

## The Crystal and Molecular Structure of 5-Methoxy-(*N,N*)-dimethyltryptamine Hydrochloride

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The hydrochloride of the strongly hallucinogenic indole amine 5-methoxy-(*N,N*)-dimethyltryptamine crystallizes in the orthorhombic space group *Pcab* with  $a=17.40$ ,  $b=22.86$ ,  $c=6.98$  Å;  $Z=8$ . The structure was determined from Patterson projections and refined by the method of least-squares to  $R=0.062$  for 2204 observed reflexions. The almost planar indole nucleus is rotated  $23.4^\circ$  to the nearly planar side chain. The configuration of the molecule is compared with other indole derivatives. The layered structure is mainly held together by van der Waals forces but there is one hydrogen bond (3.02 Å) between the  $N^+H$  of the side chain and the chloride ion.

### Introduction

The role of tryptamine derivatives has a special significance for the understanding of the biochemical mechanisms underlying various psychoses (Wooley & Shaw, 1954). Although no detailed knowledge of the steric configuration of these molecules was available attempts were made to interpret the structure-function relationship (Isenberg & Szent-Györgyi, 1959; Snyder & Merrill, 1965; Snyder & Richelson, 1968; Chotia & Pauling, 1969). Some preliminary crystal data of four indolalkylamines have recently been presented (Bergin, Carlström, Falkenberg & Ringertz, 1968). The present work gives the molecular structure of one of these compounds, the aim being to get a basis for further studies on the interrelation between molecular configuration and pharmacological activity.

### Experimental

5-Methoxy-(*N,N*)-dimethyltryptamine or methylated bufotenine was first isolated from plants by Pachter, Zacharias & Ribeiro (1959), and was later proved to be the main constituent of several South American hallucinogenic drugs (Holmstedt, Vandenheuvel, Gardiner & Horning, 1964; Holmstedt, 1965). The pharmacological activity has been investigated by Gessner & Page (1962) and Gessner (1970). The crystallization in ether and ethanol at  $0^\circ\text{C}$  of the hydrochloride salt was performed by Dr Jan Lundström (Institute of Pharmacognosy, Stockholm) resulting in highly birefringent single crystals in the form of colourless flat prisms.

The parameters of the orthorhombic unit cell were determined at room temperature from Weissenberg photographs of crystals mounted along the  $b$  and  $c$  axes. The density was measured by flotation in a chloroform-xylene mixture at  $25^\circ\text{C}$  and the melting point, determined in a hot-stage microscope, was found to be  $153^\circ$ .

### Crystal data:

5-Methoxy-(*N,N*)-dimethyltryptamine hydrochloride

$\text{C}_{13}\text{H}_{18}\text{N}_2\text{O} \cdot \text{HCl}$

M.W. 254.76

$a = 17.40 \pm 0.01$  Å

$b = 22.86 \pm 0.02$  Å

$c = 6.98 \pm 0.01$  Å

$V = 2776.39$  Å<sup>3</sup>

$D_x = 1.218$  g.cm<sup>-3</sup>

$D_m = 1.221$  g.cm<sup>-3</sup>

$Z = 8$

Systematic absences:  $hk0$  when  $k=2n+1$ ,  $h0l$  when  $h=2n+1$ ,  $0kl$  when  $l=2n+1$

Space group *Pcab*

For the preliminary structure determination integrated Weissenberg photographs were recorded with Ni-filtered Cu  $K\alpha$  radiation for the zero layer about the  $c$  axis using the multiple-film and equi-inclination technique. The photographic density of 136 independent reflexions, strong enough to be observed, and their corresponding backgrounds were measured in a microdensitometer. The intensities were corrected for film factors,  $\alpha_1$ - $\alpha_2$  separation, Lorentz and polarization factors but not for extinction or absorption. The three-dimensional set of data was collected from an optically perfect crystal measuring  $0.15 \times 0.15 \times 0.35$  mm. It was mounted about the  $c$  axis (corresponding to the long dimension of the crystal) in a Philips linear automatic single-crystal diffractometer, PAILRED. Using strictly monochromatic Mo  $K\alpha$  radiation the layers  $hk0$  through  $hk8$  were recorded within  $\sin \theta/\lambda = 0.7025$  corresponding to the Cu-sphere. This resulted in 2811 independent reflexions. Of these, 607 reflexions were not significantly different from the background intensity, and when included in the calculations these 'unobserved' reflexions were given half the threshold intensity. The corrected structure amplitudes were placed on

Table 1. Observed and calculated structure factors

The five columns in each group represent h, k, l, 10Fo, 10Fc. Unobserved reflexions are marked with letter L.

