moieties are nearly planar, constituting the rigid parts of the cations, with the terminal $-NH_3^+$ groups on opposite sides. In each cation the H atoms of the two $-NH_3^+$ groups are in different conformations (*gauche* and eclipsed) with respect to the C—N bond, as shown in Fig. 3 where the Newman projections along the N—N bonds are depicted for both $NH_3^+$ groups of the four independent cations. In each eclipsed group an H atom is involved in an intramolecular hydrogen bond with the S.

The packing of the cations, anions and water molecules in the crystal is determined by an extensive network of $NH\cdots Cl$, $-NH_3^+\cdots Cl$, $-NH_3^+\cdots O$ and $OH\cdots Cl$ hydrogen bonds.

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# Structure of 5-Azatricyclo[4.3.1.$0^{3,8}$]decan-4-one Hemihydrate, $C_9H_{13}NO.\frac{1}{2}H_2O$

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**Abstract.** $M_r = 160{\cdot}22$, monoclinic, $P2_1/c$, $a = 12{\cdot}375\ (3)$, $b = 12{\cdot}695\ (3)$, $c = 12{\cdot}521\ (3)$ Å, $\beta = 119{\cdot}29\ (2)°$, $V = 1715{\cdot}6\ (8)$ Å$^3$, $Z = 8$, $D_m = 1{\cdot}27\ (2)$, $D_x = 1{\cdot}24$ g cm$^{-3}$, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 6{\cdot}29$ cm$^{-1}$, $F(000) = 696$, $T = 295$ K. Final $R = 0{\cdot}079$ for 1494 unique observed reflections. The constraints of the tricyclic system result in a significantly non-planar character of the amide group. In the unit cell, there are two symmetric independent molecules of the lactam. These two molecules are of two conformational types: *A*, where the non-planarity of the amide group is caused mostly by a torsion around the C′—N bond, and *B*, in which there is a pyramidal arrangement of the bonds at N.

**Introduction.** The structure of 5-azatricyclo[4.3.1.$0^{3,8}$]-decan-4-one hemihydrate was determined as a part of studies on potential occurrence of non-planar amide groups in amides and peptides (Ealick & van der Helm, 1977; Bláha *et al.*, 1978; Bláha & Maloň, 1980). This lactam is a model compound in which the *cis*-amide group is embedded in a rigid tricyclic skeleton. Determination of properties characteristic for a non-planar amide group, *e.g.* dependence of chiroptical parameters on the extent and character of deviation from planarity, could be a starting point for finding other similar deviations in flexible amides (peptides) in solution (Bláha & Maloň, 1980). The synthesis of the compound (I) as well as results of the chiroptical studies in solution are reported elsewhere (Tichý, Farag, Maloň, Kálal & Bláha, 1984).

**Experimental.** Colorless prismatic crystals grown by slow evaporation from a hexane/benzene/ether mixture at room temperature; molecular formula of title compound confirmed by elemental analysis; crystal

