Bond angles within the ring of (I) are increased from 120° at C and decreased at N but not to the same degree as in (VI), where the mean C—N—C and N—C—N angles are 127·3 (5) and 112·7 (5)° respectively.

Steric hindrance between methyl groups is relieved by a small movement (up to ±0·2 Å) out of the plane of the heterocycle,* but not by the obvious mechanism of a concerted series of twists about exocyclic C—N bonds. There is indeed a twist about C(2)—N(4) which depresses C(6) and elevates C(7) relative to the plane, but the entire dimethylamino group attached to C(1) is elevated whilst the entire group at C(3) is depressed. The sum of the bond angles at each of the dimethylamino N atoms is very close to 360°, suggesting that sp^2 hybridization of N occurs. Furthermore, efficient π overlap with the ring is encouraged by the lack of twisting.

The ions and solvent molecules are held together in the unit cell (Fig. 2) by hydrogen bonding and stacking. The Cl^- ion accepts hydrogen bonds from two symmetry-related O(2) water molecules and one O(3) water molecule with O···Cl distances of 3·227 (5), 3·148 (5), and 3·264 (5) Å. The remaining water hydrogen atom, H(31), forms a hydrogen bond to the other water O atom with O···O = 2·867 (6) Å. The heterocyclic cations are formed into stacks in the **a** direction by the action of centres of symmetry. This packing mode enables dimethylamino groups on successive molecules within the stack to interleave (Fig. 2). The closest interaction is between C(1) and N(1) of adjacent rings at 3·398 (6) Å.

* See previous footnote.

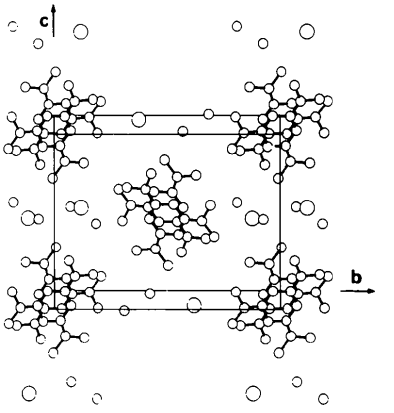

Fig. 2. *PLUTO* (Motherwell, 1972) drawing of the unit-cell contents viewed down **a**.

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Elementary Patterns in Protein–Nucleic Acid Interactions. VII. Structure of *N*-[3-(9-Adeninyl)propionyl]-DL-tryptophan Ethyl Ester, $C_{21}H_{23}N_7O_3$*

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Abstract. $M_r = 421·46$, triclinic, $P\bar{1}$, $a = 7·734$ (2), $b = 22·40$ (1), $c = 6·798$ (3) Å, $\alpha = 112·79$ (3), $\beta = 104·10$ (4), $\gamma = 88·69$ (4)°, $V = 1049·7$ Å^3, $D_m = 1·32$, $D_x = 1·333$ Mg m^{-3}, $Z = 2$, λ(Cu $K\alpha$) = 1·54184 Å; $R = 0·11$ for 1762 diffractometer-measured intensities. The molecule is extended so that there is no intramolecular stacking between the adenine and indole moieties. However, the adenine moieties related by the inversion are stacked with respect to each other, and the indolyl and ethyl groups are piled up alternately along

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the *a* axis by van der Waals contacts. The adenine N(1) atom is an acceptor of a hydrogen bond from the secondary amide NH of the peptide bond in the neighboring molecule, the N···N distance being 2·942 (8) Å.

Introduction. Stacking interactions between aromatic residues of proteins and nucleic acid bases have been postulated from spectroscopic studies in solution (Hélène & Lancelot, 1982). In model crystals that contain the adenine and indole moieties, however, hydrogen bonds are predominant and no significant stacking has been reported (Kaneda & Tanaka, 1976; Ohki, Takenaka, Shimanouchi & Sasada, 1977*a*,*b*; Bunick & Voet, 1982). Recently, stacking has been reported for the N(1)-methylated adenine derivative (Ishida, Usami, Inoue, Yamagata & Tomita, 1982). For further examination, a new model compound, *N*-[3-(9-adeninyl)propionyl]-DL-tryptophan ethyl ester, was prepared and its crystal structure has been determined by X-ray analysis.

