The Crystal and Molecular Structure of (*N*,*N*)-Dimethyltryptamine

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The hallucinogenic indolealkylamine, (*N*,*N*)-dimethyltryptamine, crystallizes in two modifications having the same monoclinic space group, $P2/a$ and $P2_1/c$ ($Z=8$). For the latter, which has two molecules in the asymmetric unit, data were collected on an automatic diffractometer. Unit-cell dimensions are $a=12\cdot99$, $b=12\cdot08$, $c=18\cdot38$ Å and $\beta=127\cdot85°$. The structure was determined by the symbolic addition procedure and refined by the method of full-matrix least squares to $R=0\cdot048$ for 2080 observed reflexions. The molecular structures of the two molecules are almost identical. The indole nuclei are planar, and the ethylamine side chain is almost fully extended (torsion angle $\tau_2=176$ and $188°$ for molecules A and B respectively) and lies near a plane which is approximately perpendicular to that of the indole ($\tau_1=102$ and $90°$). Relatively strong N–H$\cdots$N hydrogen bonds join A-molecules ($2\cdot92$ Å) and B-molecules ($2\cdot89$ Å) separately in two different helically fashioned hydrogen-bonding systems around screw axes.

Introduction

(*N*,*N*)-Dimethyltryptamine, in the following abbreviated to DMT, is a psychotomimetic substance (Szara, 1956). Its activity is probably due to interference with the function of serotonin (5-hydroxytryptamine), one of the synaptic transmitters in the central nervous system. DMT was first isolated from the seeds of *Piptadenia peregrina* (Fish, Johnson & Horning, 1955), which is a constituent in many hallucinogenic drugs used by South American Indians. The structure determination of DMT was undertaken as part of our research program on psychoactive compounds.
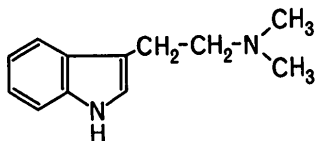
Experimental

Of the halides of DMT good crystals could only be obtained for the bromide. However, the dimensions of these crystals, which were grown in a methanol–ether solution, were too small to allow the recording of reliable intensities. Hence it was decided to determine the structure of the DMT base by using direct methods. The crystals of the base were obtained from Schuka Co., Germany and in the batch two entirely different crystal modifications could easily be distinguished by their optical properties and crystal shape. One of the modifications was found to be identical with the monoclinic DMT ($P2_1/a$) described by Bergin, Carlström, Falkenberg & Ringertz (1968). The only crystals large enough for single-crystal analysis belonged to the other modification, crystallizing in the same space group but

with eight instead of four molecules in the unit cell. Crystal data of this modification as well as DMT.HBr are given in Table 1. The space group was determined from Weissenberg photographs and the unit-cell parameters were measured at 20 °C on an automatic linear single-crystal diffractometer PAILRED (Philips) using Mo $K\alpha$ radiation ($\lambda=0\cdot7107$ Å). The density was measured by flotation in a Clerici solution at 27 °C. The melting point was determined in a hot-stage microscope.

An optically perfect and almost spherical crystal with a diameter of roughly 0·35 mm was glued with gum arabic on to a glass fibre. Since the crystal was quite hygroscopic it was sealed inside a Lindemann-glass capillary. The unique axis b (corresponding to the long dimension of the originally prismatic crystal) was oriented parallel to the ω axis of a PAILRED diffractometer equipped with a graphite monochromator. Intensities of the layers $h0l$ through $h13l$ were recorded for $\sin\theta/\lambda\leq0\cdot58$. To approximate to a fixed-count strategy, reflexions with low intensities were measured up to three times. The background intensity was measured for one min on each side of every reflexion. The scanning method was a continuous ω-scan with a scanning range of 3–4° and a scan-speed of 2·5° per min.

3743 independent reflexions were recorded, of which 2092 were significantly different from the background intensity at a 95% confidence limit, corresponding to 55·9% of the total. This relatively low percentage was due to a rapid fall-off of intensities at higher θ values, which was already apparent in the Weissenberg photographs. The intensities were corrected for background, Lorentz and polarization factors but not for absorption, owing to the low μ value (0·71 cm^{-1} for Mo $K\alpha$). The corrected structure amplitudes were placed on an approximately absolute scale by Wilson statistics. An overall temperature factor of $B=4\cdot8$ was obtained

from a Wilson plot. All calculations were performed on an IBM 360/75 computer using the X-ray crystallographic program system developed by Bergin (1971).