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density determined by flotation in $CCl_4$/heptane. Preliminary cell dimensions and space group determined from oscillation and Weissenberg photographs recorded with Cu $K\alpha$ radiation; final cell dimensions refined on 24 reflections with $15\cdot8 < 2\theta < 26\cdot5°$ from diffractometer measurements. Crystal $0\cdot2 \times 0\cdot2 \times 0\cdot3$ mm, Syntex $P2_1$ automated diffractometer with graphite monochromator. Cu $K\alpha$ radiation, $(\sin\theta/\lambda)_{\max}$ 0·4968 Å$^{-1}$. $\theta$–$2\theta$ scan technique, $-12 \leq h \leq 0$, $0 \leq k \leq 12$, $-10 \leq l \leq 12$; in range up to $2\theta = 100°$, 2006 reflections measured (including systematically absent), 1773 unique, 1494 with $I > 1\cdot96\sigma_I$. Three standard reflections ($\bar{3}00$, 020, 004) monitored after every 47 reflections showed decreasing intensity throughout data collection. In the case of the 004 reflection the intensity decreased below the intensity limit set to 65% of the initial intensity. Then a new crystal was mounted (dimensions $0\cdot2 \times 0\cdot2 \times 0\cdot25$ mm). The intensities of the three standard reflections of the second crystal decreased to 83, 78 and 74%, respectively, of the initial intensity. The measurements were reduced to the same scale with the program *INTER* (Langer, 1973). Corrections made for Lorentz and polarization factors, not for absorption. Phase problem solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and by subsequent weighted difference Fourier synthesis. Refinement on $F$ by full-matrix LS method using *SHELX*76 (Sheldrick, 1976). H atoms were calculated in the theoretical positions with the exception of those of water located on the difference map. At the end of refinement all H atoms were included in the refinement, but unstable ones were refined using riding model. Refinement was stopped when $(\Delta/\sigma)_{\max} < 0\cdot15$; total number of parameters refined 286; final $R = 0\cdot0795$, $wR = 0\cdot1131$, $w = [\sigma_F^2 + (0\cdot02F)^2]^{-1}$, where $\sigma_F$ is taken from counting statistics. Final difference Fourier synthesis on observed reflections did not show any significant feature, the maximum being 0·49 and minimum $-0\cdot23$ e Å$^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and* $B_{eq}$ (Å$^2$) *values with e.s.d.'s in parentheses*

|  | $x$ | $y$ | $z$ | $B_{\rm eq}$* |
|---|---|---|---|---|
| C(1*A*) | 3149 (7) | 5949 (6) | 7540 (7) | 8·5 (3) |
| C(2*A*) | 4140 (8) | 5109 (6) | 7941 (8) | 8·6 (3) |
| C(3*A*) | 5189 (7) | 5673 (5) | 7882 (5) | 5·7 (2) |
| C(4*A*) | 5161 (5) | 5365 (4) | 6700 (4) | 4·6 (2) |
| N(5*A*) | 4216 (4) | 5732 (3) | 5700 (4) | 5·1 (2) |
| C(6*A*) | 3457 (6) | 6581 (4) | 5779 (5) | 5·9 (2) |
| C(7*A*) | 4333 (7) | 7368 (4) | 6650 (5) | 6·5 (2) |
| C(8*A*) | 4926 (7) | 6896 (5) | 7948 (6) | 6·8 (2) |
| C(9*A*) | 3942 (7) | 6832 (6) | 8340 (6) | 8·6 (3) |
| C(10*A*) | 2563 (6) | 6213 (6) | 6182 (7) | 7·4 (3) |
| O(1*A*) | 5946 (4) | 4770 (3) | 6677 (3) | 5·6 (1) |
| C(1*B*) | 1806 (11) | 3307 (7) | 8481 (9) | 11·8 (5) |
| C(2*B*) | 572 (12) | 3443 (5) | 7341 (9) | 11·2 (5) |
| C(3*B*) | −249 (7) | 2624 (4) | 7523 (5) | 5·6 (2) |
| C(4*B*) | −391 (6) | 1720 (4) | 6704 (5) | 4·6 (2) |
| N(5*B*) | 638 (5) | 1213 (4) | 7040 (4) | 6·0 (2) |
| C(6*B*) | 1675 (8) | 1367 (7) | 8341 (8) | 9·3 (4) |
| C(7*B*) | 1102 (8) | 1436 (5) | 9190 (6) | 8·4 (3) |
| C(8*B*) | 438 (7) | 2395 (5) | 8939 (5) | 6·4 (2) |
| C(9*B*) | 1389 (6) | 3329 (5) | 9414 (5) | 7·2 (2) |
| C(10*B*) | 2404 (8) | 2227 (9) | 8485 (9) | 11·8 (4) |
| O(1*B*) | −1333 (4) | 1497 (3) | 5761 (4) | 6·2 (2) |
| O | 1653 (4) | 9411 (3) | 6408 (4) | 7·8 (2) |