Table with multiple columns of numerical data representing structure factors for various h, k, l indices. The table is organized into groups of five columns each, corresponding to h, k, l, 10Fo, and 10Fc. Reflexions are marked with 'L' for unobserved.

Table 1 (cont.)

11	6	1	213	-218	1119	5	44	7	1	0	2	185	202	13	1	4	201	-37	19	14	1	201	15	14	6	6	46	-47	15	2	4	117	-125	15	17	2	67	81	16	15	4	28L	-7	11	15	7	158	140	19	2	4	74	81
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an absolute scale by Wilson statistics. The calculations above were performed with a program system by Bergin & Ringertz (1969) and were carried out on an IBM 360/75 computer.

**Determination of the structure**

In the (001) Patterson projection, based on the preliminary photographic reflexion set, the Cl-Cl rotation peak was easily located. The calculated electron density map, based upon the chlorine signs only, showed besides the chlorine maxima, additional peaks. The location of the molecule by iterated Fourier analysis in this projection was determined. The agreement index  $R [\sum(|F_o| - |F_c|) / \sum |F_o|]$  was at this stage 0.26. A least-squares refinement reduced the  $R$  value to 0.14. The overall temperature factor was set to  $B=3.0$ . Using  $h0l$  data a second Patterson projection enabled a preliminary estimation of the  $z$  coordinates for all non-hydrogen atoms.

**Refinement procedure**

Since the unit cell contained 36 atoms in the asymmetric unit and the number of parameters to be varied was quite large, the block-diagonal least-squares program in the *X-ray-63 Program System* by Stewart & High (1965) was used. The atomic scattering factors were those listed in *International Tables for X-ray Crystallography* (1962).

For the initial steps of the refinement procedure only the 846 strongest reflexions of the entire set were used. The structure amplitudes were given unit weight. The first two cycles of the three-dimensional refinement for the non-hydrogen atoms with isotropic temperature factors resulted in an  $R$  value of 0.098. From a difference Fourier synthesis it was now possible to locate all 19 hydrogen atoms.

The weighting scheme employed was of the type:  $W_{hkl} = 1/(A + BF_o + CF_o^2)$ , if  $|F_o| \geq 2.4$ ;  $W_{hkl} = 1$ , if  $|F_o| < 2.4$ . The weights were normalized to make the maximum weight equal to 1.  $A$ ,  $B$  and  $C$  were varied slightly during the refinement in order to give a satisfactory convergence. The values assumed by  $A$  were around  $2|F_{min}|$ , those of  $B$  around 1 and those of  $C$  around  $2|F_{max}|$ . The final refinement for the observed 2204 weighted structure factors resulted in an  $R$  value of 0.062. The mean standard deviation of the atomic coordinates was 0.0034 Å for the carbon atoms and 0.0419 Å for the hydrogen atoms. The average shift to error was 0.11 for the non-hydrogen atoms and 0.13 for all 211 parameters which were varied in the last refinement cycle. Isotropic temperature factors of the hydrogen atoms, set equal to those of the 'heavier' atoms to which they were covalently bound, were not refined. The values of  $B$  ranged from 2.93 to 5.87. Observed and calculated structure factors from this last cycle are listed in Table 1. The atomic coordinates and thermal parameters for the final structure are given in Tables 2 and 3.