Determination of the structure

The 300 highest normalized structure factors ($|E| \geq 1.69$) were used to set up the equation system for phase determination based on the principle suggested by Karle & Karle (1963, 1966) of generating solutions of the triple relations between phases. The program uses the indices of the reflexions to find all the triple products ($|E_1 . E_2 . E_3| > 12.0$) up to a total of 800. The basic set for applying the formula by Sayre (1952) consisted of the three reflexions with the highest E values having a large number of combinations, thereby specifying the origin. In addition, the signs of three other reflexions were specified by symbols. The basic set used in the phase determination was:

Sign	h	k	l	$|E|$	Number of relations	Range for probability
+	4	3	10	3·770	27	0·993–0·911
+	9	3	−11	3·644	30	0·993–0·912
+	12	5	−17	3·587	30	0·998–0·915
a	10	2	−11	3·571	28	0·999–0·912
b	5	5	−14	3·425	22	0·992–0·908
c	12	4	−14	3·345	19	0·991–0·921

By an iterative procedure the Sayre relations were used to accumulate phases expressed in the phases of the basic set. Once the symbols had been assigned, 268 phases were obtained and in the resulting E maps the nineteen highest peaks corresponded to atoms of the two indole nuclei in the asymmetric unit. The electron density maps synthesized with phases based on these nineteen atomic positions revealed the nine missing atoms.

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

Values for non-hydrogen atoms are $\times 10^4$, and for hydrogen atoms $\times 10^3$.

Molecule A

	x/a	y/b	z/c
N(1)	4535 (3)	2227 (2)	1465 (2)
C(2)	4890 (3)	1276 (3)	1976 (2)
C(3)	3823 (3)	747 (3)	1773 (2)
C(4)	1378 (4)	1287 (3)	612 (2)
C(5)	565 (4)	2067 (5)	−14 (3)
C(6)	1059 (5)	2967 (4)	−180 (3)
C(7)	2371 (5)	3118 (3)	271 (3)
C(8)	3204 (3)	2316 (3)	914 (2)
C(9)	2724 (3)	1396 (3)	1088 (2)
C(10)	3804 (4)	−327 (3)	2178 (2)
C(11)	3616 (3)	−169 (3)	2906 (2)
N(12)	3506 (2)	−1230 (2)	3240 (2)
C(13)	3660 (4)	−1064 (4)	4089 (3)
C(14)	2279 (4)	−1774 (4)	2561 (3)
H(1)	510 (3)	273 (3)	152 (2)
H(2)	580 (3)	106 (3)	241 (2)
H(4)	107 (3)	60 (3)	75 (2)
H(5)	−45 (3)	206 (3)	−38 (2)
H(6)	56 (3)	354 (3)	−60 (2)
H(7)	273 (3)	377 (3)	20 (2)
H(10A)	469 (3)	−79 (3)	251 (2)
H(10B)	307 (3)	−77 (3)	166 (2)
H(11A)	439 (3)	26 (3)	345 (2)
H(11B)	281 (3)	27 (3)	264 (2)
H(13A)	300 (3)	−49 (3)	397 (2)
H(13B)	359 (3)	−183 (3)	431 (2)
H(13C)	458 (3)	−73 (3)	456 (2)
H(14A)	148 (3)	−133 (3)	238 (2)
H(14B)	214 (3)	−248 (3)	278 (2)
H(14C)	226 (3)	−199 (3)	199 (2)

Refinement of the structure

A full-matrix least-squares refinement of the coordinates of the 28 atoms with isotropic temperature factors gave an R value of 0·16 ($R = \sum||F_o| - |F_c||/\sum|F_o|$). Further refinement was carried out with anisotropic temperature factors for four cycles ($R = 0·08$). From a

Table 1. *Crystal data*

	(N,N)-Dimethyltryptamine hydrobromide DMT.HBr	(N,N)-Dimethyltryptamine DMT
Empirical formula	$C_{12}H_{16}N_2 . HBr$	$C_{12}H_{16}N_2$
Molecular weight	269·19	188·26
Melting point	114·5 °C	65·5 °C
Crystals	Transparent light-yellow prisms	Transparent colourless hexagonal prisms
Crystal system	Orthorhombic	Monoclinic
Systematic absences	$hk0$ when k is odd $h0l$ when h is odd $0kl$ when l is odd	$h0l$ when l is odd $0k0$ when k is odd
Space group	$Pcab$	$P2_1/c$
Molecules per unit cell	$Z = 8$	$Z = 8$
Unit-cell dimensions	$a = 13·23 \pm 0·03$ Å $b = 24·70 \pm 0·05$ $c = 7·70 \pm 0·01$ $V = 2517·27$ Å³	$a = 12·99 \pm 0·01$ Å $b = 12·08 \pm 0·01$ $c = 18·38 \pm 0·02$ $\beta = 127·85 \pm 0·01°$ $V = 2277·50$ Å³
D_m		1·080 g.cm⁻³
D_x	1·421 g.cm⁻³	1·074 g.cm⁻³

Table 2 (cont.)