Experimental. The title compound was synthesized by the dicyclohexylcarbodiimide method from 3-(9-adeninyl)propionic acid (prepared by the method reported by Kondo, Miyata & Takemoto, 1971) and DL-tryptophan ethyl ester (purchased from Tokyo Kasei Co.); plate crystals (from an ethanol solution), 0·2 × 0·2 × 0·015 mm, D_m by flotation in a mixture of cyclohexane and carbon tetrachloride; Rigaku automated four-circle diffractometer, Ni-filtered Cu $K\alpha$ radiation; unit-cell dimensions determined by least squares with the 2θ values of 34 high-angle reflexions; intensity data in the range $5° < 2\theta < 120°$ collected by means of ω scanning with a scan speed of 2° min^{-1} and with a scan width of 1·5°; five reference reflexions monitored periodically showed no significant deterioration; no absorption correction; 3097 measured independent reflexions, 1204 with no net intensities; observational threshold value $F_{\lim} = 3{\cdot}97$, standard deviations estimated by $\sigma^2(F_o) = \sigma_p^2(F_o) + qF_o^2$ with $\sigma_p(F_o)$ evaluated from counting statistics and q ($1{\cdot}31 \times 10^{-5}$) from variations of the monitored reflexions (McCandlish & Stout, 1975); the distribution of E's showed centrosymmetry, space group $P\bar{1}$; the structure solved by direct methods, anisotropic block-diagonal least squares, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$; all H atoms were included in the structure factor calculations; zero reflexions with $|F_c| > F_{\lim}$ included in least-squares calculation by assuming $F_o = F_{\lim}$ and $w = \sigma(F_{\lim})$; final $R = 0{\cdot}11$ ($R_w = 0{\cdot}040$) for 1762 measured reflexions [$F_o > 3\sigma(F_o)$], maximum shift of parameters in the last cycle $0{\cdot}1\sigma$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); $F(000) = 444$; programs used were *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and *XSEN* (Takenaka & Sasada, 1980).

Discussion. Atomic parameters are listed in Table 1.* The molecular structure is shown in Fig. 1. The bond distances and angles are in agreement with those found in 3-(9-adeninyl)propionamide (Takimoto, Takenaka & Sasada, 1981), 3-(9-adeninyl)propionamide : 1-methylthymine (1:1) complex dihydrate (Takimoto, Takenaka & Sasada, 1982), 3-(7-adeninyl)-propionamide monohydrate (Takimoto, Takenaka & Sasada, 1983), L-tryptophan hydrochloride (Takigawa, Ashida, Sasada & Kakudo, 1966) and DL-tryptophan ethyl ester hydrochloride (Vijayalakshmi & Srinivasan, 1975). The molecule is extended so that there is no intramolecular stacking between the two rings; the torsion angles being given in Fig. 1. The C^{β}—C^{γ} [C(10′)—C(3′)] bond lies *trans* to the C^{α}—COO^- bond and *gauche* to the C^{α}—NH bond, which is similar to one of the two possible conformations for tryptophan derivatives (Pasternak, 1956; Bye, Mostad & Rømming, 1973; Wakahara, Kido, Fujiwara & Tomita, 1973). The purine and indole rings are planar with

* Lists of structure factors, anisotropic thermal parameters of C, N and O atoms, atomic parameters of H atoms, and the least-squares planes for the rings and the peptide group have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38275 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and isotropic temperature factors*

The B values are the equivalent isotropic temperature factors calculated from the anisotropic thermal parameters using the equation $B = 8\pi^2(U_1 + U_2 + U_3)/3$ where U_1, U_2, and U_3 are the principal components of the mean-square displacement matrix **U**. Values in angle brackets are the anisotropicities defined by $[\sum(B - 8\pi^2U_i)^2/3]^{1/2}$. The e.s.d.'s in parentheses and the anisotropicities in angle brackets refer to the last decimal places.