Table 2. *Final fractional atomic coordinates and their standard deviations (in parentheses)*

Cl	0.3651 (1)	0.3029 (1)	0.9266 (1)
N(1)	0.2991 (2)	0.5229 (1)	0.2249 (5)
N(14)	0.3798 (1)	0.2931 (1)	0.4971 (3)
O(10)	0.4306 (2)	0.6221 (1)	0.8608 (4)
C(2)	0.3171 (2)	0.4649 (2)	0.2519 (5)
C(3)	0.3597 (2)	0.4584 (1)	0.4147 (5)
C(4)	0.4039 (2)	0.5367 (1)	0.6634 (5)
C(5)	0.3985 (2)	0.5959 (1)	0.7048 (5)
C(6)	0.3578 (2)	0.6343 (1)	0.5815 (6)
C(7)	0.3231 (2)	0.6144 (1)	0.4196 (6)
C(8)	0.3283 (2)	0.5550 (1)	0.3749 (5)
C(9)	0.3680 (2)	0.5159 (1)	0.4956 (4)
C(11)	0.4750 (3)	0.5874 (2)	0.9877 (6)
C(12)	0.3913 (2)	0.4026 (1)	0.4988 (5)
C(13)	0.3511 (2)	0.3499 (1)	0.4156 (4)
C(15)	0.3314 (2)	0.2436 (1)	0.4289 (5)
C(16)	0.4623 (2)	0.2820 (2)	0.4572 (6)
H(1)	0.268 (2)	0.535 (2)	0.135 (7)
H(2)	0.302 (2)	0.435 (2)	0.151 (6)
H(3)	0.432 (2)	0.507 (2)	0.747 (6)
H(4)	0.358 (2)	0.673 (2)	0.619 (6)
H(5)	0.295 (2)	0.641 (2)	0.338 (6)
H(6)	0.438 (3)	0.560 (2)	1.047 (7)
H(7)	0.517 (2)	0.569 (2)	0.917 (7)
H(8)	0.487 (2)	0.611 (2)	1.094 (7)
H(9)	0.449 (2)	0.399 (2)	0.475 (6)
H(10)	0.385 (2)	0.405 (2)	0.634 (6)
H(11)	0.354 (2)	0.348 (2)	0.279 (5)
H(12)	0.295 (2)	0.350 (2)	0.443 (5)
H(13)	0.377 (2)	0.297 (2)	0.620 (6)
H(14)	0.351 (2)	0.206 (2)	0.485 (7)
H(15)	0.341 (2)	0.242 (2)	0.297 (6)
H(16)	0.279 (2)	0.247 (2)	0.474 (6)
H(17)	0.474 (3)	0.241 (2)	0.491 (7)
H(18)	0.475 (3)	0.289 (2)	0.329 (7)
H(19)	0.494 (3)	0.309 (2)	0.514 (7)

### Description and discussion of the structure

#### Configuration of the molecule

The atomic numbering of the indole nucleus is according to international rules. The rest of the molecule has been numbered in the most convenient way (Fig. 1). The configuration of the molecule is illustrated in Fig.

2, including the thermal ellipsoids of the non-hydrogen atoms scaled to 50 per cent probability. The calculations were performed with the plot program *ORTEP* (Johnson, 1965) on an IBM 360/75 computer. The 5-MeO-DMT molecule consists of two parts: the almost planar indole nucleus with a methoxyl group attached to the C(5) atom and the side-chain with the amino group. The best plane through the indole nucleus was calculated with the C(12) and O(10) atoms included and is expressed by the equation  $0.84357X + 0.14995Y - 0.51567Z = 5.3563$  in orthogonal Ångström space. The maximum deviation of the atoms from this plane was found to be 0.029 Å and the mean deviation  $\pm 0.016$  Å. This was considered somewhat too high for a perfectly planar structure and a better fit was obtained in determining the best planes of the six- and five-membered rings separately. The mean atomic deviations were reduced to  $\pm 0.004$  and  $\pm 0.008$  Å respectively. Both values are within the limits of experimental error. The normals to the two planes make an angle of  $2.1^\circ$  and the indole nucleus is thus slightly bent along the C(8)–C(9) bond. This angle between the five- and six-membered rings is statistically highly significant.