Molecule B

	x/a	y/b	z/c
N(1)	− 346 (2)	7342 (2)	2966 (2)
C(2)	− 185 (3)	6280 (3)	2789 (2)
C(3)	959 (3)	5860 (3)	3524 (2)
C(4)	2720 (3)	6765 (3)	5111 (2)
C(5)	2991 (4)	7721 (4)	5595 (3)
C(6)	2155 (4)	8617 (3)	5222 (3)
C(7)	1000 (4)	8588 (3)	4340 (3)
C(8)	709 (3)	7620 (3)	3836 (2)
C(9)	1559 (3)	6700 (3)	4209 (2)
C(10)	1494 (3)	4736 (3)	3588 (2)
C(11)	2332 (3)	4739 (3)	3268 (2)
N(12)	2703 (2)	3626 (2)	3203 (2)
C(13)	3237 (4)	3632 (3)	2699 (3)
C(14)	3644 (4)	3128 (3)	4103 (3)
H(1)	− 102 (3)	775 (3)	260 (2)
H(2)	− 85 (3)	595 (3)	217 (2)
H(4)	336 (3)	611 (3)	539 (2)
H(5)	393 (3)	778 (3)	622 (2)
H(6)	233 (3)	934 (3)	553 (2)
H(7)	38 (3)	921 (3)	406 (2)
H(10A)	75 (3)	418 (3)	320 (2)
H(10B)	193 (3)	443 (3)	420 (2)
H(11A)	180 (3)	511 (3)	261 (2)
H(11B)	315 (3)	523 (3)	369 (2)
H(13A)	408 (3)	415 (3)	307 (2)
H(13B)	345 (3)	284 (3)	265 (2)
H(13C)	257 (3)	399 (3)	209 (2)
H(14A)	443 (3)	365 (3)	447 (2)
H(14B)	380 (3)	232 (3)	405 (2)
H(14C)	336 (3)	310 (3)	449 (2)

difference Fourier synthesis all 32 hydrogen atoms could be identified as they were found among the 45 strongest peaks. An inspection of the F_{calc} based on all 60 atomic positions revealed that the 12 strongest F_{obs} were affected by secondary extinction and they were excluded from subsequent refinements. Three cycles of refinement with the coordinates of all atoms and anisotropic temperature factors for the non-hydrogen atoms gave a final R value of 0·048 for 2080 reflexions. The isotropic temperature factor ($B = 4\cdot2$ Å^2) given to the hydrogen atoms was not refined. Owing to the great number of parameters, non-hydrogen and hydrogen atoms were refined in separate runs of the refinement procedure. The last shifts for both non-hydrogen and hydrogen atoms were less than the corresponding e.s.d.'s. The mean e.s.d. of the atomic coordinates was 0·004 Å for the non-hydrogen atoms and 0·03 Å for the hydrogen atoms.

The atomic scattering factors were taken from International Tables for X-ray Crystallography (1962). The structure amplitudes were given unit weight throughout, because of the counter strategy mentioned. Anomalous dispersion terms were not included in the calculations. The atomic coordinates and thermal parameters for the final structure are given in Tables 2 and 3. Observed and calculated structure factors from the last cycle of refinement are listed in Table 4..

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

β_{ij} are the coefficients in the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl) \times 10^{-4}]$

Molecule A

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	132 (4)	67 (4)	67 (2)	− 33 (5)	130 (4)	− 13 (3)
C(2)	129 (4)	75 (5)	56 (2)	7 (6)	114 (5)	0 (4)
C(3)	142 (4)	62 (5)	61 (2)	− 9 (6)	141 (5)	− 11 (4)
C(4)	136 (5)	112 (5)	64 (2)	− 38 (7)	126 (6)	− 32 (5)
C(5)	143 (5)	161 (7)	71 (3)	31 (9)	127 (6)	0 (6)
C(6)	196 (7)	152 (7)	73 (3)	150 (10)	152 (7)	61 (6)
C(7)	218 (7)	88 (5)	78 (3)	45 (8)	194 (7)	26 (5)
C(8)	144 (4)	64 (5)	55 (2)	1 (6)	133 (5)	− 9 (4)
C(9)	128 (4)	66 (5)	51 (2)	− 19 (6)	118 (5)	− 23 (4)
C(10)	195 (5)	66 (5)	82 (2)	22 (6)	203 (6)	14 (4)
C(11)	139 (4)	66 (5)	65 (2)	15 (5)	142 (5)	5 (4)
N(12)	115 (3)	73 (4)	58 (2)	7 (4)	118 (4)	16 (3)
C(13)	236 (7)	114 (5)	83 (3)	− 3 (8)	215 (8)	22 (5)
C(14)	142 (5)	119 (5)	94 (3)	− 65 (7)	146 (6)	1 (5)

