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Structure of *N*-Acetyl-2,3-didehydroproline, $C_7H_9NO_3$

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Abstract. $M_r = 155{\cdot}18$, orthorhombic, *Pbca*, $a = 13{\cdot}455$ (4), $b = 13{\cdot}466$ (4), $c = 8{\cdot}069$ (3)Å, $Z = 8$, $V = 1462{\cdot}0$ (8) Å^3, $D_x = 1{\cdot}410$, $D_m = 1{\cdot}41$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}90$ mm^{-1}, $F(000) = 656$, $T = 298$ K, final $R = 0{\cdot}042$ for 625 unique reflections. The molecules exhibit a non-planar conformation and are linked by hydrogen bonds to form one-dimensional chains. The conformational flexibility of this molecular system is discussed also on the basis of the known structures of related compounds and previously reported spectroscopic and theoretical results.

Introduction. α, β-Unsaturated amino acid residues are present in many natural peptides which exhibit biological activities (Rich & Bhatnagar, 1978, and references therein; Ajò, Granozzi, Tondello & Del Pra, 1980, and references therein). They are particularly interesting because of their unusual conformational (Ajò, Granozzi, Tondello & Del Pra, 1980; Ajò, Busetti & Granozzi, 1982; Ajò, Casarin & Granozzi, 1982; Busetti, Ajò & Granozzi, 1982; Ajò, Busetti, Ottenheijm & Plate, 1984) and electronic (Ajò, Granozzi, Ciliberto & Fragalà, 1980; Ajò, Casarin, Granozzi & Busetti, 1981) features.

In previous papers we reported on the crystal and molecular structure of *N*-acetyldehydroalanine (dehydro-Ala-OH) which assumes an extended conformation in the crystal state (Ajò, Granozzi, Tondello, Del Pra & Zanotti, 1979). 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).

These results encouraged us in pursuing conformational investigations of this series of compounds; *N*-acetyl-2,3-didehydroproline (dehydro-Pro-OH) could be of relevant interest, since the presence of a five-membered ring (*φ cisoid*) prevents both conformations found for dehydro-Ala-OH (*φ trans*) and dehydro-Phe-OH ($\varphi = 71{\cdot}7°$).

Conformational studies on dehydro-Pro-OH and suitable derivatives are also of interest in relation to *s-cis–s-trans* isomerization behaviour in solution, which is different both from that of other acylproline analogues and from that of some *N*-substituted α,β-unsaturated acylamino acids (Galardy, Alger & Liakopoulou-Kyriakides, 1982).

Experimental. Crystals of $C_7H_9NO_3$ provided by M. Liakopoulou-Kyriakides (Galardy, Alger & Liakopoulou-Kyriakides, 1982). D_m measured by flotation. Crystal 0·5 × 0·4 × 0·6 mm. Philips PW 1100 four-circle diffractometer. Cell dimensions from 32 high-angle reflections. θ–2θ scan mode, $2 < \theta < 23°$,

($h \leq 12$, $k \leq 12$, $l \leq 7$). Intensities and orientation of two reflections checked every 3 h: no significant variation. Lp correction, no absorption correction. 770 unique observations, 625 with $I > 2{\cdot}5\sigma(I)$. Structure solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least-squares refinement (on F), anisotropic thermal parameters for non-hydrogen atoms, unit weights. H atoms located on a difference map and included in refinement with isotropic temperature factor $U = 0{\cdot}04$ Å^2. Methyl group clearly disordered in two possible positions with occupancy 0·5. $\Delta/\sigma < 0{\cdot}3$. Final difference-map excursions between +0·13 and −0·16 e Å^{-3}. No correction for secondary extinction. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs: *SHELX*76 (Sheldrick, 1976), drawings with *ORTEP*II (Johnson, 1976).

Discussion. An *ORTEP* drawing of *N*-acetyl-2,3-didehydroproline (with numbering of the atoms and nomenclature of relevant torsion angles) is reported in Fig. 1 and the final positional parameters are in Table 1.* Bond distances and angles are shown in Fig. 2 and crystal packing is in Fig. 3: molecules are linked in one-dimensional chains by an intermolecular hydrogen-bonding system between the carboxylic O of the molecule at the origin and the amide carbonyl group at $(\frac{1}{2}-x,\ \bar{y},\ z-\frac{1}{2})$: O(2)···O(3) = 2·598 (5) Å, O(2)—H(1,O2)···O(3$^{\rm I}$) = 167 (5)°. An analogous hydrogen-bonding system [2·58(1) Å] is present in the crystal structure of *N*-propionylproline (Kamwaya, Oster & Bradaczek, 1981) but the conformation of the latter molecule is completely different (ω_1 *cis*, ψ *trans*). There is no other distance shorter than the sum of the van der Waals radii.