The methoxyl group was expected to be very nearly in the plane of the six-membered ring (Kantha, Ahmed & Barnes, 1962), but the C(11) atom is 0.08 Å out of the plane, which is significant as the standard deviation of the atoms defining the plane of the six-membered ring is 0.004 Å. The torsion angle ( $\tau$ ) as defined by Klyne & Prelog (1960) is  $2.5^\circ$  for the atoms C(6)–C(5)–O(10)–C(11).

The atoms C(12) through C(15) of the side-chain and the C(3) atom in the five-membered ring are almost in the same plane, the mean deviation being  $\pm 0.038$  Å. The plane formed by these atoms is rotated  $22.5^\circ$  with respect to the plane of the five-membered ring. The torsion angle C(2)–C(3)–C(12)–C(13) or the position of the  $\alpha$ -carbon atom, C(13), should be 0,  $+90$  or  $-90^\circ$  according to Chotia & Pauling (1969). However, the angle actually found ( $17.2^\circ$ ) differs from the predicted

Table 3. *Anisotropic parameters and standard deviations (in parentheses)*

All values are  $\times 10^5$ .  $\beta_{ij}$  are the coefficients in the expression:  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cl	409 (3)	235 (2)	1386 (15)	-1 (2)	39 (6)	-59 (4)
N(1)	455 (12)	215 (6)	2582 (75)	-18 (7)	-444 (26)	228 (18)
N(14)	331 (9)	147 (4)	1254 (46)	15 (5)	11 (17)	-40 (12)
O(10)	608 (13)	173 (5)	3282 (74)	9 (6)	-309 (26)	-199 (16)
C(2)	431 (13)	218 (8)	2216 (79)	-26 (8)	-313 (29)	28 (20)
C(3)	322 (11)	173 (6)	1760 (65)	-23 (7)	-130 (22)	32 (16)
C(4)	288 (10)	135 (6)	2159 (70)	-0 (6)	-26 (22)	25 (16)
C(5)	350 (11)	151 (6)	2562 (85)	-10 (7)	34 (26)	-34 (18)
C(6)	384 (13)	134 (6)	3265 (101)	11 (7)	107 (30)	117 (20)
C(7)	362 (12)	148 (6)	3177 (97)	7 (7)	-28 (29)	277 (20)
C(8)	277 (10)	176 (6)	2208 (72)	-18 (6)	-21 (23)	176 (18)
C(9)	248 (9)	137 (5)	1889 (64)	-19 (6)	24 (20)	76 (15)
C(11)	517 (17)	249 (9)	2913 (104)	-58 (10)	-235 (35)	-176 (25)
C(12)	420 (13)	127 (5)	1991 (69)	-13 (7)	-242 (25)	-4 (16)
C(13)	347 (11)	135 (5)	1699 (62)	14 (6)	-109 (21)	-30 (15)
C(15)	529 (16)	143 (6)	2512 (85)	-30 (8)	-200 (31)	2 (19)
C(16)	406 (14)	255 (9)	3035 (106)	89 (9)	186 (32)	89 (24)

values as is also the case in the serotonin molecule (Karle, Dragonette & Brenner, 1965). The position of the nitrogen atom relative to the  $\alpha$ -carbon atom gives an antiplanar torsion angle  $C(3)-C(12)-C(13)-N(14)$ ,  $\tau=179.2^\circ$ . This is in accordance with the situation found in serotonin. The methoxyl group is substituted in the 5-position of the DMT molecule and there is no hydrogen bond  $N^+(14)\cdots O(10)$ . Therefore the third important torsion angle  $C(12)-C(13)-N(14)-C(15)$  discussed by Chotia & Pauling (1969) is not relevant in the present structure.

The equations of all planes and atomic deviations are given in Table 4.