Molecule B

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	103 (3)	82 (5)	68 (2)	37 (5)	91 (4)	19 (3)
C(2)	109 (4)	83 (5)	62 (2)	− 6 (6)	98 (5)	− 7 (4)
C(3)	111 (4)	69 (5)	65 (2)	13 (5)	129 (5)	10 (4)
C(4)	119 (4)	94 (5)	55 (2)	17 (6)	108 (5)	24 (4)
C(5)	155 (5)	107 (5)	64 (2)	− 24 (7)	127 (6)	− 1 (5)
C(6)	200 (6)	89 (5)	82 (3)	− 51 (8)	188 (7)	− 29 (5)
C(7)	166 (5)	74 (5)	86 (3)	19 (6)	175 (7)	7 (5)
C(8)	118 (4)	72 (5)	60 (2)	3 (6)	119 (5)	9 (4)
C(9)	107 (4)	70 (5)	56 (2)	11 (5)	116 (5)	17 (4)
C(10)	143 (4)	70 (5)	80 (2)	2 (6)	164 (6)	6 (4)
C(11)	110 (4)	68 (5)	60 (2)	− 11 (5)	115 (5)	− 5 (4)
N(12)	107 (3)	67 (4)	60 (2)	− 7 (4)	116 (4)	− 3 (3)
C(13)	194 (6)	97 (5)	96 (3)	− 1 (7)	219 (7)	− 12 (5)
C(14)	163 (5)	116 (5)	86 (3)	92 (7)	156 (7)	54 (5)

Table 4. *Observed and calculated structure factors*

The five columns in each group represent h, k, l, |Fo|, Fc.

[Table of observed and calculated structure factors — dense multi-column numerical data, arranged in groups of five columns (h, k, l, |Fo|, Fc).]

Table 4 (cont.)

Description and discussion of the structure

Molecular geometry

Bond distances and angles with estimated standard deviations are given in Tables 5, 6 and 7. In Fig. 1 the indole nuclei are numbered according to international rules; the ethylamine chains, however, are numbered in the most convenient way. The configurations of the two molecules are represented in Fig. 2 with thermal ellipsoids of the non-hydrogen atoms scaled to 33% probability because of the high thermal movements. The hydrogen atoms are represented by spheres having a diameter of 0·2 Å. For comparison, all values below are given for the two molecules of the asymmetric unit labelled *A* and *B*, with the latter in parentheses.

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

	Molecule *A*	Molecule *B*
N(1)–C(2)	1·372 (4) Å	1·371 (5) Å
C(2)–C(3)	1·355 (3)	1·351 (4)
C(3)–C(9)	1·425 (4)	1·421 (4)
C(9)–C(8)	1·403 (4)	1·413 (4)
C(8)–N(1)	1·370 (3)	1·363 (4)
C(9)–C(4)	1·401 (3)	1·400 (4)
C(4)–C(5)	1·356 (6)	1·366 (6)
C(5)–C(6)	1·388 (6)	1·380 (5)
C(6)–C(7)	1·374 (5)	1·376 (6)
C(7)–C(8)	1·393 (5)	1·394 (5)
C(3)—C(10)	1·503 (4)	1·498 (4)
C(10)–C(11)	1·512 (4)	1·522 (2)
C(11)–N(12)	1·464 (4)	1·458 (4)
N(12)–C(13)	1·460 (4)	1·458 (3)
N(12)–C(14)	1·446 (4)	1·453 (5)
N(1)—H(1)	0·92 (3)	0·86 (3)
C(2)—H(2)	0·97 (2)	1·00 (3)
C(4)—H(4)	1·03 (3)	1·03 (3)
C(5)—H(5)	1·05 (2)	1·04 (3)
C(6)—H(6)	0·93 (3)	0·98 (3)
C(7)—H(7)	0·96 (3)	0·98 (3)
C(10)–H(10*A*)	1·07 (2)	1·02 (3)
C(10)–H(10*B*)	1·00 (3)	0·97 (3)
C(11)–H(11*A*)	1·02 (3)	1·05 (3)
C(11)–H(11*B*)	1·00 (2)	1·04 (3)
C(13)–H(13*A*)	1·02 (3)	1·07 (3)
C(13)–H(13*B*)	1·04 (3)	1·01 (3)
C(13)–H(13*C*)	1·04 (3)	1·00 (3)
C(14)–H(14*A*)	1·03 (2)	1·03 (3)
C(14)–H(14*B*)	1·01 (3)	1·02 (3)
C(14)–H(14*C*)	1·07 (3)	0·97 (2)
N(1)···N(12ⁱ)	2·924 (3)	2·885 (3)
H(1)···N(12ⁱ)	2·01 (2)	2·03 (3)

