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3-(9-Adenyl)propionyltryptamine Monohydrate

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Abstract. $C_{18}H_{19}N_7O.H_2O$, FW 367·41, triclinic, $P\bar{1}$, $a = 9{\cdot}289$ (2), $b = 20{\cdot}013$ (3), $c = 5{\cdot}018$ (1) Å, $\alpha = 96{\cdot}81$ (1), $\beta = 96{\cdot}22$ (2), $\gamma = 78{\cdot}08$ (2)°, $Z = 2$, $D_x = 1{\cdot}351$, $D_m = 1{\cdot}350$ g cm^{-3}, μ(Mo $K\alpha$) = 1·01 cm^{-1}. The structure was solved by the direct method using diffractometer data and was refined by a block-diagonal least-squares method. The final R value was 0·137 for 2493 reflexions. The molecule is fully extended. Two adenine bases, related by a centre of symmetry, are paired through two N(6)H···N(1) hydrogen bonds. The adenine moiety links to the indole in a different molecule through an N(3)···HN(indole) hydrogen bond. This mode of interaction is the same as that found in the 9-ethyladenine–indole complex, implying that a typical interaction mode between adenine and tryptophane is present.

Introduction. The interaction between adenine and aromatic amino acids has been studied in connexion with biological processes (Montenay-Garestier & Hélène, 1971; Hélène, Dimicoli & Brun, 1971; Brun, Toulmé & Hélène, 1975; Morita, 1967, 1974). In order to establish the structural chemistry of the elementary patterns of such interactions, the title compound was synthesized from 9-β-carboxyethyladenine (Kondo, Miyata & Takemoto, 1971) and tryptamine by the dicyclohexylcarbodiimide method, and the structure of a crystal of the monohydrate was determined by X-ray analysis.

Prismatic crystals were obtained from an aqueous solution. The crystal density was measured by flotation in a mixture of cyclohexane and carbon tetrachloride. A crystal 0·07 × 0·15 × 0·40 mm was used for data collection on a Rigaku four-circle automated diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The unit-cell dimensions were determined by least-squares calculations with the 2θ values of 22 high-angle reflexions, measured on the diffractometer. Intensities of 3141 independent reflexions (up to 50° in 2θ) were obtained, of which 1007 were zero-reflexions. The normalized structure factors were derived and their distribution was found to be centric; hence the space group was $P\bar{1}$.

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966). The atomic parameters were refined by a block-diagonal least-squares method; the quantity minimized was $\Sigma\, w(|F_o| - |F_c|)^2$, with $w = 1/(\sigma_p^2 + qF_o^2)$, where σ_p is due to counting statistics and q is $1{\cdot}25 \times 10^{-5}$ (derived from the intensity variances of the monitored reflexions). In

Table 1. *Final positional parameters (heavy atoms* $\times 10^4$, *hydrogen and disordered atoms* $\times 10^3$), *with their standard deviations in parentheses*

	x	*y*	*z*
N(1)	5693 (6)	4245 (3)	1722 (11)
C(2)	6697 (8)	3693 (4)	2344 (15)
N(3)	6625 (6)	3220 (3)	3948 (11)
C(4)	5321 (7)	3368 (3)	5051 (13)
C(5)	4175 (7)	3920 (3)	4630 (13)
C(6)	4383 (7)	4379 (3)	2836 (13)
N(6)	3379 (6)	4929 (3)	2198 (12)
N(7)	3013 (6)	3904 (3)	6122 (12)
C(8)	3474 (8)	3356 (4)	7403 (14)
N(9)	4861 (6)	3006 (3)	6834 (11)
C(9)	5656 (8)	2348 (4)	7793 (15)
C(10)	5256 (8)	1750 (3)	6011 (14)
C(11)	6100 (8)	1053 (4)	6963 (16)
O(1)	6317 (7)	977 (3)	9378 (10)
N(10)	6536 (8)	594 (3)	4997 (12)
C(14)	9064 (9)	−1117 (4)	3852 (16)
C(15)	10194 (9)	−1327 (4)	5739 (17)
N(11)	10772 (6)	−2027 (3)	5150 (12)
C(16)	10002 (7)	−2275 (4)	2903 (14)
C(17)	8918 (8)	−1702 (4)	2028 (15)
C(18)	7993 (9)	−1805 (4)	−296 (16)
C(19)	8192 (9)	−2462 (5)	−1661 (16)
C(20)	9258 (8)	−3033 (4)	−790 (15)
C(21)	10161 (8)	−2922 (4)	1521 (15)
O(2)	10119 (7)	4686 (3)	7354 (13)
C(12*A*)	769 (1)	−4 (1)	595 (3)
C(12*B*)	706 (1)	−18 (1)	524 (3)
C(13*A*)	849 (2)	−30 (1)	412 (3)
C(13*B*)	790 (1)	−47 (1)	314 (3)
H(2)	757 (6)	370 (3)	164 (11)
H(61)	353 (7)	519 (3)	117 (12)
H(62)	230 (8)	504 (4)	283 (14)
H(8)	292 (7)	323 (3)	886 (13)
H(91)	542 (6)	231 (3)	933 (10)
H(92)	687 (6)	230 (3)	781 (11)
H(101)	532 (7)	168 (3)	417 (14)
H(102)	409 (8)	159 (4)	594 (15)
H(15)	1055 (7)	−100 (3)	734 (13)
H(11)	1153 (7)	−227 (3)	610 (13)
H(18)	721 (7)	−142 (3)	−96 (13)
H(19)	772 (7)	−250 (3)	−301 (13)
H(20)	935 (7)	−350 (3)	−182 (13)
H(21)	1080 (7)	−337 (3)	226 (13)