#### Bond lengths and bond angles

The bond lengths and bond angles with estimated standard deviations are listed in Tables 5 and 6 and illustrated in Fig. 1. No corrections have been made for thermal motion. The average C-C bond length in the undistorted benzene ring is 1.397 Å. The C(6)-C(7) bond (1.360 Å) is significantly shorter than the average value when tested with the criteria of significance pre-

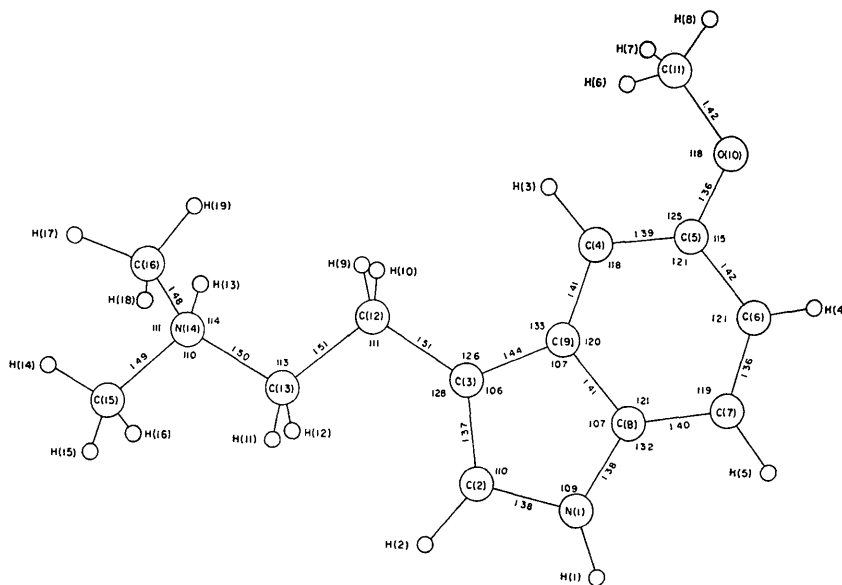


Fig. 1. Diagram showing bond lengths (in Å) and bond angles (in degrees) for non-hydrogen atoms.

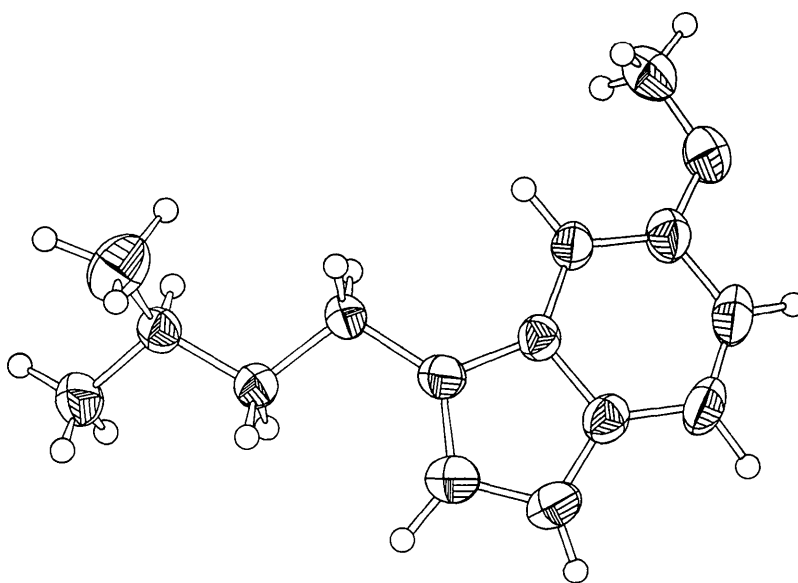


Fig. 2. Thermal ellipsoids representation of the 5-MeO-DMT molecule. The ellipsoids enclose 50 per cent probability. The hydrogen atoms are indicated by small spheres. The chlorine atom is not included in the drawing.

Table 4. Equations of the best planes with the formula  $m_1x + m_2y + m_3z = d$  in orthogonal Ångström space

	Plane	$m_1$	$m_2$	$m_3$	$d$
A	N(1), O(10), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9) C(12)	0.84357	0.14995	-0.51567	5.3563
B	C(4), C(5), C(6), C(7), C(8), C(9), C(10)	0.83884	0.16935	-0.51737	5.5802
C	N(1), C(2), C(3), C(9), C(8), C(12)	0.84219	0.13338	-0.52242	5.1495
D	C(15), N(14), C(13), C(12), C(3)	0.62671	-7.2065	-0.77591	0.93642

## Deviations (Å) from the best planes

	A		B		C		D
N(1)	-0.016	C(4)	0.002	N(1)	-0.007	C(15)	0.047
O(10)	0.002	C(5)	0.002	C(2)	0.004	N(14)	-0.030
C(2)	0.015	C(6)	0.003	C(3)	-0.008	C(13)	-0.065
C(3)	-0.003	C(7)	0.002	C(9)	-0.009	C(12)	0.034
C(4)	-0.025	C(8)	-0.006	C(8)	0.013	C(3)	0.014
C(5)	0.001	C(9)	0.002	C(12)	0.006		
C(6)	0.024	O(10)	-0.005				
C(7)	0.019						
C(8)	-0.016						
C(9)	-0.029						
C(12)	0.028						

## Angles between planes

A-D	23.37°	B-C	2.09°
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sented by Cruickshank (1966). The mean C-N distance in the five-membered ring is 1.376 Å and the C-C distance is 1.404 Å. One of the three C-N bonds around the quaternary nitrogen atom, N(14)-C(13), is significantly longer than the others. The mean C-N bond length, 1.492 Å, is, however, in good agreement with the average value for a C-N<sup>+</sup> single bond (Hahn, 1957). The angles between the N(14) atom and its attached carbon atoms, C(13), C(15) and C(16), are 110.3, 113.5 and 110.9° respectively, *i.e.* fairly close to the normal tetrahedral angle, 109.47°. The C-H bond lengths range from 0.92 to 1.03 Å and the two N-H distances are 0.86 and 0.87 Å.

Table 5. Interatomic distances and standard deviations (in parentheses)

N(1)-C(2)	1.376 (5) Å	C(2)-H(2)	1.01 (4) Å
C(2)-C(3)	1.365 (5)	C(4)-H(3)	1.01 (4)
C(3)-C(9)	1.437 (4)	C(6)-H(4)	0.92 (4)
C(9)-C(4)	1.411 (4)	C(7)-H(5)	0.96 (4)
C(4)-C(5)	1.385 (4)		
C(5)-C(6)	1.419 (5)	C(12)-H(9)	1.03 (4)
C(6)-C(7)	1.360 (5)	C(12)-H(10)	0.95 (4)
C(7)-C(8)	1.396 (4)	C(13)-H(11)	0.96 (4)
C(8)-N(1)	1.375 (4)	C(13)-H(12)	1.00 (4)
C(8)-C(9)	1.409 (4)	C(11)-H(6)	1.00 (4)
		C(11)-H(7)	0.97 (4)
C(5)-O(10)	1.363 (4)	C(11)-H(8)	0.95 (4)
O(10)-C(11)	1.419 (5)	C(15)-H(14)	1.00 (4)
		C(15)-H(15)	0.94 (4)
C(3)-C(12)	1.509 (4)	C(15)-H(16)	0.97 (4)
C(12)-C(13)	1.508 (4)	C(16)-H(17)	0.99 (5)
C(13)-N(14)	1.503 (4)	C(16)-H(18)	0.94 (5)
N(14)-C(15)	1.489 (4)	C(16)-H(19)	0.92 (5)
N(14)-C(16)	1.484 (5)		
		Cl...H(13)	2.16 (4)
N(1)-H(1)	0.87 (4)	Cl...N(14)	3.017 (2)
N(14)-H(13)	0.86 (4)		

A comparison of the 5-MeO-DMT molecule with other indole amines and related amino acids is presented in Table 7. There are vast differences in accuracy between these structure determinations but valuable information can still be found in comparing the bond lengths and bond angles of the indole nuclei. Of greatest interest is naturally the serotonin (5-hydroxytryptamine) molecule as this substance is supposed to be a transmitter of the synaptic junctions in the brain and therefore has an activity opposite to that of the hallucinatory effects of 5-MeO-DMT. In both molecules the indole nucleus is almost planar and the amino-chain slightly out of the plane of the ring system. The inclination between the normals to the chain-plane and to the indole-plane in serotonin is 11.7°.

