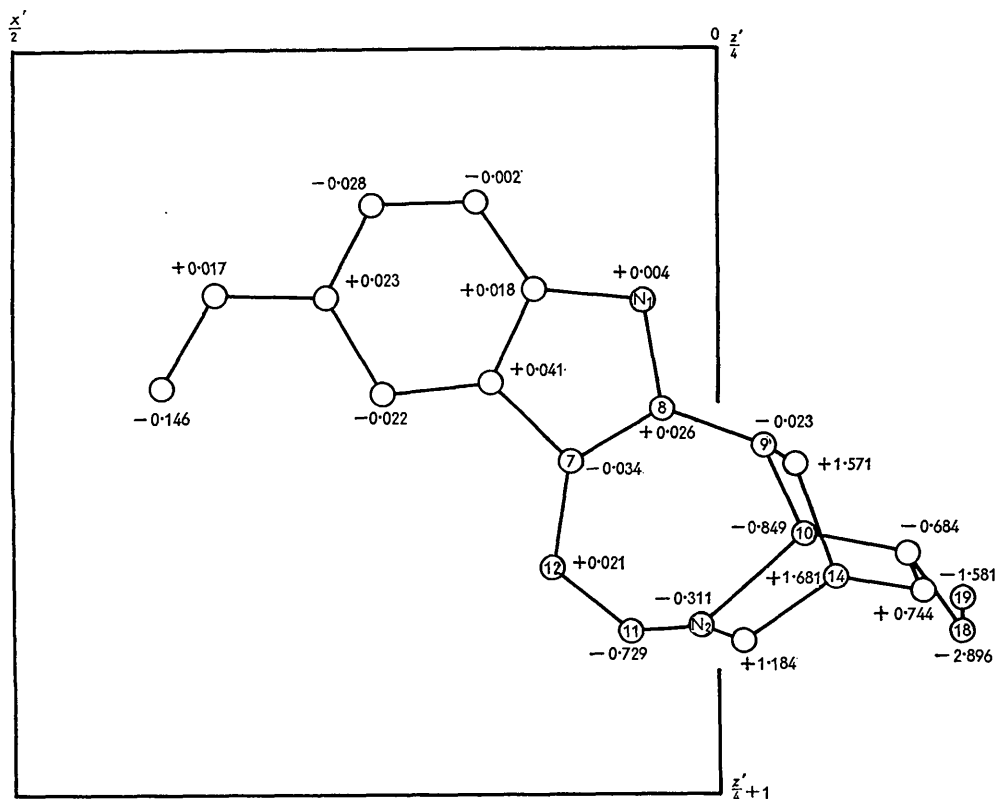This plane makes angles of 57°, 88° and 72° to (100),

Fig. 3. Atomic positions relative to the plane of the indole rings.
Figures give height in Å above or below the indole plane.

Table 5. *Intramolecular distances*

Bond	(Å)	(σ)	Bond	(Å)	(σ)
C_1-C_2	1·39	0·042	C_8-C_9	1·49	0·034
C_2-C_3	1·36	0·043	C_9-C_{15}	1·65	0·037
C_3-C_4	1·42	0·042	C_9-C_{10}	1·51	0·038
C_4-O	1·39	0·037	C_{10}-N_2	1·58	0·036
O-C_{20}	1·45	0·043	N_2-C_{13}	1·51	0·035
C_4-C_5	1·45	0·041	C_{13}-C_{14}	1·56	0·038
C_5-C_6	1·48	0·037	C_{14}-C_{15}	1·59	0·037
C_6-C_1	1·40	0·038	C_{14}-C_{16}	1·52	0·042
C_6-C_7	1·51	0·037	C_{16}-C_{17}	1·50	0·046
C_7-C_8	1·41	0·036	C_{17}-C_{10}	1·48	0·043
C_8-N_1	1·39	0·034	C_{17}-C_{18}	1·55	0·049
N_1-C_1	1·40	0·037	C_{18}-C_{19}	1·39	0·059
C_7-C_{12}	1·48	0·036			
C_{12}-C_{11}	1·55	0·036	Br-N_2	3·23	0·020
C_{11}-N_2	1·49	0·033	Br-N_1	3·34	0·024

Table 6. *Intermolecular distances under 4 Å*

Bond	(Å)	(σ)	Bond	(Å)	(σ)
Br_I-$Cl1_I$	3·59	0·026	$C3_I$-$C7_{II}$	3·70	0·040
Br_I-$Cl2_{II}$	3·98	0·025	$C3_I$-$Cl1_{II}$	3·72	0·039
Br_I-$Cl3_I$	3·74	0·029	$C3_I$-$Cl2_{II}$	3·67	0·038
Br_I-$Cl8_I$	3·78	0·038	$C4_I$-$Cl1_{II}$	3·81	0·040
Br_I-$C20_{III}$	3·73	0·039	$C6_I$-$Cl3_{II}$	3·82	0·039
Cl_I-$Cl3_{II}$	3·61	0·040	$C8_I$-$Cl3_{II}$	3·98	0·037
Cl_I-$Cl4_{II}$	3·82	0·038	$Cl1_I$-O_{II}	3·55	0·033
$C2_I$-$C5_{II}$	3·80	0·041	$Cl3_I$-Nl_{II}	3·72	0·037
$C2_I$-$Cl4_{II}$	3·73	0·040	$Cl7_I$-O_{III}	3·83	0·037
$C3_I$-$C6_{II}$	3·95	0·039			