The dimensions of the peptide group are to some extent different from those usually found in simple peptides (Marsh & Donohue, 1967). Also, comparison with dehydro-Ala-OH and dehydro-Phe-OH gives contradictory results: the N—C$_\alpha$ bond length is 1·416 (5) Å, to be compared with the reported ones for dehydro-Ala-OH [1·409 (5) Å] and dehydro-Phe-OH [1·438 (6) Å]; the C$_\alpha$=C$_\beta$ bond length is 1·313 (6) Å [1·318 (7) in dehydro-Phe-OH and 1·328 (5) Å in dehydro-Ala-OH].

The conformation of dehydro-Pro-OH is described by the following torsion angles (see Fig. 1):

ω_1[C(1)—C(2)—N(1)—C(4)] = − 172·5 (5)°
φ [C(2)—N(1)—C(4)—C(3)] = − 26·3 (7)
ψ [N(1)—C(4)—C(3)—O(2)] = − 58·3 (6)
ω_2[C(4)—C(3)—O(2)—H(O2)] = − 160 (4).

The maximum displacement of the dihydropyrrole ring from the N(1)—C(4)—C(5)—C(6)—C(7) plane is 0·060 (5) Å.

Two main differences are evident with respect to the corresponding fragment in the antibiotic virginiamycin (Durant, Evrard, Declercq & Germain, 1974), in which the 2,3-didehydroproline residue is esterified. The first concerns ψ (*cisoid* in the title compound, *transoid* in virginiamycin): identical behaviour emerges from the comparison of dehydro-Phe-OH ($\varphi = 71{\cdot}7$, $\psi = 13{\cdot}9°$) and dehydro-Phe-OEt ($\varphi = 80{\cdot}8$, $\psi = -177{\cdot}4°$) (Ajò, Busetti, Ottenheijm & Plate, 1984); the *cisoid* conformation of ψ in dehydro-Phe-OH and dehydro-Pro-OH in the crystal state seems to be related, in these rather conformationally flexible systems, to the formation of intermolecular hydrogen bonds. The second difference is represented by the deviation of torsion angle ψ from 0 or 180°; this distortion is greater in dehydro-Pro-OH ($\psi = -147{\cdot}1°$ in virginiamycin), and, consistently, the deviation for φ is smaller ($\varphi = 46{\cdot}8°$ for virginiamycin). This behaviour is clearly related to repulsive interactions between the acylamido and carboxy groups, previously invoked to explain the relatively low barrier to *s-cis–s-trans* isomerization in solution. This interaction, in any case, prevents a fully planar conformation for these systems: in Fig. 4 we report the results of conformational calculations, carried out by the previously described method, and torsional potentials (Ajò, Granozzi, Tondello, Del Pra & Zanotti, 1979; see p. 929). The conformational-energy minimum is at $\psi = \pm 90°$ when $\varphi = 0°$, but it shifts towards $\psi = 0°$ or

Table 1. *Fractional positional parameters* ($\times 10^4$ *for non-hydrogen atoms,* $\times 10^3$ *for hydrogen atoms) and isotropic thermal parameters* (Å$^2 \times 10^3$), *with e.s.d.'s in parentheses*

$U_{\rm eq}$ = one third the trace of the diagonalized anisotropic temperature factor matrix.