	x	y	z	B(Å^2)
N(1)	−0·1188 (7)	0·0953 (2)	0·4366 (8)	2·9 ⟨7⟩
C(2)	−0·1379 (9)	0·0762 (3)	0·597 (1)	3·1 ⟨10⟩
N(3)	−0·2174 (7)	0·0206 (2)	0·5748 (8)	2·8 ⟨11⟩
C(4)	−0·2803 (8)	−0·0175 (3)	0·361 (1)	2·4 ⟨12⟩
C(5)	−0·2611 (9)	−0·0063 (3)	0·180 (1)	2·7 ⟨7⟩
C(6)	−0·1768 (9)	0·0527 (3)	0·225 (1)	2·8 ⟨10⟩
N(6)	−0·1510 (8)	0·0721 (2)	0·0683 (8)	3·7 ⟨25⟩
N(7)	−0·3386 (8)	−0·0581 (2)	−0·0145 (8)	3·8 ⟨20⟩
C(8)	−0·4029 (9)	−0·0994 (3)	0·051 (1)	3·9 ⟨19⟩
N(9)	−0·3722 (7)	−0·0773 (2)	0·2775 (8)	2·8 ⟨9⟩
C(11)	−0·4346 (9)	−0·1112 (3)	0·399 (1)	3·1 ⟨7⟩
C(12)	−0·2980 (9)	−0·1537 (3)	0·462 (1)	2·8 ⟨8⟩
C(13)	−0·2645 (8)	−0·2093 (3)	0·262 (1)	2·7 ⟨9⟩
O(13)	−0·3892 (6)	−0·2429 (2)	0·1094 (7)	4·1 ⟨15⟩
N(1′)	0·3651 (8)	−0·2791 (3)	0·6895 (9)	4·6 ⟨18⟩
C(2′)	0·3100 (9)	−0·2461 (3)	0·552 (1)	4·0 ⟨9⟩
C(3′)	0·2346 (9)	−0·2906 (3)	0·340 (1)	3·5 ⟨13⟩
C(4′)	0·189 (1)	−0·4152 (4)	0·186 (1)	6·0 ⟨20⟩
C(5′)	0·217 (1)	−0·4675 (4)	0·250 (1)	7·9 ⟨32⟩
C(6′)	0·297 (1)	−0·4580 (4)	0·467 (1)	8·0 ⟨41⟩
C(7′)	0·351 (1)	−0·3975 (4)	0·632 (1)	6·5 ⟨20⟩
C(8′)	0·3237 (9)	−0·3451 (3)	0·565 (1)	3·9 ⟨15⟩
C(9′)	0·2388 (9)	−0·3531 (3)	0·343 (1)	3·7 ⟨12⟩
C(10′)	0·1633 (9)	−0·2721 (3)	0·145 (1)	3·6 ⟨14⟩
C(11′)	−0·0411 (9)	−0·2721 (3)	0·092 (1)	3·0 ⟨11⟩
C(12′)	−0·1060 (9)	−0·2628 (3)	−0·132 (1)	3·5 ⟨10⟩
C(13′)	−0·217 (1)	−0·3222 (3)	−0·515 (1)	4·5 ⟨23⟩
C(14′)	−0·265 (1)	−0·3916 (3)	−0·665 (1)	5·8 ⟨28⟩
N(2′)	−0·0927 (7)	−0·2185 (3)	0·2659 (8)	3·0 ⟨7⟩
O(1′)	−0·0938 (7)	−0·2126 (2)	−0·1496 (7)	4·9 ⟨25⟩
O(2′)	−0·1613 (6)	−0·3214 (2)	−0·2892 (7)	3·9 ⟨15⟩