$* \; B_{\rm eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

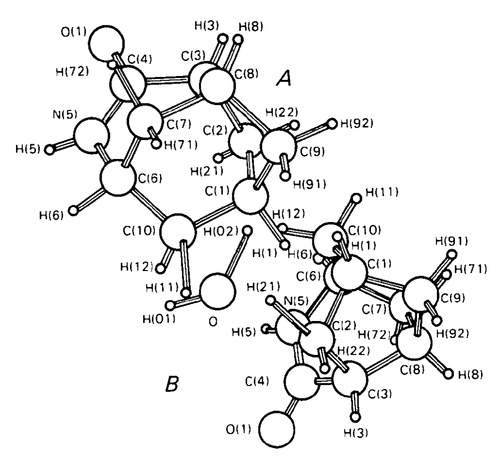
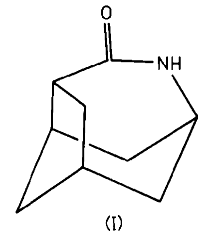


Fig. 1. Projection of the structure with numbering scheme.

**Discussion.** The molecule of the lactam (I) consists of two six-membered rings and one five-membered ring.



(I)

A view of the independent part of the structure (molecules *A* and *B* of the title lactam and a molecule of water) is shown in Fig. 1 which serves also as a numbering scheme. The fractional atomic coordinates and $B_{\rm eq}$ values are given in Table 1, bond lengths and angles in Table 2.* These values were calculated with the program *SHELX*76. The crystal packing can be seen in Fig. 2. Although the molecules *A* and *B* are chemically identical, their molecular geometries (conformations) differ as their environments are different. Hydrogen bonds are given in Table 3.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles involving H atoms and weighted mean planes for the amide group have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39320 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *for A and B lactam molecules*

| | *A* | *B* | | *A* | *B* | | *A* | *B* |
|---|---|---|---|---|---|---|---|---|
| C(1)—C(2) | 1·514 (10) | 1·506 (13) | C(3)—C(8) | 1·596 (8) | 1·574 (8) | C(6)—C(7) | 1·485 (8) | 1·543 (11) |
| C(1)—C(9) | 1·504 (10) | 1·491 (11) | C(4)—N(5) | 1·312 (6) | 1·299 (7) | C(6)—C(10) | 1·498 (9) | 1·371 (11) |
| C(1)—C(10) | 1·525 (10) | 1·556 (12) | C(4)—O(1) | 1·242 (6) | 1·219 (6) | C(7)—C(8) | 1·540 (8) | 1·415 (8) |
| C(2)—C(3) | 1·515 (10) | 1·547 (11) | N(5)—C(6) | 1·464 (7) | 1·514 (9) | C(8)—C(9) | 1·523 (10) | 1·569 (8) |
| C(3)—C(4) | 1·514 (8) | 1·491 (7) | | | | | | |
| C(9)—C(1)—C(2) | 98·4 (6) | 99·3 (9) | C(3)—C(4)—O(1) | 122·4 (5) | 125·4 (5) | C(8)—C(7)—C(6) | 108·3 (5) | 108·0 (6) |
| C(10)—C(1)—C(2) | 113·0 (6) | 111·4 (7) | N(5)—C(4)—O(1) | 122·4 (5) | 121·4 (5) | C(7)—C(8)—C(3) | 109·2 (4) | 110·1 (5) |
| C(10)—C(1)—C(9) | 112·2 (6) | 111·1 (7) | N(5)—C(4)—C(3) | 115·1 (6) | 113·0 (5) | C(9)—C(8)—C(3) | 100·4 (6) | 100·3 (5) |
| C(3)—C(2)—C(1) | 103·1 (6) | 102·6 (6) | C(6)—N(5)—C(4) | 119·9 (5) | 117·7 (6) | C(9)—C(8)—C(7) | 108·5 (6) | 108·7 (6) |
| C(4)—C(3)—C(2) | 108·3 (5) | 106·3 (6) | C(7)—C(6)—N(5) | 106·5 (5) | 108·4 (7) | C(8)—C(9)—C(1) | 100·9 (5) | 99·9 (5) |
| C(8)—C(3)—C(2) | 104·8 (6) | 105·0 (6) | C(10)—C(6)—N(5) | 113·4 (5) | 113·7 (8) | C(6)—C(10)—C(1) | 114·7 (6) | 114·9 (7) |
| C(8)—C(3)—C(4) | 113·2 (5) | 116·7 (5) | C(10)—C(6)—C(7) | 110·9 (5) | 111·0 (7) | | | |