Symmetry code

i $1-x, \frac{1}{2}+y, \frac{1}{2}-z$

The two molecules are almost identical (see Fig. 2). For the non-hydrogen atoms the differences in bond lengths and bond angles do not exceed 0·01 Å and 1·2° respectively. One exception is, however, the C(4)–C(5)–C(6) angle where the difference is 1·6°. In both molecules the C(4)–C(5) bond, 1·356 Å (1·366 Å), is significantly shorter than the standard C–C bond in

Table 6. *Interatomic angles and standard deviations (in parentheses) for all non-hydrogen atoms*

	Molecule *A*	Molecule *B*
N(1)–C(2)–C(3)	110·4 (3)°	110·4 (3)°
C(2)–C(3)–C(9)	106·5 (3)	106·7 (3)
C(3)–C(9)–C(8)	107·1 (3)	106·9 (3)
C(9)–C(8)–N(1)	107·7 (3)	107·4 (3)
C(8)–N(1)–C(2)	108·3 (3)	108·6 (3)
C(4)–C(5)–C(6)	120·4 (5)	122·0 (4)
C(5)–C(6)–C(7)	122·7 (5)	121·5 (4)
C(6)–C(7)–C(8)	116·7 (4)	117·3 (4)
C(7)–C(8)–C(9)	121·5 (3)	121·7 (3)
C(8)–C(9)–C(4)	119·4 (3)	118·9 (3)
C(9)–C(4)–C(5)	119·3 (4)	118·6 (4)
N(1)–C(8)–C(7)	130·7 (3)	130·9 (3)
C(3)–C(9)–C(4)	133·5 (3)	134·1 (3)
C(2)—C(3)—C(10)	126·6 (3)	126·3 (3)
C(9)—C(3)—C(10)	126·9 (3)	127·0 (3)
C(3)—C(10)–C(11)	113·0 (3)	112·0 (3)
C(10)–C(11)–N(12)	111·7 (3)	112·3 (3)
C(11)–N(12)–C(13)	110·0 (3)	110·9 (3)
C(11)–N(12)–C(14)	112·1 (3)	112·3 (3)
C(13)–N(12)–C(14)	109·9 (3)	109·3 (3)
N(1)—H(1) ··· N(12)	173·9	173·4
N(1)···N′(12)—C′(11)	109·8	107·7
N(1)···N′(12)—C′(13)	110·9	103·3
N(1)···N′(12)—C′(14)	104·1	113·1

Table 7. *Interatomic angles and standard deviations (in parentheses) for all bonds involving hydrogen atoms*

	Molecule *A*	Molecule *B*
C(8)–N(1)–H(1)	127 (2)°	125 (2)°
C(2)–N(1)–H(1)	125 (2)	126 (2)
N(1)–C(2)–H(2)	121 (2)	120 (2)
C(3)–C(2)–H(2)	129 (2)	130 (2)
C(5)–C(4)–H(4)	124 (2)	121 (2)
C(9)–C(4)–H(4)	117 (2)	120 (2)
C(4)–C(5)–H(5)	124 (2)	116 (2)
C(6)–C(5)–H(5)	116 (2)	121 (2)
C(5)–C(6)–H(6)	126 (2)	125 (2)
C(7)–C(6)–H(6)	112 (2)	113 (2)
C(6)–C(7)–H(7)	124 (2)	123 (2)
C(8)–C(7)–H(7)	119 (2)	119 (2)
C(3)——C(10)–H(10*A*)	113 (2)	110 (2)
C(3)——C(10)–H(10*B*)	107 (2)	111 (2)
C(11)——C(10)–H(10*A*)	105 (2)	109 (2)
C(11)——C(10)–H(10*B*)	109 (2)	114 (2)
H(10*A*)–C(10)–H(10*B*)	109 (3)	101 (3)
C(10)——C(11)–H(11*A*)	109 (2)	109 (2)
C(10)——C(11)–H(11*B*)	109 (2)	111 (2)
N(12) —C(11)–H(11*A*)	109 (2)	108 (2)
N(12) —C(11)–H(11*B*)	109 (2)	111 (2)
H(11*A*)–C(11)–H(11*B*)	109 (3)	105 (3)
N(12) —C(13)–H(13*A*)	109 (2)	107 (2)
N(12) —C(13)–H(13*B*)	108 (2)	108 (2)
N(12) —C(13)–H(13*C*)	107 (2)	107 (2)
H(13*A*)–C(13)–H(13*B*)	115 (3)	112 (3)
H(13*A*)–C(13)–H(13*C*)	108 (3)	108 (3)
H(13*B*)–C(13)–H(13*C*)	110 (3)	114 (3)
N(12) —C(14)–H(14*A*)	113 (2)	107 (2)
N(12) —C(14)–H(14*B*)	114 (2)	111 (2)
N(12) —C(14)–H(14*C*)	108 (2)	114 (2)
H(14*A*)–C(14)–H(14*B*)	101 (3)	118 (3)
H(14*A*)–C(14)–H(14*C*)	114 (3)	103 (3)
H(14*B*)–C(14)–H(14*C*)	107 (3)	103 (3)