## Environment of the molecule

In the present structure there is only one hydrogen bond. This bond connects the N<sup>+</sup> ion with the Cl<sup>-</sup> ion and runs almost parallel to the *c*-axis direction. The hydrogen atom is nearly on the line between these two atoms, the N(14)-H(13)···Cl angle being 177°. The N···Cl distance, 3.02 Å, is slightly shorter than normally found and the H(13)···Cl distance, 2.16 Å, is accordingly appreciably shorter than the sum of van der Waals radii (3.05 Å). The uncharged nitrogen atom of the indole nucleus does not take part in any hydrogen bonding. No other unusually short contacts between non-bonded atoms were found; the shortest intermolecular C-C and C-N distances are 3.79 and 3.32 Å respectively.

There are eight molecules per unit cell and they are arranged in a double-layered system with the indole

nuclei inclined at  $36.7^\circ$  to the *ab* plane. The crystal arrangement shows a resemblance to the packing of L-tryptophan HCl (Takigawa, Ashida, Sasada & Kakudo, 1966): the polar groups are held in position by hydrogen bonds and the non-polar indole nuclei by van der Waals forces. The packing of the molecules in half

a unit cell ( $x=0$  to  $x=\frac{1}{2}$ ) projected on the *bc* plane is shown in Fig. 3.

We wish to thank Professor Bo Holmstedt for supplying the raw material and for valuable criticism of the manuscript, Dr Jan Lundström for the crystalliza-

Table 6. *Interatomic angles and standard deviations (in parentheses)*

N(1)—C(2)—C(3)	110.1 (3) <sup>o</sup>	O(10)—C(11)—H(6)	105 (3) <sup>o</sup>
C(2)—C(3)—C(9)	106.4 (3)	O(10)—C(11)—H(7)	109 (3)
C(3)—C(9)—C(8)	107.2 (3)	O(10)—C(11)—H(8)	107 (3)
C(9)—C(8)—N(1)	107.3 (3)	H(6)—C(11)—H(7)	116 (4)
C(8)—N(1)—C(2)	109.0 (3)	H(7)—C(11)—H(8)	118 (4)
		H(6)—C(11)—H(8)	101 (4)
C(4)—C(5)—C(6)	120.8 (3)		
C(5)—C(6)—C(7)	121.2 (3)	C(3)—C(12)—H(9)	111 (2)
C(6)—C(7)—C(8)	118.8 (3)	C(13)—C(12)—H(9)	110 (2)
C(7)—C(8)—C(9)	121.1 (3)	C(3)—C(12)—H(10)	108 (2)
C(8)—C(9)—C(4)	119.9 (3)	C(13)—C(12)—H(10)	111 (2)
C(9)—C(4)—C(5)	118.2 (3)	H(9)—C(12)—H(10)	106 (3)
C(11)—O(10)—C(5)	118.3 (3)	C(12)—C(13)—H(11)	113 (2)
O(10)—C(5)—C(4)	124.6 (3)	N(14)—C(13)—H(11)	109 (2)
O(10)—C(5)—C(6)	114.6 (3)	C(12)—C(13)—H(12)	112 (2)
		N(14)—C(13)—H(12)	105 (2)
N(1)—C(8)—C(7)	131.6 (3)	H(11)—C(13)—H(12)	104 (3)
C(4)—C(9)—C(3)	132.8 (3)		
		C(13)—N(14)—H(13)	106 (2)
C(9)—C(3)—C(12)	125.7 (3)	C(15)—N(14)—H(13)	111 (2)
C(2)—C(3)—C(12)	127.9 (3)	C(16)—N(14)—H(13)	105 (2)
C(3)—C(12)—C(13)	110.9 (3)		
C(12)—C(13)—N(14)	112.9 (3)	N(14)—C(15)—H(14)	110 (2)
C(13)—N(14)—C(15)	110.3 (2)	N(14)—C(15)—H(15)	104 (3)
C(13)—N(14)—C(16)	113.5 (3)	N(14)—C(15)—H(16)	112 (3)
C(15)—N(14)—C(16)	110.9 (3)	H(14)—C(15)—H(15)	107 (4)
		H(14)—C(15)—H(16)	105 (4)
C(8)—N(1)—H(1)	127 (3)	H(15)—C(15)—H(16)	120 (4)
C(2)—N(1)—H(1)	123 (3)		
N(1)—C(2)—H(2)	119 (2)	N(14)—C(16)—H(17)	109 (3)
C(3)—C(2)—H(2)	131 (2)	N(14)—C(16)—H(18)	112 (3)
C(9)—C(4)—H(3)	118 (2)	N(14)—C(16)—H(19)	112 (3)
C(5)—C(4)—H(3)	124 (2)	H(17)—C(16)—H(18)	110 (4)
C(5)—C(6)—H(4)	115 (3)	H(17)—C(16)—H(19)	114 (4)
C(7)—C(6)—H(4)	123 (3)	H(18)—C(16)—H(19)	99 (4)
C(6)—C(7)—H(5)	121 (3)		
C(8)—C(7)—H(5)	120 (3)	N(14)—H(13)...Cl	177 (3)

