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The Crystal and Molecular Structure of *N*-Acetyl-5-methoxy-tryptamine (Melatonin)

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The structure of melatonin has been determined by X-ray methods using 2543 observed reflections collected by counter methods. The crystals are monoclinic, space group $P2_1/c$, with unit cell dimensions $a = 7.71_4$ Å; $b = 9.27_6$ Å; $c = 17.11_8$ Å and $\beta = 96.9_1$°. The refinements yielded a conventional R-factor of 5 %; standard deviations in bond lengths and in angles not involving hydrogen atoms are 0.002 Å and 0.1°, respectively. The molecular geometry and the hydrogen bond system in the crystal is discussed. The molecule has also been studied by X-ray methods by Quarles [1] and by Wakahara, Fujiwara and Tomita.[2]

As a part of a series of structure investigations of tyrosine and tryptophan derivatives the crystal and molecular structure of *N*-acetyl-5-methoxytryptamine (melatonin) has been determined. The compound occurs naturally in mammals and its biological activity is believed to involve changes in certain neurones in the central nervous system. Bioactive monoamines, which includes melatonin, have in the recent years received increased interest and much work has been devoted to reach information useful for an explanation of the relation between structure and biological activity. We have studied the melatonin molecule in order to obtain data relevant in this discussion, for the study of the conformation of such compounds in the crystalline phase and for the comparison with several theoretical calculations made on analogous molecules. During the refinement of the structure model we became aware of studies of the same molecule by Quarles [1] and also by Wakahara *et al.*[2] However, even if the present determination yields the same general structural information it is based on more than twice of their number of data, and less than half of their standard deviations in bond lengths were obtained.

EXPERIMENTAL

Large prismatic crystals of melatonin were formed by slow evaporation of an ethanolic solution at room temperature. A preliminary study showed the crystals to be monoclinic, space group $P2_1/c$.

The intensity data were recorded on an automatic Picker diffractometer using graphite crystal monochromated MoK-radiation. The specimen was cut from a large crystal to the dimensions $0.3 \times 0.3 \times 0.3$ mm^3 and was mounted on a glass fibre with the crystallographic a-axis along the ϕ-axis. The $\omega - 2\theta$ scanning mode was employed with a 2θ scan speed of 2° min^{-1} through a scan range from 0.5° below $2\theta(\alpha_1)$ to 0.5° above $2\theta(\alpha_2)$. Background counts were taken for 10 s at each of the scan range limits. The intensities of three standard reflections measured for every 150 reflections of the data set showed slow changes of up to 10 % and the intensity data were accordingly adjusted. The estimate of the standard deviations of the measurements was based on counting statistics with an additional term of 2 % of the intensity. Out of 3306 unique reflections with $\sin \theta/\lambda$ less than 0.7, 2543 reflections were found to have intensities larger than twice their standard deviation and were regarded as observed. The remaining reflections were excluded from the refinement procedure.

The intensity data were corrected for Lorentz and polarization effects. Atomic scattering factors used during the calculations (for computer programs *cf.* Ref. 3) were those of Hansen *et al.*[4] for oxygen, nitrogen, and carbon, and of Stewart *et al.*[5] for hydrogen. Unit cell dimensions were calculated from diffractometer measurements on 17 general reflections.

Table 1. Observed and calculated structure factors. The columns are h, k, l, $10F_o$, and $10|F_c|$.