the present refinement, the zero-reflexions were included by assuming $|F_o| = F_{\text{lim}}$ and $w = w(F_{\text{lim}})$, where F_{lim} is 1·97, an observational threshold value. However, the zero-reflexions for which $|F_c| < F_{\text{lim}}$ were omitted. When the R value reached 0·12 a difference synthesis revealed the H atoms, except for those of C(12), C(13) and the water molecule. C(12) and C(13) appeared to have large anisotropic thermal ellipsoids, and relevant bond lengths were unreasonable. These atoms were therefore assumed to occupy A and B sites with half weight and were refined with isotropic temperature factors. The final R value was 0·137 (R = 0·109 for $F_o \geq 3/\sqrt{w}$).* Atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962). The positional parameters are given in Table 1.

Discussion. Bond lengths and angles are shown in Fig. 1 (their standard deviations are 0·01 Å and 0·6° – those involving disordered atoms are about twice these values). The dimensions of the adenine ring agree with those found in related compounds. N(10)–C(12) is abnormally long, but N(10)–C(12*A*) and N(10)–C(12*B*) are 1·562 and 1·545 Å respectively. The bond lengths and angles of the indole ring are somewhat different from the usual values. These differences may be attributed to the slight disorder of the ring accompanied by the two alternative arrangements of the methylene bridge. The molecule is fully extended; the torsions around the C(9)–C(10) and C(12)–C(13) bonds correspond to a staggered arrangement.

The crystal structure viewed along **a** is given in Fig. 2, and the hydrogen-bond lengths are listed in Table 2. The extended molecule lies nearly along $[1\bar{1}0]$, and is bound to the molecules in the next cells along **c** through an N(10)H···O(1) hydrogen bond between

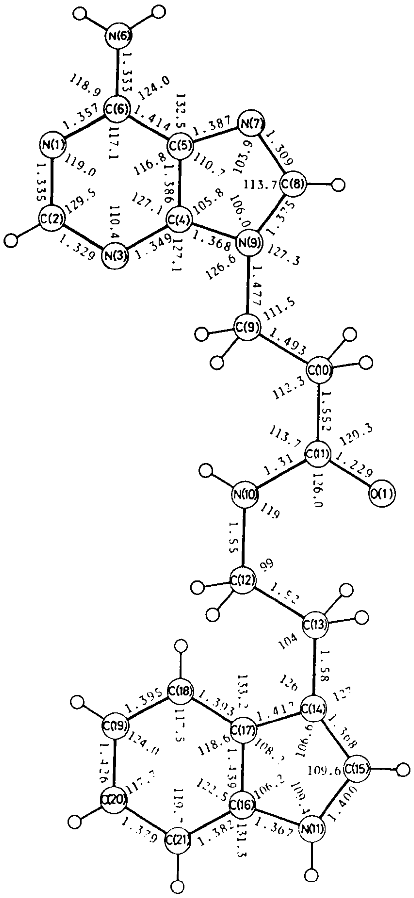

Fig. 1. Bond lengths (Å) and angles (°). Average values are given for the disordered part.