I x, y, z
II $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$
III $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$
IV $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$

Table 7. *Bond angles*

	(°)	(σ)		(°)	(σ)
1-2-3	123	2·88	10-N2-11	118	1·91
2-3-4	119	2·79	N2-11-12	119	2·11
3-4-5	123	2·66	11-12-7	114	2·16
3-4-O	115	2·63	14-13-N2	108	2·08
4-O-20	119	2·47	13-N2-11	112	1·93
4-5-6	113	2·34	13-N2-10	113	1·98
5-6-1	123	2·43	N2-10-17	110	2·29
6-1-2	119	2·62	10-17-18	121	2·75
7-8-9	131	2·27	10-17-16	107	2·62
8-7-12	131	2·39	16-17-18	105	2·74
			17-18-19	109	3·37
N1-1-6	106	2·39	17-16-14	117	2·77
1-6-7	109	2·30	16-14-13	107	2·23
6-7-8	105	2·19	16-14-15	109	2·23
7-8-N1	109	2·19	13-14-15	105	2·03
8-N1-1	111	2·30	14-15-9	108	1·98
			15-9-8	104	1·95
8-9-10	124	2·23	15-9-10	108	2·05
9-10-N2	106	2·10	9-10-17	113	2·45

Table 8. *Standard deviations of atomic parameters*

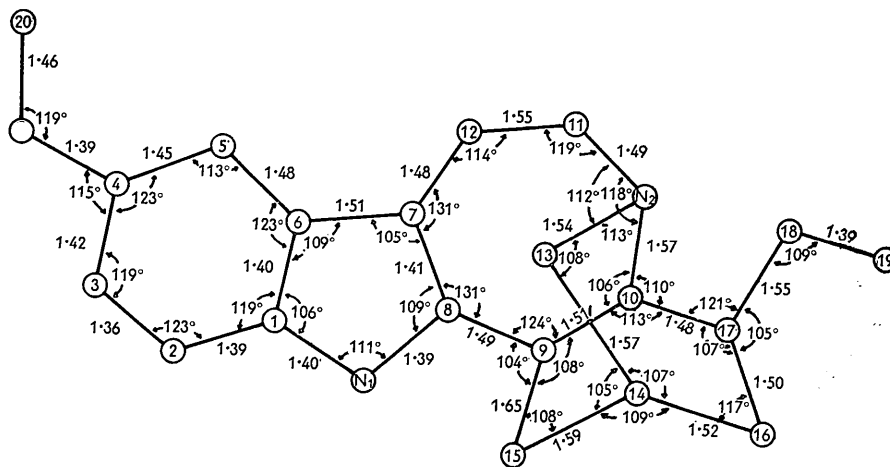|	(Å)		(Å)		(Å)
C_1	0·028	C_9	0·024	C_{17}	0·031
C_2	0·031	C_{10}	0·029	C_{18}	0·038
C_3	0·029	C_{11}	0·026	C_{19}	0·045
C_4	0·031	C_{12}	0·025	C_{20}	0·039
C_5	0·027	C_{13}	0·028	N_1	0·024
C_6	0·026	C_{14}	0·025	N_2	0·020
C_7	0·027	C_{15}	0·027	O	0·021
C_8	0·025	C_{16}	0·034	Br	0·004

Fig. 4. Bond lengths and angles for ibogaine in the hydrobromide.

(010) and (001) respectively. The perpendicular distance of the crystallographic origin to this plane is 2·4 Å.

In Fig. 3, the distances of the atoms from the indole plane are given. Within less than twice the standard deviations, the atoms in the indole rings and the adjacent substituent atoms, O, C_9 and C_{12}, are coplanar. The seven-membered ring is as flat as is compatible with the valence angles, corresponding to a distorted chair-shaped configuration. If the mid-point of C_7–C_8 is considered in conjunction with C_9, C_{10}, N_2, C_{11} and C_{12} the analogy with a chair-shaped cyclohexane ring is very apparent. The central axis of the iso-quinuclidine tricyclic structure, i.e. C_{10}–C_{14}, makes an angle of 74° to the indole plane. The substituent ethyl group C_{18}, C_{19}, is cis with respect to the iso-quinuclidine nitrogen, contrary to a tentative assignment as trans from chemical evidence (Bartlett, Dickel & Taylor, 1958).

The bond lengths and valence angles are shown in Fig. 4. They are not sufficiently precise to permit a discussion of valence bond structure. The mean C–C length in the indole system is 1·43 Å with a maximum spread of 0·08 Å which is about twice the standard deviation. In the remainder of the molecule the mean bond length is 1·53 Å with a maximum spread of 0·12 Å. These mean bond lengths are in agreement with the lengths expected for the conjugated bonds of the indole rings and the single bonds of the seven-membered ring and the iso-quinuclidine structure.