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0	0	4	250	-	231
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0	0	8	289		259
0	0	10	167	-	158
0	0	12	291	-	288
0	0	14	97		92
0	0	16	287		299
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0	1	19	45	-	41
0	1	17	23		20
0	1	16	57	-	64
0	1	15	173	-	173
0	1	14	86		87
0	1	13	36		37
0	1	12	53	-	54
0	1	11	133	-	123
0	1	10	93	-	97
0	1	9	113		109
0	1	8	423		376
0	1	7	173		160
0	1	6	69		61
0	1	5	95	-	90
0	1	4	224	-	214
0	1	3	251		250
0	1	2	275	-	249
0	1	1	457	-	459
0	2	0	939	-	924
0	2	1	423	-	398
0	2	2	333	-	297
0	2	3	341		362
0	2	4	691		651
0	2	5	114	-	111
0	2	6	377	-	334
0	2	7	3	-	36
0	2	8	325	-	294
0	2	9	121	-	114
0	2	10	103	-	102
0	2	11	106		106
0	2	12	135		130
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0	2	14	83	-	83
0	2	15	33	-	35
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0	2	20	55		50
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0	3	19	65	-	57
0	3	18	43	-	44
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0	3	15	70	-	76
0	3	14	93	-	87
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0	3	10	63		62
0	3	9	153		148
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0	4	1	263		252
0	4	2	269	-	237
0	4	3	9	-	2
0	4	5	193	-	182
0	4	6	155		144
0	4	7	134		133
0	4	8	83		86
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0	4	17	35		34
0	4	18	15		19
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0	5	16	16		16
0	5	15	51		57
0	5	14	123		171
0	5	13	141	-	145
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0	5	11	236	-	242
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0	5	9	142		138
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1	1	7	137	-	125
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1	0	-18	37	-	33
2	0	-18	101	-	111
2	0	-16	151	-	151
2	0	-14	144		146
2	0	-12	70	-	71
2	0	-10	261		254
2	0	-8	121		111
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2	5	-19	21	-16
2	5	-20	43	36
7	6	-3	21	20
7	5	-10	40	41
7	4	-11	35	31

CRYSTAL DATA

Melatonin (N-acetyl-5-methoxytryptamin) $C_{13}H_{16}N_2O_2$, monoclinic. $a=7.714(0.002)$ Å; $b=9.276(0.002)$ Å; $c=17.118$ (0.004) Å; $\beta=96.91$ (0.03). $V=1214$ Å^3; $M=232.28$; $F(000)=496$; $Z=4$; $D_{\text{calc}}=1.27$ gcm^{-3}. Absent reflections: ($h0l$) for l odd, ($0k0$) for k odd; space group $P2_1/c$.

STRUCTURE DETERMINATION

The structure was determined by the application of the symbolic addition procedure and

Table 2. Fractional atomic coordinates and thermal parameters with standard deviations ($\times 10^5$) for non-hydrogen atoms.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O5	6647(16)	−25333(11)	37530(7)	2729(27)	1008(13)	460(5)	−879(30)	−29(19)	−283(13)
O13	61358(14)	48624(10)	73724(5)	2794(25)	701(10)	316(4)	−462(26)	312(16)	−26(11)
N1	27247(16)	31323(12)	37572(6)	2030(25)	909(14)	296(5)	−31(30)	148(17)	−264(13)
N12	50897(16)	26613(11)	70553(6)	2206(26)	630(12)	240(4)	−183(28)	118(16)	33(11)
C2	33649(19)	33006(14)	45301(8)	1766(27)	784(15)	317(5)	−61(33)	210(19)	41(15)
C3	31897(17)	20627(13)	49447(7)	1455(24)	753(15)	255(5)	30(32)	127(17)	23(14)
C4	18833(18)	−4044(14)	44452(7)	1530(25)	838(15)	255(5)	30(32)	127(17)	23(14)
C5	11844(18)	−11065(15)	37747(8)	1562(26)	916(16)	340(6)	−86(34)	123(19)	−174(15)
C6	9623(20)	−4022(17)	30442(8)	1790(29)	1299(21)	288(5)	51(40)	−80(20)	−278(17)
C7	14300(19)	10096(17)	29723(8)	1783(28)	1364(21)	225(5)	363(40)	46(19)	134(16)
C8	21407(17)	17329(14)	36436(7)	1378(23)	890(15)	262(5)	264(31)	185(16)	107(14)
C9	23855(16)	10404(13)	43808(7)	1271(22)	812(14)	232(5)	138(29)	184(16)	−11(13)
C10	37056(18)	17623(14)	58001(7)	1692(26)	778(15)	253(5)	−106(33)	139(17)	−2(14)
C11	43736(21)	30646(14)	62666(7)	2366(32)	759(15)	240(5)	−107(36)	96(20)	27(14)
C13	59679(18)	35796(13)	75510(7)	1703(26)	727(14)	253(5)	−45(32)	343(18)	−62(13)
C14	67334(22)	30028(16)	83307(8)	2214(32)	1015(18)	289(5)	−297(39)	8(21)	33(16)
C15	8773(24)	−33064(17)	44714(11)	2300(35)	866(18)	577(9)	−177(42)	279(28)	70(20)

Sayre's equation and refined by Fourier- and full-matrix least-squares methods. Final refinements included individual isotropic thermal parameters for hydrogen atoms and anisotropic temperature factors expressed by $\exp-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$ for the other atoms in addition to all positional parameters. The final conventional R-factor is 0.052.

The observed and calculated structure factors are listed in Table 1; positional and thermal parameters of non-hydrogen atoms are listed in Table 2 and those of hydrogen atoms in Table 3. Bond lengths and angles are tabulated in Table 4; estimated standard deviations were calculated from the correlation matrix. An analysis of the rigid body vibrations of the indol nucleus was carried out and the bond lengths corrected for thermal librations are given in Table 4.

Table 3. Fractional atomic coordinates ($\times 10^3$) with standard deviations and thermal parameters for hydrogen atoms.

	x	y	z	B
HN1	282(2)	378(2)	338(1)	4.1 (0.3)
HC2	376(2)	429(2)	472(1)	3.6 (0.3)
HC4	204(2)	−84(2)	494(1)	4.1 (0.3)
HC6	45(2)	−92(2)	259(1)	4.3 (0.4)
HC7	124(2)	145(2)	249(1)	3.2 (0.3)
H110	269(2)	137(2)	605(1)	3.4 (0.3)
H210	461(2)	103(2)	587(1)	3.8 (0.3)
H111	348(2)	379(2)	629(1)	4.4 (0.4)
H211	532(2)	349(2)	601(1)	4.2 (0.3)
H115	18(3)	−285(2)	489(1)	6.5 (0.5)
H215	46(3)	−425(2)	432(1)	6.8 (0.5)
H315	207(2)	−333(2)	471(1)	4.7 (0.4)
HN12	502(2)	178(2)	720(1)	3.0 (0.3)
H114	680(3)	200(2)	835(1)	6.2 (0.5)
H214	613(2)	340(2)	873(1)	5.3 (0.4)
H314	788(3)	338(3)	845(1)	7.4 (0.5)

DESCRIPTION OF THE STRUCTURE

The structure of the melatonine molecule as found in the present determination is shown in Fig. 1. The bond lengths and angles in the indole-ethylamine part of the molecule is in very good agreement with those given by Falkenberg[6] as the averaged structure based on several precise structure analyses of compounds containing this group. In the indole nucleus there are consistent and systematic variations in the bond lengths and angles indicating a reduced aromatic character; the same variations are also found in the theoretically calculated structure.[7] The C11−N12 bond length of 1.445 Å may be considered normal for a $C(sp^3)-N(sp^2)$ distance and the N-acetyl group shows dimensions typical for a peptide.

The methoxy group is close to the plane of the indole moiety and the conformation about the O5−C15 bond is strictly staggered. It is

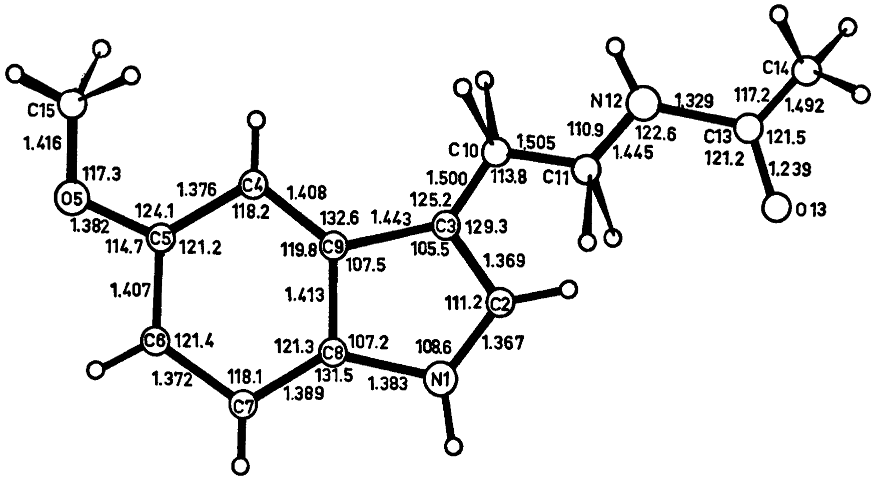

Fig. 1. Conformation of the melatonin molecule. Corrected bond lengths (Å) and angles (°) are indicated.

interesting to note that the external angles at C5 differ in a way (C4 – C5 – O5 = 124.1°, ∠C6 – C5 – O5 = 114.7) corresponding to that found at the OH group in phenols in which the H-atom is situated in the plane of the aromatic ring. The opening of the angles C15 – O5 – C5, O5 – C5 – C4 and also of C5 – C4 – HC4 relative to their standard values indicate a steric strain; nevertheless the arrangement of the atoms involved is planar, the dihedral angle C4 – C5 – O5 – C15 is 0° within the accuracy of determination.

The six- and five-membered rings are each strictly planar, the deviations from the corre-

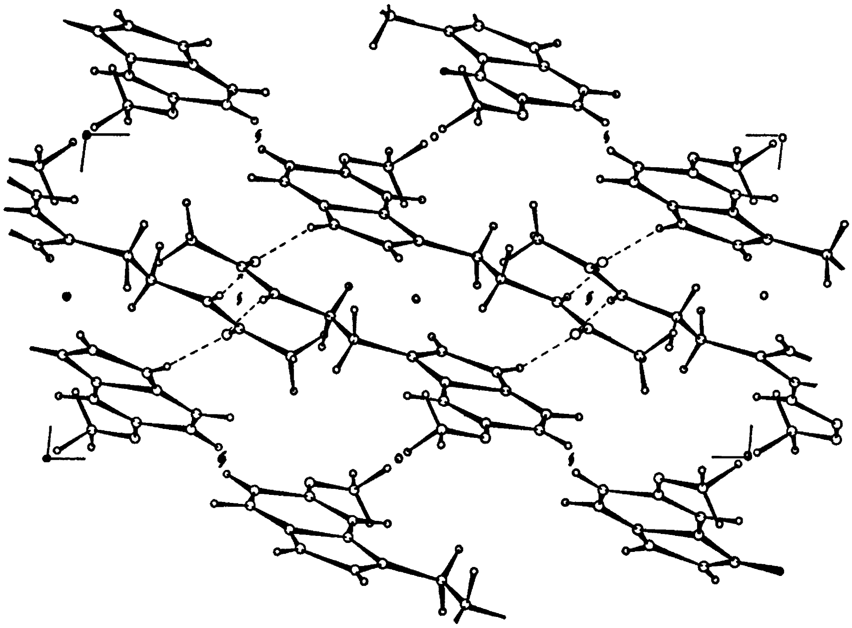

Fig. 2. The crystal structure of melatonin as viewed along the *b* axis.

Table 4. Interatomic distances (Å) and bond angles (°) with estimated standard deviations. For the indole part bond lengths corrected for rigid-body librations are given in parentheses. Standard deviations are 0.002 Å in bonds and 0.1° in angles between heavy atoms, 0.02 Å and 1.0°, respectively, if one hydrogen atom is involved.