benzene, 1·397 Å, while the average of the other five bond lengths in the benzene portion of the indole nucleus, 1·392 Å (1·393 Å), is equal to the standard bond length.

In the pyrrole ring, the C–N distances C(2)–N(1), 1·372 ± 0·003 Å (1·371 ± 0·005 Å), and C(8)–N(1), 1·370 ± 0·003 Å (1·363 ± 0·004 Å), are equivalent within two standard deviations. They are not significantly shorter than the C–N bond lengths of 5-methoxy-(N,N)-dimethyltryptamine and earlier determined indole nuclei (Falkenberg & Carlström, 1971). The C(2)–C(3) bond, 1·355 Å (1·351 Å) is significantly shorter than the C(3)–C(9) bond, which indicates a stronger double-bond character in the former. This is consistent with the results of earlier work (Falkenberg

& Carlström, 1971) although it is more pronounced in the present structure.

The C(3)–C(10) bond of the ethylamine chain, 1·503 Å (1·498 Å), is somewhat shorter than the C(10)–C(11) bond, 1·512 Å (1·522 Å). Both are significantly shorter than the standard paraffinic single bond, 1·541 Å.

The bond distance between the tertiary amino nitrogen N(12) and the α-carbon atom, C(11), is 1·464 Å (1·458 Å), which is close to the corresponding bond, 1·457 Å, in 5-methoxytryptamine (Quarles, 1971). The mean of all C–N bonds around N(12) in both molecules is 1·457 Å, which is somewhat shorter than the 3-covalent N–C standard bond of 1·472 Å (*Table of Interatomic Distances and Configuration in Molecules*
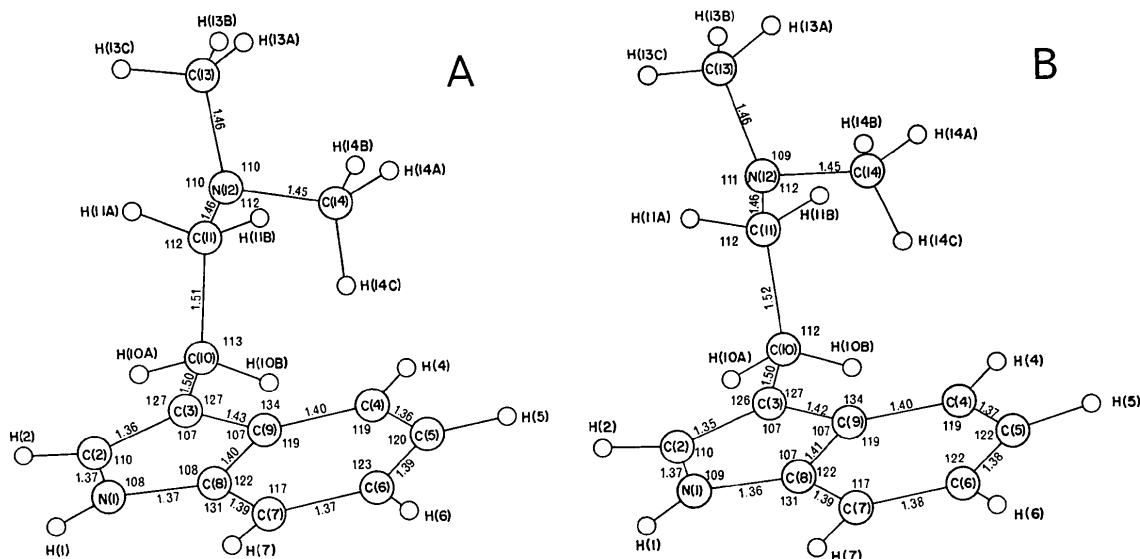
Fig. 1. Atom numbering, bond lengths (Å) and bond angles (°) for non-hydrogen atoms in molecules *A* (left) and *B* (right) of (N,N)-dimethyltryptamine.
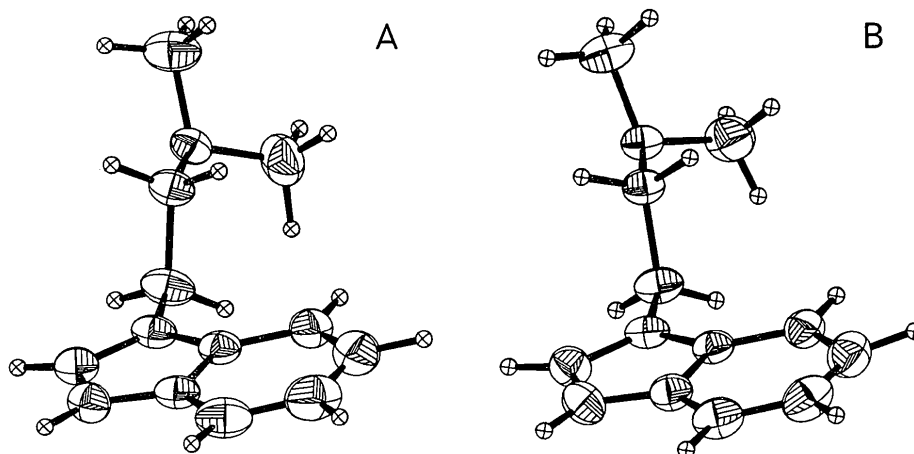
Fig. 2. Molecular conformation of molecules *A* (left) and *B* (right) of (N,N)-dimethyltryptamine. The non-hydrogen atoms are represented by 33 % probability thermal ellipsoids and the hydrogen atoms indicated by small spheres with a radius of 0·1 Å. The drawings were performed using the program *ORTEP* (Johnson, 1970).

and Ions, 1965) and much shorter than the C–N$^+$ bond of 1·505 Å (Hahn, 1957). As might be expected, the amino nitrogen is thus unprotonized. The angles around N(12) are all nearly tetrahedral with a close resemblance to ammonia with a lone electron pair. Identical results were found in chlorpromazine, which also has a dimethylated amino group in the side chain (McDowell, 1969). The indole nuclei of the two DMT molecules are planar within the limits of experimental error. This is shown in Table 8 where the equations of the best planes are also given. Since it has been re-

ported that the benzene and pyrrole rings in some indole derivatives are slightly bent along the C(8)–C(9) bond (Bergman, Abrahamsson & Dahlén, 1971; Falkenberg & Carlström, 1971), the angles between the planes of the two parts of the indole nuclei were also calculated. However, the angles 0·17° (0·91°) do not differ significantly from planarity.

There is considerable interest in the torsion angles of the ethylamine chain in this group of compounds with regard to receptor stereospecificity. The position of the α-carbon atom is described by the torsion angle $\tau_1 =$

Table 8. *Equations of the best planes with the formula* $m_1X + m_2Y + m_3Z = d$ *in orthogonal space*

Plane	m_1	m_2	m_3	d
Molecule A				
Pyrrole ring	−0·470060	0·512232	0·718792	0·91526
Benzene ring	−0·470108	0·514578	0·717083	0·91780
Indole nucleus	−0·469794	0·514006	0·717699	0·91714
Molecule B				
Pyrrole ring	0·863196	0·350919	−0·362972	−1·72598
Benzene ring	0·865552	0·358811	−0·349390	−1·58694
Indole nucleus	0·864780	0·355338	−0·354813	−1·65589

Deviations (in Å) from the best planes.
Distances marked with asterisks refer to atoms defining the plane.