Similarly with respect to bond angles, the mean angle in the benzene ring is 120°, in the pyrrole ring 108°, and for the remainder of the molecule 111°, excluding $C_8C_7C_{12}$ and $C_7C_8C_9$. These two angles of 130° are associated with the junction of the seven membered ring to the five membered ring and are significantly greater than the 120°, which is the corresponding angle of the benzene bonds on the other side of the pyrrole ring.

The bromine ion is coordinated to two nitrogen

atoms only, an indole and an iso-quinuclidine nitrogen on different molecules. The former distance is significantly greater than the latter, in accordance with the greater basicity of the latter. This coordination appears to account for the anisotropic thermal motion of the bromine atom which is not accompanied by a similar anisotropy in the ibogaine molecule ions. The environment of the bromine ion, which is illustrated in Fig. 5, is compatible with the anisotropic thermal parameters which are least in the z direction (3·0 Å⁻²) and greatest in x and y (5·9 and 7·1 Å⁻²).
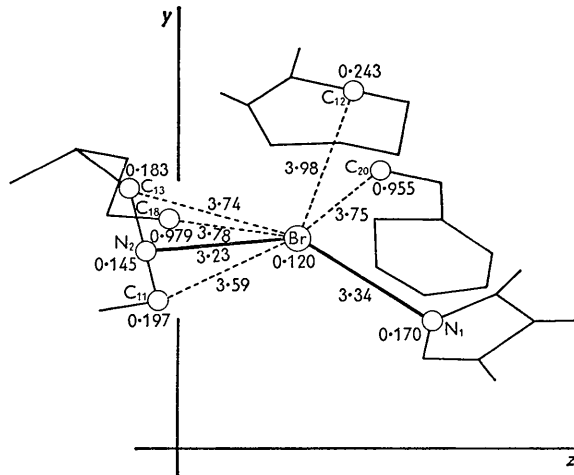

Fig. 5. Environment of the bromine ions in ibogaine hydrobromide.

On the basis of the 0·10 Å difference in the bromine to nitrogen distances and the chemical evidence, it is reasonable to postulate that the hydrobromide structure in the crystal is best represented formally as $N_{(2)}H$ · · · Br^- · · · H–$N_{(1)}$ with the more ionic binding to the iso-quinuclidine nitrogen (N_2).

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Short Communication

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

Observations on Chayes' discussion of the intermediate plagioclase felspars. By HELEN D. MEGAW, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

Chayes (1958) has propounded a tentative hypothesis that the positions of the subsidiary reflexions (*e* type maxima) in the intermediate plagioclase felspars may depend on average run lengths in Si and Al atoms, that is, on the average numbers of consecutive atoms of the same kind in tetrahedral sites. He seeks a relation between these and the observed quantities δ_c, the displacements of the layer lines of *e* type maxima (on oscillation photographs about [001]) from the nearest layer lines of principal or *a* type maxima; these displacements may alternatively be defined as the differences of reciprocal-space coordinates (in angular measure) along c^*. It appears to be implied, though not explicitly stated, that the relation is expected to take the form

$$360/\delta_c = E' , \qquad (1)$$

where E' is the average run length in Si. E' can be evaluated for the case of complete disorder, since Chayes has shown that its value $E(\bar{\imath}_{Si})$ is then mathematically given by

$$E(\bar{\imath}_{Si}) = 1/\alpha , \qquad (2)$$

where α is the ratio of the number of Al atoms to the total number of tetrahedral atoms. When a graph is drawn using the values of δ_c measured by Gay (1956) it is shown that a reasonable (not perfect) fit is obtained for

$$360/\delta_c = E(\bar{\imath}_{Si}) . \qquad (3)$$

Chayes comments: 'To a remarkable extent the "repeat distance" calculated from the δ_c spacing behaves as if it were governed by the same rules which determine average run lengths in a run sequence characterized by short-range disorder'. This, which strictly only says that both are inversely proportional to the composition parameter α, might be taken as a claim that the graph of (3) provides evidence tending to support (1), or even predicts the form of (1) (which has never been explicitly stated), as well as allowing an estimate of the state of order. It is important to realize that this is not true, which can be shown as follows.

Suppose we start with the very much simpler hypothesis,

$$\delta_c/360 = \alpha , \qquad (4)$$

which assumes the displacement, in cycles, to be equal to the relative number of Al atoms, *irrespective of their degree of order*. This gives

$$360/\delta_c = 1/\alpha , \qquad (5)$$

which is identical with (3) except for the labelling of one axis, and must therefore fit the experimental results equally well. Admittedly it is empirical as it stands, but it is so much simpler than (1), and without the need for any accessory postulates about order, that it would require strong theoretical reasons in favour of (1) to allow the latter any weight in the absence of direct independent evidence for it. In other words, any reasons for belief in (1) must come from considerations other than the empirical fit with experimental results shown in the graph, which can be accounted for more easily without it.

Chayes mentions experiments (Abelson, 1957) in which