Table 3. *Hydrogen-bond geometry* (Å *and* deg)

| $X$—H···$Y$ | $X$—H | H···$Y$ | $X$···$Y$ | $X$—H···$Y$ |
|---|---|---|---|---|
| N(5$A$)—H(5$A$)···O(1$A^{i}$) | 0·90 (6) | 2·08 (6) | 2·952 (6) | 162 (6) |
| O—H(O2)···O(1$A^{ii}$) | 1·11 (8) | 1·72 (9) | 2·795 (6) | 161 (7) |
| N(5$B$)—H(5$B$)···O$^{iii}$ | 0·86 (5) | 2·15 (6) | 2·900 (7) | 146 (5) |
| O—H(O1)···O(1$B^{iv}$) | 0·88 (6) | 1·93 (6) | 2·794 (6) | 167 (6) |

Symmetry code: (i) $\bar{x}+1, \bar{y}+1, \bar{z}+1$; (ii) $\bar{x}+1, y+\frac{1}{2}, \bar{z}+\frac{3}{2}$; (iii) $x, y-1, z$; (iv) $\bar{x}, \bar{y}+1, \bar{z}+1$.

Table 4. *Parameters and angles* (°) *describing the geometry of the amide group*

| Parameter | Definition | Values for the title lactam | |
|---|---|---|---|
| | | Molecule *A* | Molecule *B* |
| $\omega_1 = \omega[C(3)—C(4)—N(5)—C(6)]$ | | 14·7 (8) | 18·2 (9) |
| $\omega_2 = \omega[O(1)—C(4)—N(5)—H(5)]$ | | 10 (5) | 2 (4) |
| $\omega_3 = \omega[O(1)—C(4)—N(5)—C(6)]$ | | −168·4 (6) | −166·6 (7) |
| $\omega_4 = \omega[C(3)—C(4)—N(5)—H(5)]$ | | −167 (5) | −172 (5) |
| $\tau' = 2\tau = \omega_1 + \omega_2$ | (mod $2\pi$) | 25 (5) | 20 (4) |
| $\chi_C = \omega_1 - \omega_3 + \pi$ | | 3 (1) | 5 (1) |
| $\chi_N = \omega_2 - \omega_3 + \pi$ | | −2 (5) | −11 (4) |

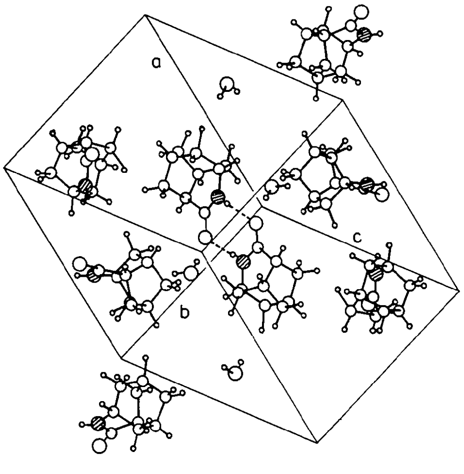

Fig. 2. The crystal packing. N atoms are shaded. The hydrogen bonds forming the cyclic dimer are shown.

### *The non-planar amide group*

The conformation of the amide group is determined by restrictions caused by the rigid tricyclic skeleton and by the crystal environment of this group. In the normal case, the atoms of this group are planar or nearly so, but sometimes non-planarity can occur. We can define the four torsion angles about the C′—N bond and the deformation of the *cis*-amide group is then described by the three independent parameters $\tau'$ (Winkler & Dunitz, 1971), $\chi_C$ and $\chi_N$ (Warshel, Levitt & Lifson, 1970). The definition of the four torsional angles about the amide bond and their relationship to $\tau'$, $\chi_C$ and $\chi_N$ are in Table 4. These torsional angles were calculated with the program *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The calculated values of $\tau'$, $\chi_C$ and $\chi_N$ for both *A* and *B* molecules are given in Table 4. The parameter $\tau'$ describes rotation about the C′—N bond and the values of $\chi_C$ and $\chi_N$ describe the non-planar arrangement of bonds about C′ and N atoms respectively. In most cases where the non-planar amide group occurs, the surroundings of C′ have been found to be almost planar, whereas the pyramidal distortion at N was highly significant (Ealick & van der Helm, 1977), in agreement with the predicted energy requirements given by Winkler & Dunitz (1971).