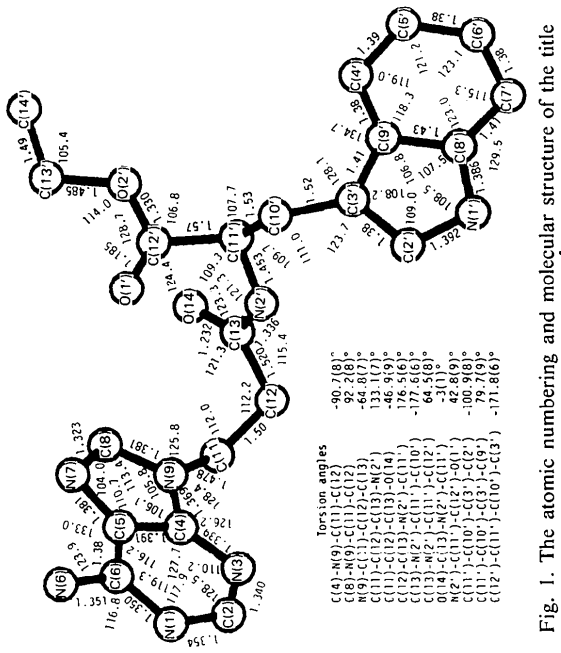

Fig. 1. The atomic numbering and molecular structure of the title compound. E.s.d.'s are 0·008–0·014 Å for bond distances and 0·6–0·9° for bond angles.

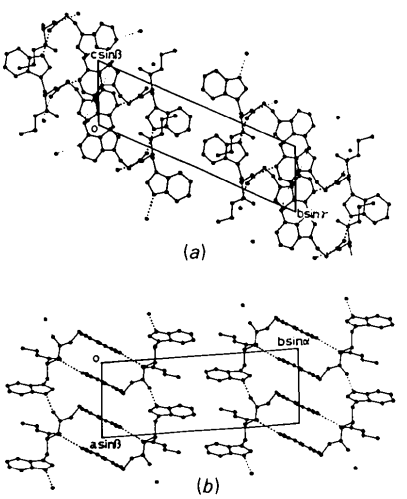

Fig. 2. The crystal structure of the title compound projected (*a*) along the *a* axis and (*b*) along the *c* axis.

Table 2. *Hydrogen-bond distances* (Å) *and angles* (°)

Standard deviations are given in parentheses.

N(1)···N(2′)	2·942 (8)	C(2)–N(1)···N(2′)	96·3 (4)
N(3)···N(6^{ii})	3·006 (8)	C(6)–N(1)···N(2′)	145·2 (4)
O(14)···N(1′^{iv})	2·837 (7)	C(2)–N(3)···N(6^{ii})	88·9 (4)
		C(4)–N(3)···N(6^{ii})	160·5 (4)
		N(3^{iii})···N(6)–C(6)	139·2 (4)
		C(13)–O(14)···N(1′^{iv})	154·4 (4)
		N(1^{i})···N(2′)–C(13)	107·8 (4)
		N(1^{i})···N(2′)–C(11′)	127·4 (4)
		O(14^{v})···N(1′)–C(2′)	132·2 (5)
		O(14^{v})···N(1′)–C(8′)	116·8 (4)

Symmetry code: (i) $-x,-y,1-z$; (ii) $x,y,1+z$; (iii) $x,y,-1+z$; (iv) $-1+x,y,-1+z$; (v) $1+x,y,1+z$.

respective maximum shifts of 0·04 Å at N(1) and −0·02 Å at C(9′) from their least-squares planes.

The crystal structure is shown in Fig. 2, and the hydrogen-bond distances and angles are listed in Table 2. The adenine moieties related by the inversion at $(0,0,\frac{1}{2})$ are stacked with respect to each other with a spacing of 3·45 (1) Å; the interatomic distance is 3·453 (9) Å between C(2) and C(4). On the other hand, indolyl and ethyl groups are piled up alternately along the *a* axis by van der Waals contacts, and these stacked columns face each other near the inversion centres at $y=\frac{1}{2}$. Thus, direct intermolecular stacking between adenine and indole rings is not observed in the present crystal.

The NH group of the indole ring is hydrogen-bonded to the carbonyl O atom of the peptide bond in the molecule at $(1+x,y,1-z)$; the NH···O distance is 2·837 (7) Å. The molecules are connected along the *c* axis through the head-to-tail N(6)H···N(3) hydrogen bonds [3·006 (8) Å] between adenine rings. The other N(6)H group points to O(1′) of the ethyl ester group at $(-x,-y,-z)$, but the distance N···O is 3·495 (8) Å. The adenine N(1) is an acceptor of the hydrogen bond from the secondary amide NH of the peptide bond in the neighboring molecule at $(-x,-y,1-z)$, the N···N distance being 2·942 (8) Å. The twisting angle φ[C(13)–N(2′)···N(1)–C(2)] is 99·9 (6)°, which is defined in the same way as the torsion angle (Takenaka, Ohki & Sasada, 1980). Similar hydrogen-bonding geometries have been found in 3-(7-adeninyl)propionamide monohydrate (Takimoto *et al.*, 1983) and 3-(9-adeninyl)propionamide : 1-methylthymine (1:1) complex dihydrate (Takimoto *et al.*, 1982), in spite of the different crystal fields.