	x	y	z	$U_{\rm eq}$
O(1)	658 (2)	−628 (3)	1488 (4)	51 (1)
O(2)	1618 (2)	711 (2)	1172 (4)	42 (1)
O(3)	2036 (2)	296 (2)	4593 (4)	45 (1)
N(1)	712 (3)	1304 (2)	4388 (4)	34 (1)
C(1)	1821 (6)	1492 (5)	6758 (8)	53 (2)
C(2)	1527 (4)	987 (3)	5179 (6)	38 (2)
C(3)	877 (3)	212 (4)	1841 (5)	36 (2)
C(4)	281 (3)	832 (3)	2994 (5)	32 (2)
C(5)	−654 (4)	1093 (3)	2828 (6)	44 (2)
C(6)	−967 (4)	1812 (4)	4130 (7)	50 (2)
C(7)	−17 (4)	2009 (4)	5088 (7)	47 (2)
H(1,O2)	221 (4)	26 (4)	68 (7)	
H(1,C1)	159 (6)	233 (6)	690 (9)	
H(2,C1)	140 (11)	122 (8)	755 (16)	
H(3,C1)	262 (8)	146 (6)	695 (10)	
H′(1,C1)	142 (9)	148 (9)	744 (19)	
H′(2,C1)	216 (6)	218 (7)	654 (10)	
H′(3,C1)	248 (7)	107 (6)	742 (10)	
H(1,C5)	−110 (3)	79 (3)	197 (5)	
H(1,C6)	−142 (3)	154 (3)	482 (5)	
H(2,C6)	−126 (3)	237 (3)	363 (5)	
H(1,C7)	23 (3)	261 (3)	503 (5)	
H(2,C7)	−3 (3)	194 (3)	629 (5)	

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38945 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$\psi = 180°$ when φ deviates from 0° within the limited conformational flexibility of the *unsaturated* five-membered ring. The conformation of *N*-propionylproline represents the extreme element of this series: in this case the flexibility of the *saturated* five-membered ring allows a greater deviation of φ ($\varphi = -75{\cdot}5°$), and, consistently, a nearly planar conformation (175·5°) around ψ.

On the basis of the above considerations we suggest for dehydro-Pro-OH a high (although less than in proline derivatives) conformational flexibility; the actual crystal-state conformation is mainly determined by intermolecular (in particular, hydrogen-bonding) interactions.

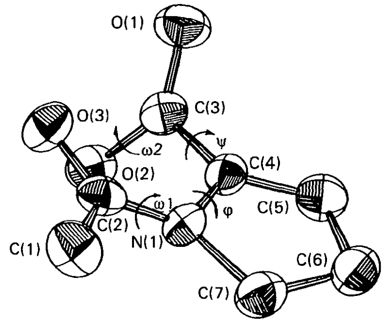

Fig. 1. An *ORTEP* drawing of the title compound with the atom-numbering scheme and torsion angles.

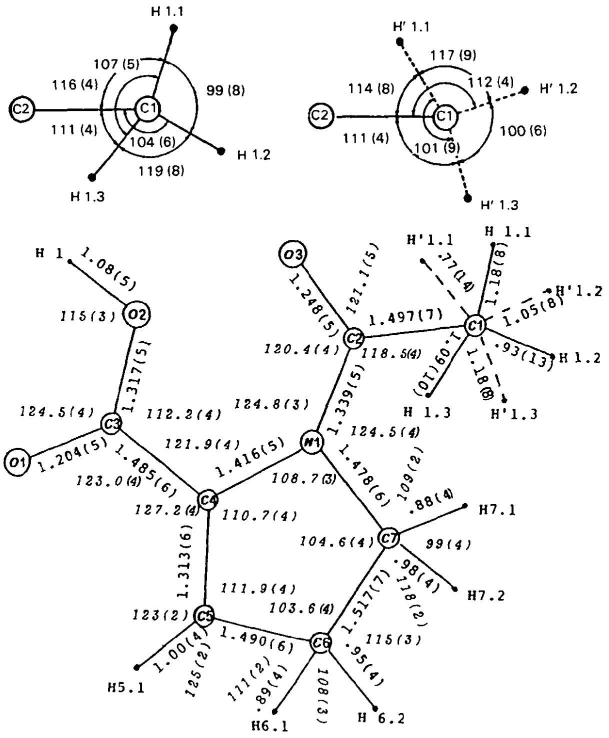

Fig. 2. A schematic view of the title molecule showing bond distances (Å) and angles (°); e.s.d.'s are in parentheses.

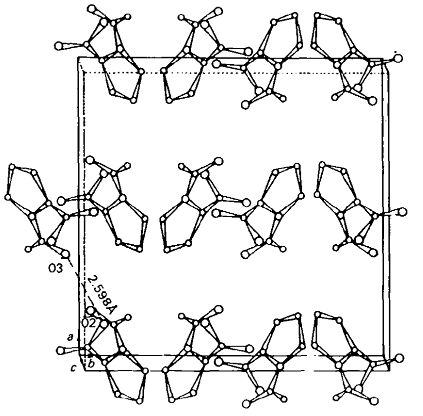

Fig. 3. Molecular packing in the unit cell.