Distances

N1–C2	1.365	(1.367)	C15–H115	1.03
C2–C3	1.365	(1.369)	C15–H215	0.95
C3–C9	1.440	(1.443)	C15–H315	0.96
C9–C4	1.403	(1.408)	C2–HC2	1.01
C4–C5	1.373	(1.376)	C4–HC4	0.96
C5–C6	1.403	(1.407)	C6–HC6	0.96
C6–C7	1.368	(1.372)	C7–HC7	0.91
C7–C8	1.386	(1.389)	C10–H110	1.01
C8–C9	1.408	(1.413)	C10–H210	0.97
C8–N1	1.380	(1.383)	C11–H111	0.97
C3–C10	1.497	(1.500)	C11–H211	0.98
C5–O5	1.382		C14–H114	0.93
O5–C15	1.416		C14–H214	0.94
C10–C11	1.505		C14–H314	0.95
C11–N12	1.445		N1–HN1	0.90
N12–C13	1.329		N12–HN12	0.85
C13–O13	1.239			
C13–C14	1.492			

N1 ···O13	(1 – *x*,1 – *y*,1 – *z*)	2.895	N12–O13	(1 – *x*,*y* – ½,3/2 – *z*)	2.969
HN1···O13	(1 – *x*,1 – *y*,1 – *z*)	2.03	HN12–O13	(1 – *x*,*y* – ½,3/2 – *z*)	2.19

Angles

N1–C2–C3	111.2	C5–C4–HC4	123
C2–C3–C9	105.5	C6–C7–HC7	120
C3–C9–C8	107.5	C7–C6–HC6	119
C9–C8–N1	107.2	C8–C7–HC7	122
C8–N1–C2	108.6	C9–C4–HC4	117
C3–C9–C4	132.6	C8–N1–HN1	126
C9–C4–C5	118.2	C2–N1–HN1	125
C4–C5–C6	121.2	N1–C2–HC2	118
C5–C6–C7	121.3	C3–C2–HC2	130
C6–C7–C8	118.1	C3–C10–H110	111
C7–C8–C9	121.3	C3–C10–H210	111
C8–C9–C4	119.8	H110–C110–H210	106
C7–C8–N1	131.5	C11–C10–H110	108
C4–C5–O5	124.1	C11–C10–H210	108
C6–C5–O5	114.7	C10–C11–H111	112
C5–O5–C15	117.3	C10–C11–H211	108
C2–C3–C10	129.3	H111–C11–H211	108
C9–C3–C10	125.2	N12–CH–H111	110
C3–C10–C11	113.8	N12–C11–H211	108
C10–C11–N12	110.9	C11–N12–HN12	119
C11–N12–C13	122.6	C13–N12–HN12	119
N12–C13–O13	121.3	C13–C14–H114	113
N12–C13–C14	117.2	C13–C14–H214	110
C14–C13–O13	121.5	C13–C14–H314	111
O5–C15–H115	120	H114–C14–H314	109
O5–C15–H215	103	H114–C14–H214	113
O5–C15–H315	112	H214–C14–H314	103
H115–C15–H215	112		
H115–C15–H315	113		
C5–C6–HC6	119		

sponding least-squares planes being less than 0.01 Å; the angle between the two planes is 1.4°. The non-hydrogen atoms of the longer side-chain are also roughly co-planar; a plane through these atoms does not quite coincide with the pyrrole-plane, however, the dihedral angle C2 – C3 – C10 – C11 being 5.5°.

The molecular arrangement in the crystal and the hydrogen bond system is illustrated in Fig. 2. Two hydrogen donors, N1 and N12, each with one hydrogen atom are available for hydrogen bond formation. There are also two potential acceptor atoms, but O13 is the acceptor for two hydrogen bonds and O5 for none. Each molecule is hydrogen bonded to three neighbouring molecules. The structure may be described as centrosymmetric hydrogen bonded dimers which are again hydrogen bonded to four neighbouring dimers forming helices along a set of screw axes. In this way the crystal consists of layers of hydrogen bonded molecules parallel to the $b-c$ plane. Between these layers there are only weak van der Waals interactions.

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