Table 7. *A comparison of the bond lengths (in Å) for the indole nucleus in crystallographic and theoretical determinations of indolamines and related amino acids*

Structure	N(1)—C(2)	C(2)—C(3)	C(3)—C(9)	C(9)—C(4)	C(4)—C(5)	C(5)—C(6)	C(6)—C(7)	C(7)—C(8)	C(8)—C(9)	C(8)—N(1)	Mean $\sigma$
<i>A</i>	1.430	1.338	1.418	1.405	1.411	1.353	1.390	1.399	1.388	1.307	0.014
<i>B</i>	1.401	1.342	1.470	1.434	1.400	1.396	1.409	1.422	1.407	1.385	0.018
<i>C</i>	1.40	1.34	1.49	1.37	1.37	1.42	1.39	1.40	1.39	1.38	---
<i>D</i>	1.39	1.38	1.47	1.41	1.42	1.38	1.40	1.43	1.40	1.39	---
<i>E</i>	1.377	1.344	1.451	1.412	1.397	1.386	1.399	1.400	1.382	1.391	0.015
<i>F</i>	1.372	1.362	1.445	1.416	1.445	1.381	1.380	1.394	1.370	1.432	0.020
<i>G</i>	1.375	1.378	1.433	1.428	1.382	1.420	1.383	1.428	1.419	1.379	---
<i>H</i>	1.376	1.365	1.437	1.411	1.385	1.419	1.360	1.396	1.409	1.375	0.004

*A* Glycyl-L-tryptophan dihydrate, Pasternak (1956).

*B* 3-Indolylacetic acid, Karle, Britts & Gum (1964).

*C* Skatole in complex with indole and *s*-Trinitrobenzene, Hanson (1964).

*D* Serotonin-creatinine sulphate complex, Karle, Dragonette & Brenner (1965).

*E* L-Tryptophan HCl, Takigawa, Ashida, Sasada & Kakudo (1966).

*F* L-Tryptophan HBr, Ayyar & Chandrasekharan (1967).

*G*. Indole ( $C_s$ ) bond orders, Fraga & Melgarejo (1969), transformed into bond lengths according to Pauling (1960).

*H* This work.

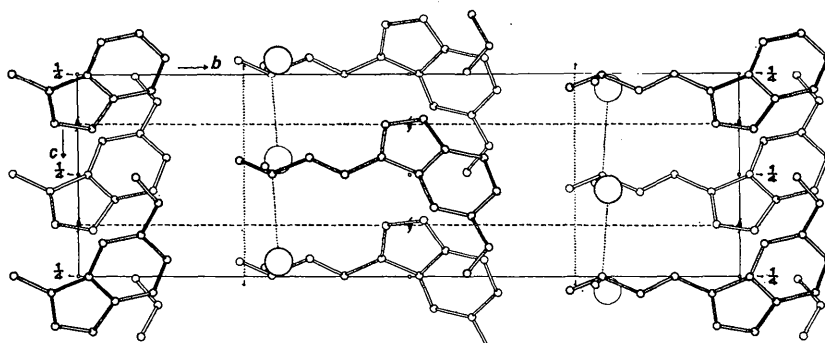


Fig. 3. The packing of the molecules in half a unit cell ( $x=0$  to  $x=\frac{1}{2}$ ) seen along the  $a$  axis.

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