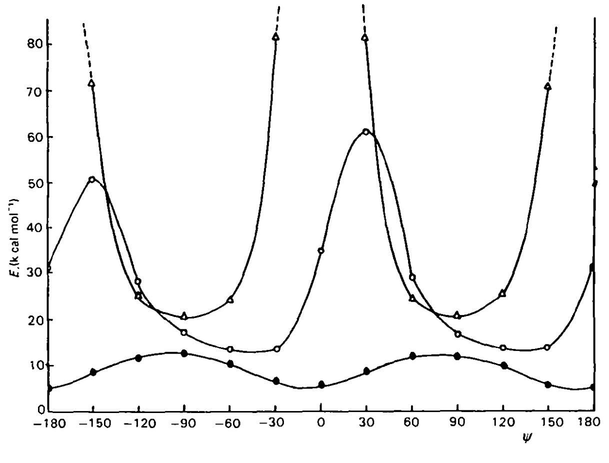

Fig. 4. Conformational-energy curves of dehydro-Pro-OH. (1 kcal mol^{-1} ≡4·2kJ mol^{-1}.) Triangles: $\varphi = 0°$; open circles: $\varphi = -30°$; filled circles: $\varphi = -60°$.

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Structure of Methyl 8-Isopropyl-3,3a,8,8a-tetrahydroindeno[2,1-*c*]pyrazole-8a-carboxylate, $C_{15}H_{18}N_2O_2$

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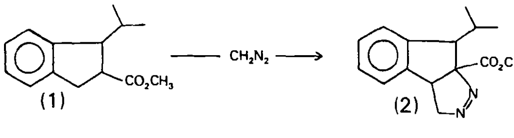
Abstract. $M_r = 258{\cdot}8$, triclinic, $P\bar{1}$, $a = 5{\cdot}764\,(4)$, $b = 15{\cdot}400\,(3)$, $c = 15{\cdot}810\,(4)$ Å, $\alpha = 97{\cdot}45\,(6)$, $\beta = 100{\cdot}39\,(5)$, $\gamma = 100{\cdot}82\,(6)°$, $V = 1375\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}25$, $D_m = 1{\cdot}27$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}078$ mm^{-1}, room temperature, $F(000) = 552$, $R_w = 0{\cdot}065$ for 1518 reflexions (6616 unique observations). There are two crystallographically independent molecules in the asymmetric unit. The isopropyl and methoxycarbonyl groups are *cis*.

Introduction. The cycloaddition reaction of diazomethane with compound (1) leads to the tricyclic compound (2). Knowledge of the stereochemistry of this compound was necessary to explain the stereospecificity of the reaction (Vebrel, Cetutti & Carrie, 1979; Vebrel & Carrie, 1983). An X-ray analysis was therefore necessary.



Experimental. Crystal (cubic form: 0·2 × 0·2 × 0·2 mm) grown from a saturated solution in ethanol. Unit cell: least-squares refinement of a set of 25 reflections. Automated Enraf–Nonius CAD-4 diffractometer, monochromatized Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode. $\theta_{\max} = 28°$. Range of *hkl*: $\bar{7}$, 7; $\overline{20}$, 20; 0, 21. Standard reflections (024, $\bar{1}01$, 040): ± 1%. 6853 reflections measured, 6616 unique [1518 with $I > \sigma(I)$], $R_{\rm int} = 0{\cdot}024$. Structure solved by direct methods (Germain, Main & Woolfson, 1971) after computing normalized structure factors. All heavy atoms of the two independent molecules obtained with the best set. After refinements, a Fourier synthesis revealed all the H atoms (between 0·315 and 0·153 e Å^{-3}). The isotropic thermal parameters assigned to the H atoms were not refined. The last refinement (on F) with $1/w = \sigma^2/F = 1/4\,[(\sigma^2/I) + (0{\cdot}04)^2I]$ lowered R_w to 0·065 and R to 0·069. $\Delta/\sigma = 0{\cdot}9$ for H atoms, 0·08 for non-H atoms. No correction for secondary extinction or absorption. All calculations performed on a Digital PDP 11/60 computer with the *SDP* package (Frenz, 1978).

Discussion. Atomic parameters are given in Table 1.* Bond distances and angles are in Fig. 1. These data agree with normal values, and differences between corresponding bond distances in molecules *A* and *B* are not statistically significant. The two pyrazoline rings have a classical conformation: the dihedral angles are respectively 25·5 and 24·6°.

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms and atomic coordinates for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38963 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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