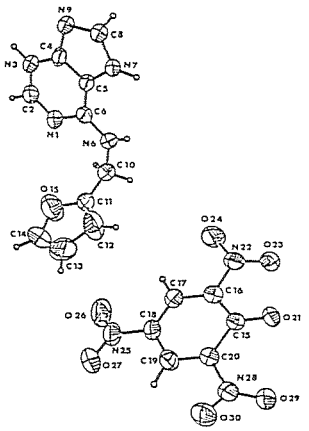
03.2–14 CRYSTAL AND MOLECULAR STRUCTURE OF KINETIN-PICRATE: A NOVEL COMPOUND CONTAINING A N(3)H AND N(7)H TAUTOMERIC FORM OF PURINE. By Manuel Soriano-García and R.A. Toscano, Instituto de Química,Universidad Nacional Autónoma de México, Circuito Exterior,Ciudad Universitaria, 04510 México D.F. México.

6-furfurylaminopurine (Kinetin) is a highly potent growth factor (cytokinin) which is implicated in many aspects of plant growth. It promotes cell division and differentiation. A 1:1 crystal complex of kinetin and picric acid was crystallized and we present its crystal and molecular structure as an appropiate model compound for studying the structural properties of cytokinins in an ionic environment.

The complex, $C_{16}H_{12}N_8O_8$, crystallizes in the monoclinic system, space group $P2_1/n$, with cell dimensions (at 18 ±2 °C) a= 4.995(1) Å, b= 13.931(3) Å, c= 26.065 (8) Å, β= 90.99(2)°, ρ= 1.63 g/cm^3 and Z= 4. The structure was solved from diffractometer data by direct methods and refined by a cascade matrix least-squares techniques to R= 0.05 using 2040 observed reflections.

The present structure provides the first description of the adenine moiety with the N(3)H and N(7)H tautomers The molecular geometry of the adenine ring found in this structure differs considerably from the assumed in theoretical calculations on the N(3)H tautomer of purine. The kinetin cation assumes a similar conformation from that found in the crystal structure of kinetin (M. Soriano-Garcia and R. Parthasarathy, Biochem. Biophys.Res. Commun., 64, 1062 (1975); M. Soriano-García and R. Parthasarathy, Acta Crystallogra. B33, 2674 (1977)). The molecular geometry within the picrate ion is not significantly different from those found for the picric acid and picrate salts. In the crystal, the kinetin cations and the picrate anions are aggregated separately into alternating layers. The molecules of kinetin cations are held together in pairs across centers of symmetry by N(3)-H···N(9) hydrogen bonds. The two layers of unlike molecules are interconnected primarily through a specific ion-pair interaction between the N(7) of the imidazole ring and the deprotonated oxygen atom O(21) of the picrate ion.



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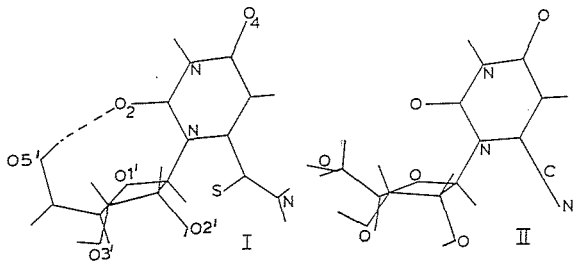
03.2–15 POLYMORPHS OF CYCLOAMANIDE A, CYCLIC (LPro-LVal-LPhe-LPhe-LAla-Gly), CONTAINING AN UNUSUAL β-BEND. By Isabella L. Karle and Chian Chian Chiang. Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375, USA.

Cycloamanide A, $C_{33}H_{42}N_6O_6$, isolated from *Amanita phalloides*, occurs in more than one crystalline pseudo polymorph. Form I (Chiang, Karle and Wieland, Int. J. Peptide Protein Res. (1982) 20, 414-420) has 4 H_2O solvent molecules while Form II has 1 H_2O and 3 C_2H_5OH solvent molecules. The crystals are not isomorphous, although the peptide molecules are isostructural. Both crystals have space group $P2_12_12_1$ with a = 13.307(2) A, b = 24.820(4) A and c = 11.231(1) A for Form I and a = 16.716(2) A, b = 24.007(3) A, and c = 10.918(1) A for Form II. The unusual intramolecular hydrogen bond in the β-bend encompassing the sequence LPhe-LAla occurs in both crystal forms. The β-bend has torsional angles characteristic of a Type II' bond (for a D,L sequence) rather than the expected Type I (for an L,L sequence). The ϕ,ψ values for L-Phe^4 and L-Ala^5 are +60°, -122° and -86°, -5° respectively (in Form II). The aberrant residue, L-Phe^4, lies in the D-region of the ϕ,ψ map that is forbidden to L- residues. In the present structure, C_4^β in the atypical β-bend is at a distance of only 2.84 A from N_5. To achieve a separation even as large as 2.84 A required an increase of 2-4° in the values for the $C_4'C_4^\alpha C_4^\beta$ and $C_4^\alpha C_4'N_5$ angles from the average values that have been observed in other peptides. One water molecule is buried in an excessively hydrophobic region to provide hydrogen bonds to two amide and two carbonyl moieties. The stability of the conformation of cyclic peptides in different solvent environments is demonstrated.