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Structure of *N-tert*-Butoxycarbonyl-L-alanyl-2-methylalanine, $C_{12}H_{22}N_2O_5$

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Abstract. $M_r = 274{\cdot}32$, monoclinic, $P2_1$, $a = 5{\cdot}434$ (7), $b = 18{\cdot}765$ (7), $c = 7{\cdot}699$ (3) Å, $\beta = 99{\cdot}66$ (5)°, $V = 773{\cdot}9$ (7) Å^3, $Z = 2$, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·057 mm^{-1}, $D_x = 1{\cdot}18$ (1) Mg m^{-3}, $F(000) = 296$. The structure was determined by direct methods from diffractometer data. Final $R = 0{\cdot}046$ for 2577 reflexions with $|F| > 0$. Significant deviations from tetrahedral angles at C_α of the Aib residue seem to be correlated with the conformation of the dipeptide, which itself is affected by the hydrogen-bonding network.

Introduction. About 10 different types of peptide antibiotics (Jung, Brückner & Schmitt, 1981, and references therein) are known at present; these contain a high percentage of the α,α-dialkylated amino acid α-aminoisobutyric acid (Aib, 2-methylalanine). 2-Methylalanyl residues have restricting effects on the conformational freedom of a peptide. It has been shown by X-ray crystallography that shorter Aib peptides preferentially adopt type III β bends and 3_{10} helices. However, α-helical structures are formed in the case of longer Aib-containing sequences (Butters, Hütter, Jung, Pauls, Schmitt, Sheldrick & Winter, 1981; Schmitt, Winter, Bosch & Jung, 1982). In order to obtain additional information about the conformational influence of this unusual amino acid, the structure of the dipeptide *N-tert*-butoxycarbonyl-L-alanyl-2-methylalanine (Boc-L-Ala-Aib-OH) was determined by X-ray crystallography. This N-protected dipeptide acid is a useful building block for the synthesis of the polypeptide antibiotic alamethicin and analogous membrane-modifying peptides.

Experimental. Boc-L-Ala-Aib-OH was obtained *via* saponification of Boc-L-Ala-Aib-OMe as described (Schmitt, Winter, Bosch & Jung, 1982) with the following modification. To Boc-L-Ala-Aib-OMe (170 g) in methanol (600 ml) was added 2*M* NaOH (900 ml). After 2h at 313 K the saponification was complete, and the mixture was worked up as described (yield 148 g, 91%).

Single crystals by slow evaporation (methanol), 0·6 × 0·25 × 0·3 mm, CAD-4 four-circle diffractometer (Enraf–Nonius), ω/θ technique, Mo $K\alpha$ radiation at room temperature, 2904 reflexions, $\theta = 3° - 25°$ (h: −6 to 6; k: −22 to 22; l: −9 to 9), 2591 unique reflexions with $|F| > 0$, direct methods (*MULTAN* 80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), isotropic refinement with *SHELX* 76 (Sheldrick, 1976) ($R = 0{\cdot}118$), methyl groups refined as rigid groups [d(C—H) = 0·96 Å], common isotropic temperature factor for H atoms (non-H atoms anisotropic), final $R = 0{\cdot}046$ ($R_G = 0{\cdot}046$, unit weights), exclusion of 14 strong low-angle reflexions (extinction effects) in the final least-squares cycles, ratio of maximum least-squares shift to error: ±0·03, $R_{int} = 0{\cdot}0342$, flat analysis of variance (with respect to h,k,l, $|F_o|$ and $\sin\theta/\lambda$), only spurious peaks (<0·25 e Å^{-3}) in final difference Fourier synthesis; scattering factors were from Cromer & Mann (1968); the values of f' and f'' were those of Cromer & Liberman (1970).

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