Planes	Pyrrole ring		Benzene ring		Indole nucleus	
Molecule	A	B	A	B	A	B
N(1)	0·0002*	0·0020*	0·0001	−0·0175	0·0019*	0·0002*
C(2)	−0·0015*	−0·0013*	−0·0055	−0·0335	−0·0027*	−0·0102*
C(3)	0·0022*	0·0001*	−0·0028	−0·0200	−0·0001*	−0·0013*
C(4)	0·0019	−0·0230	0·0014*	−0·0020*	0·0021*	0·0001*
C(5)	−0·0019	−0·0395	0·0014*	−0·0003*	0·0008*	−0·0059*
C(6)	−0·0083	−0·0366	−0·0021*	0·0022*	−0·0031*	−0·0037*
C(7)	−0·0055	−0·0216	−0·0000*	−0·0017*	−0·0004*	−0·0001*
C(8)	0·0012*	−0·0019*	0·0028*	−0·0007*	0·0037*	0·0087*
C(9)	−0·0020*	0·0011*	−0·0034*	0·0025*	−0·0020*	0·0123*
C(10)	−0·0137	0·0267	−0·0227	−0·0014	−0·0190	0·0211
C(11)	1·3440	1·4476	1·3337	1·4166	1·3376	1·4405
N(12)	1·2793	1·4887	1·2652	1·4471	1·2699	1·4757

Angles between pyrrole and benzene rings
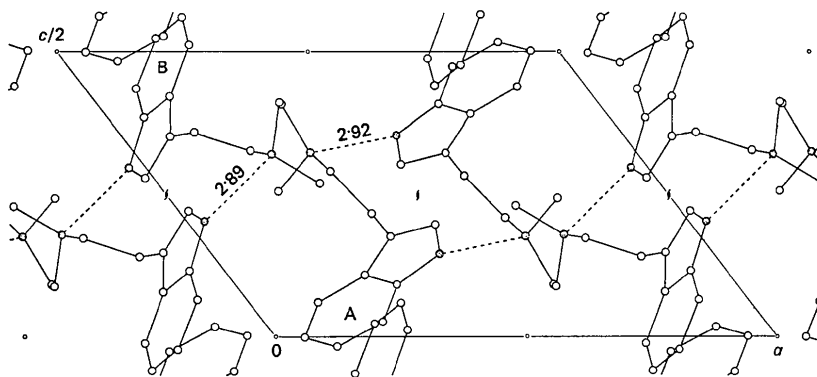
Molecule A 0·17°
Molecule B 0·91

Fig. 3. Molecular packing in DMT viewed along the b axis. Half a unit cell is shown. Carbon and nitrogen atoms are represented by open and dotted circles respectively. Hydrogen bonds are dashed and the distances are given in Å.

C(2)–C(3)–C(10)–C(11), which was found to be 102° (90°). This means that the plane defined by C(3)–C(10)–C(11) is nearly perpendicular to the plane of the indole nucleus. The torsion angle τ_2 = C(3)–C(10)–C(11)–N(12) is 176° (188°), and the amino nitrogen atom is thus as far as possible from the centre of the pyrrole ring (Fig. 2).

Description of the crystal structure

The crystal structure viewed along the *b* axis is shown in Fig. 3. The *A*-molecules are linked together by N(1)–H(1)···N(12) hydrogen bonds which run in a helical fashion around a screw axis. The *B*-molecules are connected by the same type of hydrogen bond in a nearly identical manner and the two hydrogen bonds thus give rise to N–N distances of 2·92 Å and 2·89 Å respectively. In both cases the hydrogen atoms involved lie almost on the straight line between the nitrogen atoms (see Table 6). In both hydrogen bonding systems, the hydrogen bonds form nearly tetrahedral angles with the carbon atoms around the acceptor amino nitrogen atom (Table 6). There are no connexions between the *A*- and *B*-molecules other than ordinary van der Waals contacts, the shortest intermolecular distance being 3·5 Å for non-hydrogen atoms.

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The Crystal and Molecular Structure of an Addition Compound of Cholic Acid and Ethanol

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A 1:1 addition compound of cholic acid and ethanol, $C_{26}H_{46}O_6$, crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The cell constants are $a = 14\cdot661$, $b = 11\cdot759$, and $c = 15\cdot066$ Å. The structure was solved using acentric direct methods. Refinement of the parameters of all nonhydrogen atoms by a full-matrix least-squares procedure reduced the conventional *R* index to 0·113. The carbon atoms in the rings were assigned isotropic temperature factors; all carbon and oxygen atoms not in the rings were assigned anisotropic temperature factors. A hydrogen bonding scheme has been formulated which involves three molecules of cholic acid around one ethanol with five hydrogen bonds being formed.

Introduction

The bile acids are physiologically important steroids. We have carried out a single-crystal structural analysis of an addition compound of cholic acid and ethanol, $C_{26}H_{46}O_6$, which takes the form of a one to one complex. The purpose of this study was to elucidate any unusual structural features of the molecule which

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