In our case, the highly non-planar character of the amide group was detected: the distances of O(1) and H(5) from the mean plane [C(3),C(4),N(5),C(6)] are −0·209 (4), 0·17 (6) Å (molecule *A*) and −0·201 (5), 0·11 (6) Å (molecule *B*). The $\chi^2$ values 306·6 and 412·5 show the significant non-planarity of these groups. The pyramidality at N is not significant in molecule *A*, but is more pronounced in molecule *B* (see Table 4). A slightly pyramidal arrangement of bonds can be seen at C′ in both *A* and *B* molecules. The most prominent contribution to the non-planarity of the amide group in *A* is the rotation about the C′—N bond. There is an essential difference between both conformational types *A* and *B* as a function of the hydrogen bonds. Molecules *A* are connected by the inter-amide hydrogen bonds into the cyclic dimers (see Fig. 2), while molecules *B* are connected indirectly by means of water molecules into chains. This causes different electron distributions in the amide groups and their different deviations from planarity.

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# Structure of (*Z*)-*N*-Acetyl-α,β-didehydrophenylalanyl-L-alanine Hydrate, $C_{14}H_{16}N_2O_4.\frac{1}{3}H_2O$

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**Abstract.** $M_r = 282{\cdot}25$, hexagonal, $P6_5$, $a = b = 10{\cdot}534$ (4), $c = 23{\cdot}753$ (11) Å, $V = 2283$ (2) Å$^3$, $Z = 6$, $D_m = 1{\cdot}230$ (by flotation in aqueous KBr solution), $D_x = 1{\cdot}232$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}836$ cm$^{-1}$, $F(000) = 896$, $T = 298$ K, $R = 0{\cdot}052$ for 950 reflections with $I > 2{\cdot}5\sigma(I)$. Molecules, linked by intermolecular hydrogen bonds, are arranged in helices along the *z* axis. The tendency of the phenyl ring to be planar with the C—C—N system causes a change to the expected bond angles. The conformational flexibilities of the saturated and unsaturated amino acids are discussed.

**Introduction.** Many biologically important peptides contain α,β-unsaturated amino-acid residues which are particularly interesting because of their unusual conformational and electronic features.

In previous papers we reported on the molecular structure of *N*-acetyldehydroalanine (dehydro-Ala-OH) which assumes an extended conformation in the crystal state (Ajò, Granozzi, Tondello, Del Pra & Zanotti, 1979) and, at least as far as the torsion angle $\varphi$ is concerned, also in the gas phase (Ajò, Granozzi, Ciliberto & Fragalà, 1980). In contrast, we have shown that (*Z*)-*N*-acetyldehydrophenylalanine (dehydro-Phe-OH) is non-planar both in the solid state and in the vapour phase (Ajò, Casarin, Granozzi & Busetti, 1981).

This behaviour is in agreement with theoretical conformational predictions for these compounds having a free or esterified carboxyl group (Ajò, Granozzi, Tondello, Del Pra & Zanotti, 1979; Ajò, Casarin, Granozzi & Busetti, 1981).

The dependence of crystal-state conformation on intermolecular (in particular, hydrogen-bonding) interactions has also been discussed for this class of compounds (Ajò, Busetti, Granozzi & Liakopoulou-Kyriakides, 1984; Ajò, Busetti, Ottenheijm & Plate, 1984).

Conformational studies of dehydrophenylalanine and its derivatives are of interest not only from a biological point of view (Rich & Bhatnagar, 1978, and references therein; Ajò, Granozzi, Tondello & Del Pra, 1980, and references therein) but also in order to investigate the

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