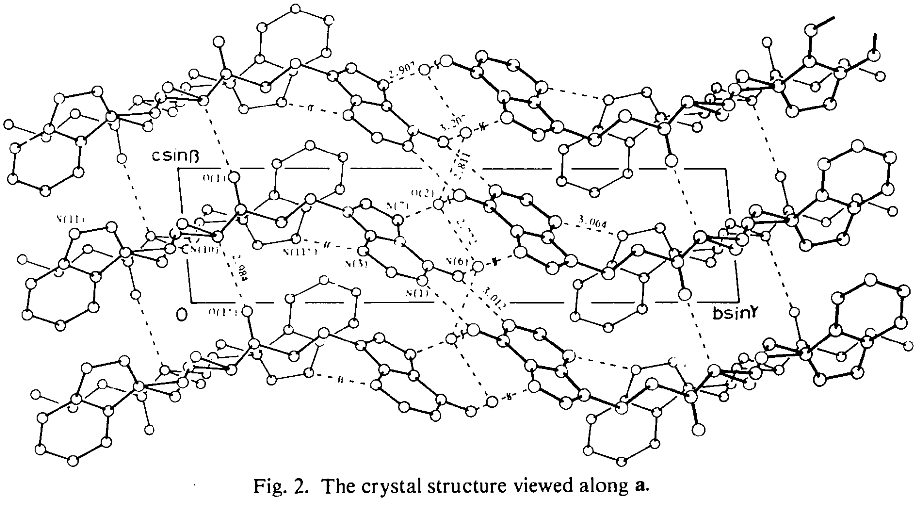

Fig. 2. The crystal structure viewed along **a**.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32725 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Hydrogen-bond distances*

O(2)···N(7)^{i}	2·907 Å	N(10)···O(1)^{ii}	2·984 Å
N(6)···N(1)^{iii}	3·012	N(6)···O(2)^{iv}	3·207
O(2)···O(2)^{iv}	2·772	O(2)···O(2)^{v}	2·811
N(11)···N(3)^{vi}	3·064		

Symmetry code

(i) x, y, z
(ii) $x, y, -1 + z$
(iii) $1 - x, 1 - y, -z$
(iv) $-x, 1 - y, 1 - z$
(v) $-x, 1 - y, 2 - z$
(vi) $2 - x, -y, 1 - z$

the amide groups. The water molecule O(2) forms hydrogen bonds with two water molecules, each O···O line passing through the centre of symmetry. Therefore, there must be disorder about one H atom of the water molecule which was not observed in the difference map. The other water H atom is donated to N(7) of adenine. At the same time, O(2) accepts an H atom from the amino group of adenine. Two adenine bases, related by the centre of symmetry at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, are paired by two N(6)H···N(1) hydrogen bonds. This type of hydrogen bonding is typical for crystals of adenine derivatives.

Furthermore, N(3) of adenine is hydrogen-bonded with N(11) of the indole. This mode of interaction is the same as that found in the 9-ethyladenine–indole complex (Kaneda & Tanaka, 1976). It may be suggested that the N(3)···HN(indole) hydrogen bond is one of the typical interaction modes between adenine and tryptophane moieties. On the other hand, the intermolecular stacking presumed from spectroscopic studies (Brun, Toulmé & Hélène, 1975; Morita, 1974) is not observed in the present crystal.

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3-(9-Adenyl)propionyltyramine Dihydrate

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Abstract. $C_{16}H_{18}N_6O_2.2H_2O$, FW 362·39, monoclinic, $P2_1/c$, a = 13·303 (4), b = 10·819 (5), c = 12·856 (3) Å, β = 107·57 (2)°, Z = 4, D_x = 1·364, D_m = 1·361 g cm^{-3}, μ(Mo $K\alpha$) = 1·09 cm^{-1}. The structure was solved by the direct method using diffractometer data and was refined by a block-diagonal least-squares method. The final R value was 0·062 for 3642 reflexions. The molecule is fully extended. The adenine rings are related by a centre-of-symmetry overlap at a spacing of 3·35 Å. Water molecules participate in all the hydrogen bonds, except for N(6)H···N(3) between adenines.

Introduction. As part of a study of the elementary patterns of interaction between amino acids and purine–pyrimidine bases, the title compound was synthesized from 9-β-carboxyethyladenine (Kondo, Miyata & Takemoto, 1971) and tyramine by the dicyclohexylcarbodiimide method, and the structure of a crystal of the hydrate was determined by X-ray analysis.

Prismatic crystals were grown from a methanol–water solution. The crystal density was measured by flotation in a mixture of cyclohexane and carbon tetrachloride. Weissenberg photographs showed systematic absences, $h0l$, $l = 2n + 1$ and $00l$, $l = 2n + 1$, indicating the space group $P2_1/c$. The precise unit-cell dimensions and the intensities of the reflexions were measured on a Rigaku four-circle automated diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ =