

Fig. 2. Schematic drawing of the hydrogen bonding.

the two types of intermolecular hydrogen bonds: N(3)—H(3)···O(31) and N(1)···H(31)—O(31). The distances and angles for the hydrogen bonds are N(3)···O(31) = 2.951 (6), N(1)···O(31) = 2.955 (6) Å, N(3)—H(3)···O(31) = 163 (6) and N(1)···H(31)—O(31) = 165 (6)°. (I) partially tautomerizes to the 1,4-dihydro form on the loss of the solvent molecules, suggesting that the hydrogen bonds with the 2-propanol molecules can stabilize the 3,4-dihydro form. There are no unusually short contacts except for the hydrogen bonds. From these results it seems that the replacement of N(1) in (II), which was not involved in any hydrogen bonds, by a CH group has little influence on the molecular and crystal structure.

The colorless crystals of the (I) 2-propanol solvate turned red on exposure of UV light in spite of the structural similarity with (II) 2-propanol solvate, in which photocoloration was inhibited by the hydro-

gen bonds. The different photochemical behaviors of the triazine and (I) cannot be explained in terms of any differences in crystal structures between the two heterocycles. A different pathway of photocoloration reaction which is not inhibited by the hydrogen bonds connecting (I) and 2-propanol molecules alternately, is suggested for the solvated crystal of (I). The details of the photochemical reactions of (I) will be discussed elsewhere.

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Structures of *N*²-Acetyl-DL-alaninamide and *N*²-Acetyl-DL-leucinamide

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Abstract. *N*²-Acetyl-DL-alaninamide (NAAA), C₅H₁₀N₂O₂, *M_r* = 130.15, monoclinic, *P*2₁/*c*, *a* = 5.9798 (4), *b* = 16.690 (2), *c* = 7.7615 (4) Å, β = 107.18 (2)°, *V* = 740.1 (1) Å³, *Z* = 4, *D_x* = 1.168 Mg m⁻³, λ(Cu *Kα*) = 1.54178 Å, μ = 0.73 mm⁻¹, *F*(000) = 280, room temperature, final *R* = 0.045 for 1386 reflections with *I* > 3σ(*I*). *N*²-Acetyl-DL-leucinamide (NALA), C₈H₁₆N₂O₂, *M_r* = 172.23, monoclinic, *P*2₁/*c*, *a* = 16.807 (2), *b* =

7.2188 (8), *c* = 8.9716 (9) Å, β = 102.61 (1)°, *V* = 1062.2 (4) Å³, *Z* = 4, *D_x* = 1.077 Mg m⁻³, λ(Cu *Kα*) = 1.54178 Å, μ = 0.60 mm⁻¹, *F*(000) = 376, room temperature, final *R* = 0.041 for 1423 reflections with *I* > 3σ(*I*). In both structures the packing is ruled by two-dimensional networks of three intermolecular hydrogen bonds, which involve all the polar groups and interconnect L and D molecules, giving rise to characteristic structures arranged in layers. In the

two molecules, the backbone conformations are rather similar and fall in the β -sheet region.

Introduction. D-Amino acid residues are not rare in nature. They are present, alternate with L residues, in some peptides or molecules containing peptide chains having antibiotic activity, found especially in microorganisms and fungi (*e.g.* gramicidin A and S, actinomycin D, cyclosporin A, *etc.*) (Benedetti, 1982). The crystal packings, molecular parameters and preferred conformations in the solid state of the pure L enantiomers of *N*-acetyl amides of alanine and leucine have been recently determined and discussed together with that of the *N*-acetyl amides of glycine (Puliti, Mattia, Barone & Giancola, 1989) as well as that of L-valine (Puliti, Mattia, Barone, Della Gatta & Ferro, 1990). The thermodynamics of phase transitions (sublimation and fusion) of some D or L enantiomers have also been reported (Ferro, Della Gatta & Barone, 1988; Puliti *et al.*, 1990). Both the amino acid dipolar ions and the corresponding protected peptides (amides of *N*-acetyl amino acids) still show a weak chiral recognition in very dilute aqueous solution, at least for the less hydrophilic homologues (Barone, Castronuovo, Elia & Giancola, 1985; Barone, Castronuovo, Del Vecchio, Elia & Giancola, 1987; Barone, Castronuovo, Del Vecchio, Elia & Puzziello, 1989). In this paper the crystal structures of the racemic forms of the *N*-acetyl amides of alanine and leucine are reported as part of a program concerning the physico-chemical properties of uncharged model peptides in the solid state and in solution. The properties of the racemic crystals differ strongly from those of the optically active crystals, primarily owing to differences in the intermolecular distances and also to topological correlations between groups of atoms.

In solution, especially in water, the interactions between solute molecules are made weaker by solvation. However, an accurate determination of the molecular and conformational parameters in the racemic crystals can offer a helpful basis to formulate hypotheses on the interactions in solution between pairs of enantiomers. The molecular and conformational parameters, found for the crystals of pure enantiomers and racemes, can also be very useful for the determination of cohesive energy, the theoretical evaluation of spectroscopic and thermodynamic properties and for conformational calculations of polypeptide chains.

Experimental. The L enantiomers were prepared according to Blackburn, Lilley & Walmsley (1980). The D enantiomers were synthesized by a modified procedure, starting from the D enantiomer of each amino acid (Fluka products). The methyl ester hydrochloride was prepared by reaction at room

temperature of the amino acid solution with a large excess of methanol containing stoichiometric quantities of thionyl chloride. The products (purified by crystallization from benzene-ethyl ether mixtures) were treated at 273 K with equimolar quantities of acetic anhydride and pyridine to obtain the *N*-acetyl derivatives of the methyl ester. After solvent removal and purification, the *N*-acetyl amides were finally obtained by ammonolysis at 273 K in anhydrous methanol previously saturated with gaseous ammonia. The final products were purified to constant melting point, by repeated crystallizations from methanol-ethyl ether mixtures. At each step the homogeneity of the products was tested by TLC (3:7 methanol:chloroform eluent) and polarimetry. Enthalpies and temperatures of fusion were determined by means of a Mettler TA-3000 apparatus using indium as a reference.

Single crystals of the DL forms were grown as colourless prisms by slow evaporation of the solvents (chloroform for NAAA and ethanol-ethyl ether mixture for NALA) from solutions containing an equimolecular ratio of both enantiomers. No optical rotation was shown by solutions prepared with those crystals. No indication of the presence of mixtures of crystals of pure enantiomers was detected.

Enraf-Nonius CAD-4F diffractometer; room temperature. Cell parameters from 25 reflections at medium θ ; ω - θ scan, as suggested by peak-shape analysis; three monitoring reflections for each data collection, intensity variation $\leq 5\%$; Lp correction, absorption ignored. Structures solved by *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982); anisotropic full-matrix least squares [$\sum w(\Delta F)^2$ minimized]; $w = 1/[\sigma^2(F) + (aF)^2 + b]$ (Killeen & Lawrence, 1969), where a and b are: 0.01 and 3 for NAAA, 0.02 and 1 for NALA; $\sigma(F)$ from counting statistics. H atoms from ΔF synthesis and geometrical considerations, refined isotropically, imposing the same thermal parameter to H atoms bonded to the same atom. A correction for secondary extinction was introduced. The most significant refinement parameters and the crystal data for the two structures are summarized in Table 1. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf-Nonius *SDP* software (B. A. Frenz & Associates, Inc., 1985) and MicroVAX computer of the 'Centro di Metodologie Chimico-fisiche dell'Università di Napoli'. Final atomic parameters for the two structures are listed in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters for each structure have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53913 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. X-ray data collection and refinement parameters

	NAAA	NALA
Crystal size (mm)	0.30 × 0.28 × 0.16	0.38 × 0.32 × 0.04
θ_{\max} (°)	75	70
Range of h, k, l	0, 0, -9 to 7, 20, 9	0, 0, -10 to 20, 8, 10
No. of independent reflections	1522	2007
No. of reflections with $I > 3\sigma(I)$	1386	1423
No. of parameters refined	118	158
Extinction coefficient	$3.40(2) \times 10^{-5}$	$4.3(1) \times 10^{-6}$
Final R	0.045	0.041
Final wR	0.051	0.047
Max. final Δ/σ	0.02	0.03
S	1.60	0.85
Max. and min. $\Delta\rho$ (e Å ⁻³)	0.18, -0.16	0.15, -0.11

Table 2. Fractional coordinates and equivalent isotropic thermal parameters (Å²) with e.s.d.'s in parentheses for non-H atoms
$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
NAAA				
O(1)	0.1012 (2)	0.24768 (7)	0.9799 (1)	5.80 (3)
O(2)	-0.1715 (2)	0.01512 (7)	0.7320 (2)	6.31 (3)
N(1)	0.0424 (2)	0.12384 (7)	0.7204 (2)	4.29 (3)
N(2)	0.1314 (3)	0.15093 (8)	1.1841 (2)	4.78 (3)
C(1)	0.1969 (3)	0.11581 (9)	0.9015 (2)	4.34 (3)
C(2)	0.1358 (3)	0.17679 (9)	1.0258 (2)	3.89 (3)
C(3)	-0.1322 (2)	0.07312 (9)	0.6483 (2)	4.15 (3)
C(4)	-0.2792 (4)	0.0910 (1)	0.4602 (3)	6.34 (5)
C(5)	0.4507 (4)	0.1287 (2)	0.9048 (3)	7.61 (6)
NALA				
O(1)	0.3192 (1)	0.1049 (2)	0.5735 (1)	5.23 (3)
O(2)	0.3824 (1)	-0.1276 (2)	0.1017 (1)	4.12 (3)
N(1)	0.3636 (1)	-0.1311 (2)	0.3423 (2)	3.70 (3)
N(2)	0.3246 (1)	0.3178 (2)	0.3930 (2)	4.76 (4)
C(1)	0.2958 (1)	-0.0000 (3)	0.3148 (2)	3.59 (4)
C(2)	0.3144 (1)	0.1468 (3)	0.4389 (2)	3.69 (4)
C(3)	0.4006 (1)	-0.1877 (2)	0.2342 (2)	3.32 (3)
C(4)	0.4673 (1)	-0.3269 (3)	0.2812 (2)	4.43 (4)
C(5)	0.2159 (1)	-0.1004 (3)	0.3158 (3)	4.99 (5)
C(6)	0.1403 (2)	0.0215 (4)	0.2791 (3)	6.50 (7)
C(7)	0.1248 (2)	0.0980 (6)	0.1175 (4)	10.1 (1)
C(8)	0.0659 (2)	-0.0890 (6)	0.3001 (5)	12.0 (1)

Discussion. In Fig. 1 are reported views, approximately in the same orientation, with the atomic numbering schemes of the molecules of NAAA and NALA. In both structures a molecule of the *L* enantiomer was chosen as the asymmetric unit, to which all the conformational parameters, discussed in the following, are referred. The geometrical parameters, involving non-H atoms, are given in Table 3. The values of the corresponding bond lengths and bond angles on average agree between the two structures within experimental errors and they show no significant discrepancies from those generally found for this kind of compound (Benedetti, 1977; Puliti *et al.*, 1989). N—H and C—H bond distances lie in the ranges 0.88 (2)–0.93 (2) and 0.90 (3)–1.10 (3) Å, respectively.

The molecular backbone conformations (see torsion angles in Table 3) fall in the regions *F* (NAAA)

Table 3. Bond lengths (Å), bond angles (°) and some torsion angles (°) with e.s.d.'s in parentheses

O(1)—C(2)	1.235 (2)	1.230 (2)
O(2)—C(3)	1.226 (2)	1.240 (2)
N(1)—C(1)	1.442 (2)	1.460 (2)
N(1)—C(3)	1.332 (2)	1.326 (2)
N(2)—C(2)	1.310 (2)	1.324 (2)
C(1)—C(2)	1.519 (2)	1.520 (2)
C(1)—C(5)	1.525 (3)	1.527 (3)
C(3)—C(4)	1.495 (2)	1.496 (3)
C(5)—C(6)	—	1.522 (3)
C(6)—C(7)	—	1.520 (5)
C(6)—C(8)	—	1.530 (5)
C(1)—N(1)—C(3)	123.2 (1)	123.3 (1)
N(1)—C(1)—C(2)	110.6 (1)	107.5 (1)
N(1)—C(1)—C(5)	110.6 (1)	110.2 (2)
C(2)—C(1)—C(5)	108.6 (1)	111.5 (2)
O(1)—C(2)—N(2)	122.5 (1)	123.3 (2)
O(1)—C(2)—C(1)	120.6 (1)	120.4 (2)
N(2)—C(2)—C(1)	116.8 (1)	116.2 (1)
O(2)—C(3)—N(1)	121.8 (1)	122.5 (2)
O(2)—C(3)—C(4)	121.7 (1)	121.2 (2)
N(1)—C(3)—C(4)	116.5 (1)	116.3 (1)
C(1)—C(5)—C(6)	—	114.7 (2)
C(5)—C(6)—C(7)	—	112.2 (2)
C(5)—C(6)—C(8)	—	109.8 (2)
C(7)—C(6)—C(8)	—	109.5 (2)
N(1)—C(1)—C(2)—N(2)	136.0 (1)	116.0 (2)
C(2)—C(1)—N(1)—C(3)	-104.4 (2)	-131.8 (2)
C(1)—N(1)—C(3)—C(4)	178.8 (2)	-178.2 (2)
N(1)—C(1)—C(2)—O(1)	-46.6 (2)	-64.0 (2)
C(3)—N(1)—C(1)—C(5)	135.2 (2)	106.4 (2)
O(1)—C(2)—C(1)—C(5)	75.0 (2)	56.8 (2)
N(1)—C(1)—C(5)—C(6)	—	-176.7 (2)
C(2)—C(1)—C(5)—C(6)	—	64.0 (2)
C(1)—C(5)—C(6)—C(7)	—	64.1 (3)
C(1)—C(5)—C(6)—C(8)	—	-174.0 (2)

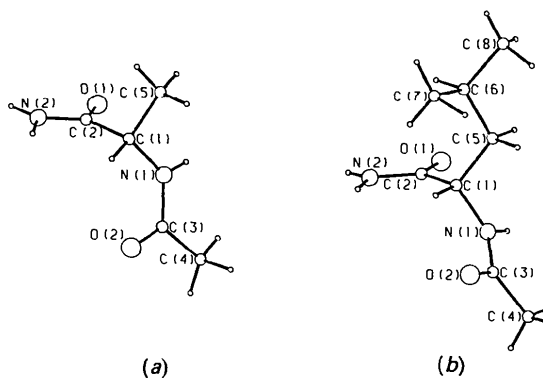


Fig. 1. Perspective views of the molecules with the atomic numbering schemes: (a) NAAA, (b) NALA.

and *E* (NALA) of the φ - ψ map, as defined by Zimmerman, Pottle, Némethy & Scheraga (1977), but are rather similar to each other. The NAAA molecule assumes about the same overall conformation as in the *L* crystal (Puliti *et al.*, 1989) and this conformation corresponds to one of the most common for the Ala residue in proteins (Némethy & Scheraga, 1977).

In the leucine derivative, the main-chain conformation [$\varphi = -131.8(2)$, $\psi = 116.0(2)^\circ$] differs from that, close to the β -bend type, observed in the pure L enantiomer [$\varphi = -67.6(7)$, $\psi = -30.3(6)^\circ$] (Puliti *et al.*, 1989). The Leu side chain is in the $t(g^+t)$ conformation where, according to Benedetti, Morelli, Némethy & Scheraga (1983), the first letter denotes the orientation of C(6) with respect to N(1) and the two letters in parentheses indicate the positions of C(7) and C(8) with respect to C(1). This extended conformation and the twisted one [$g^-(tg^-)$] adopted by the same molecule in the pure L crystal, are the only two conformations found in crystals of small peptides containing Leu residues (Benedetti *et al.*, 1983).

In the two structures, the crystal packing (Figs. 2 and 3) is ruled by six shared intermolecular hydrogen bonds, all the donor groups being involved. The

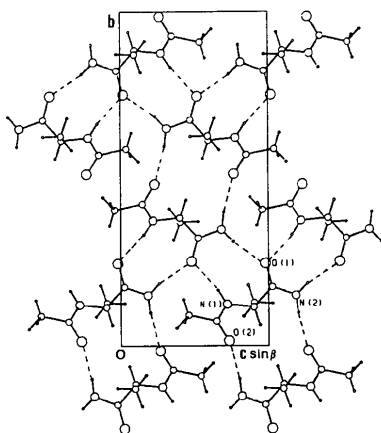


Fig. 2. Crystal structure of NAAA projected along the *a* direction. Only atoms involved in hydrogen bonds are numbered. Dashed lines indicate hydrogen bonds; the symmetry of hydrogen-bonded atoms is reported in Table 4.

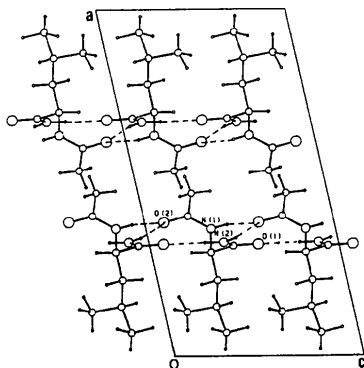


Fig. 3. Crystal packing of NALA projected on the *ac* plane. Only atoms involved in hydrogen bonds are numbered. Dashed lines indicate hydrogen bonds; the symmetry of hydrogen-bonded atoms is reported in Table 4.

Table 4. Hydrogen-bonding geometry (\AA and $^\circ$)

D—H...A	D...A	H...A	D—H...A	Code
NAAA				
N(1)—H...O(1)	2.932 (2)	2.06 (2)	171 (2)	(i)
N(2)—H...O(1)	2.900 (2)	1.99 (2)	163 (1)	(ii)
N(2)—H...O(2)	2.841 (2)	1.96 (2)	173 (2)	(iii)
NALA				
N(1)—H...O(2)	2.868 (2)	2.02 (2)	162 (2)	(iv)
N(2)—H...O(1)	2.902 (2)	2.00 (2)	177 (2)	(i)
N(2)—H...O(2)	2.942 (2)	2.08 (2)	170 (2)	(ii)

Symmetry of acceptor: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x, -y, -z + 2$; (iv) $x, -y - \frac{1}{2}, z + \frac{1}{2}$.

hydrogen-bond patterns are two-dimensional and link together molecules of different chirality. In the NAAA crystal (see Fig. 2 and Table 4) pairs of centrosymmetrically related molecules are held together by a double bridge N(2)—H...O(2), while the amidic oxygen O(1) behaves as a double acceptor toward N(1) and N(2) of glide-related molecules. In this structure, each enantiomer is hydrogen bonded with three molecules of opposite chirality, giving rise to polar layers parallel to the *bc* plane. These layers separate apolar regions which contain both C(4) and C(5) methyl groups at distances $\geq 4.180(3) \text{\AA}$.

The crystals of NAAA show values of enthalpy and entropy of fusion higher than those recently determined in our laboratory for the crystals of the highly purified L enantiomer [25.3 (1) and 58.3 (3) against 23.9 (4) kJ mol^{-1} and 55.0 (9) $\text{J mol}^{-1} \text{K}^{-1}$, respectively], even if the melting point is lower [433.6 (1) K for the raceme against 434.7 (5) K for the L enantiomer]. These data seem to indicate a slightly larger stability for racemic crystals, also supported by the shorter lengths found for the intermolecular hydrogen bonds (in the two structures the hydrogen bonds occur between the same three pairs of donor-acceptor atoms).

In the NALA structure the hydrogen bonds interconnect molecules related only by glide symmetry (Table 4). The peptidic oxygen O(2) is engaged as acceptor in two hydrogen bonds, while O(1) accepts only one hydrogen bond. In this case, however, each molecule is interconnected with four molecules of opposite chirality, translated along *b* and *c*, making a two-dimensional network of hydrogen bonds which extends parallel to the *bc* plane. The polar layers separate, along the *a* direction, two different apolar regions, one (at $x = 0$) containing the leucine side chains and the other (at $x = 0.5$) containing the methyls of the acetate groups, at van der Waals distances [$\geq 3.850(3) \text{\AA}$]. Unlike the NAAA structure, the hydrogen-bond planes in this structure do not include the inversion center. This gives rise to different patterns of hydrogen bonds in the same space group.

The NALA structure is rather different from that of the pure L enantiomer. The latter optimizes the packing by forming wrinkled polar sheets, whose concavities accommodate very well the twisted side chains. Therefore the L enantiomer forms a slightly denser crystal (1.125 compared with 1.077 Mg m⁻³), but only two hydrogen bonds are established.

The melting point of the racemic NALA is also a little lower than those of the D-NALA and L-NALA crystals [401.0 (4) K against 404.1 and 403.2 K recently redetermined]. This temperature, however, results from an enthalpy-entropy ratio, where these two thermodynamic parameters are much smaller for the raceme than those recently found for the pure L enantiomer [2.8 (1) and 7.0 (3) against 16.5 (4) kJ mol⁻¹ and 40.9 (9) J mol⁻¹ K⁻¹, respectively]. These differences of an order of magnitude are unexpected; no solid-solid transitions were found in the range 250–404 K. It is possible that this discrepancy depends on a higher organization of the racemic liquid.

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Structure of Three Di-pyrrole Compounds

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Abstract. All measurements with Mo K α radiation ($\lambda = 0.71073$ Å). (I) *p*-Phenylenebis(2,5-dimethylpyrrole), C₁₈H₂₀N₂, $M_r = 264.40$, orthorhombic, *Cc*mb, $a = 7.273$ (2), $b = 12.463$ (4), $c = 16.559$ (4) Å, $V = 1501.1$ Å³, $Z = 4$, $D_x = 1.17$ Mg m⁻³, $F(000) = 568$, $T = 295$ K, molecular symmetry 2/m. $R = 0.056$ ($wR = 0.053$) for 454 reflections having $I \geq 3\sigma(I)$ with the coordinates of all atoms refined, anisotropic thermal parameters for C and N atoms, and a fixed value of U_{iso} for H atoms. (II) 2,2',5,5'-Tetramethyl-1,1'-bipyrrole, C₁₂H₁₆N₂, $M_r = 188.27$, orthorhombic, *Cc*2a, $a = 11.773$ (3), $b = 25.154$ (6), $c = 11.841$ (3) Å, $V = 3507$ (1) Å³, $Z = 12$, $D_x = 1.07$ Mg m⁻³, $F(000) = 1224$, $T = 292$ K, molecular symmetry 2 for three

independent molecules. $R = 0.078$ ($wR = 0.080$) for 605 reflections having $I \geq 3\sigma(I)$ with isotropic refinement for C, N and H atoms in calculated positions. (III) 13,14-Diazatetracyclo[8.2.1^{1,10}.-1^{4,7}.0^{13,14}]tetradeca-4,6,10,12-tetraene, C₁₂H₁₂N₂, $M_r = 182.6$, monoclinic, *P2*₁/*a*, $a = 7.667$ (2), $b = 8.191$ (2), $c = 8.231$ (2) Å, $\beta = 112.04$ (2)°, $V = 479.1$ (2) Å³, $Z = 2$, $D_x = 1.26$ Mg m⁻³, $F(000) = 196$, $T = 292$ K, molecular symmetry $\bar{1}$. $R = 0.087$ for 354 reflections having $I \geq 3\sigma(I)$ with C and N atoms refined anisotropically and H atoms in calculated positions. There is disorder in the —CH₂—CH₂— groups. In all three compounds, each 2,5-substituted pyrrole group is planar with unexceptional bond lengths and angles. In (I) the two pyrroles are strictly orthogonal to the benzene ring, in (II) they are

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