03.2–16 CONFORMATIONAL ANALYSIS OF 6-SUBSTITUTED URIDINE INHIBITORS OF OROTIDYLATE DECARBOXYLASE: CRYSTAL STRUCTURES OF 6-THIOCARBOXAMIDOURIDINE AND 6-CYANOURIDINE. By Vivian Cody, Medical Foundation of Buffalo, Inc., Buffalo, NY 14203, and Thomas I. Kalman, Medicinal Chemistry Department, SUNY/Buffalo, Amherst,NY 14260 USA

To investigate the mechanism of the orotidylate (OMP) decarboxylase catalyzed reaction, inhibitors of the enzyme were synthesized and tested against yeast OMP decarboxylase. The 6-carboxamido and 6-thiocarboxamido derivatives of uridine monophosphate (UMP), analogues of the substrate, were designed as molecular probes of the carboxylate binding-site of the enzyme. These studies showed that thiocarboxamido-UMP is >30,000-fold more potent than carboxamido-UMP as an inhibitor of the decarboxylase. These compounds are active only as the monophosphates. We report the crystal structure analysis of 6-thiocarboxamidouridine (I) and 6-cyanouridine (II), a synthetic intermediate, as part of this study. Both compounds crystallize in the orthorhombic space group P212121 with z = 4. The lattice parameters for I ($C_9H_{11}O_6N_3S$) are a = 9.201(3), b = 14.522(5), c = 9.033 (3)Å, and for II ($C_9H_{10}O_6N_3$) are a = 10.068(2), b = 16.219(2), c = 7.048(1)Å. These data show that the presence of the 6-substituent causes the glycosyl bond to adopt a syn conformation in each structure (χ = 251° and 252°, for I and II, respectively). The furanose ring conformation in I is C3'-endo-C4'-exo and in II it has a C3'-endo pucker. The phase angle P of the sugars is 62° and 29°, and the amplitude of the ring pucker, τ_m, is 35° and 25° for I and II, respectively. The values seen for II are smaller than normally observed. Comparison of these structures with 6-methyluridine (JACS 94:6520 (72);102: 5586(80)) and orotidine (6-carboxyuridine, ACA abs.2:35(74)), shows that all of these compounds adopt a syn conformation because of the steric interactions with the sugar and the 6-substituent. Since all of these groups have different electronic properties, it is the

bulk that influences the conformation, rather than the nature of the group. The plane of the thiocarboxamido group is nearly perpendicular to the pyrimidine plane with C–S = 1.655A, and C–N = 1.318A, typical for such functional groups. The conformation of the glycoside 5'–hydroxy is gauche–gauche with respect to the furanose ring and has the 5'–hyroxyl hydrogen pointed toward, and 2.84A from, O2 to form an intramolecular hydrogen bond. This intramolecular hydrogen bonding is observed in many of the uridine structures studied, in particular those with a 6–substituent. This feature is considered a stabilizing effect for a syn conformation. The closest intramolecular contacts that the thiocarboxamido makes is S...O1' = 3.66A and N...O2' = 3.98A. However, in the cyano compound, the 5'–hydroxyl is in a gauche–trans conformation and its hydrogen forms an intermolecular hydrogen bond. The cyano group is nearly coplanar (24°) with the pyrimidine ring. In both structures, the furanose hydroxyls form a newtwork of intermolecular hydrogen bonds with adjacent molecules in the lattice.



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03.2–17 THE STRUCTURE OF N–ACETYL–α,α–DIETHYLGLYCINE–N'–METHYLAMIDE MONOHYDRATE, $C_9H_{18}N_2O_2 \cdot H_2O$. By Z. Gałdecki* and B. Luciak, Institute of General Chemistry* and Institute of Physics, Technical University of Łódź, Żwirki 36, 90–924 Łódź, Poland.

In recent years an interest in α,α–dialkylamino acids and their peptides has increased because of the presence of α–methylalanine and α–ethylalanine in ionophore antibiotics and in peptide hormone analogues. It was stated that diethylglycine (Deg) incorporation into peptide chain is more difficult than methylalanine. It is accounted for steric hindrances (Redliński A., private communication). In order to explain this problem and to determine the conformation of Deg residues in linear peptide, crystal structure investigations of the title compound (Ac–Deg–NHMe) have been undertaken. The compound crystallizes in two forms. We examined a structure of the more stable form, with melting point at 684K, which crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters: $a = 7.139(1)$, $b = 11.823(2)$, $c = 15.778(3)$ Å, $\beta = 122.23(1)^\circ$, $Z = 4$, $D_m = 1.20$, $D_x = 1.204 Mgm^{-3}$. The intensities of 1523 independent reflections were collected using CuKα radiation. The structure was solved by direct methods (MULTAN) and refined by full–matrix least–squares to a final $R = 0.046$. The positions of all H atoms were found from ΔF syntheses and were refined isotropically. The parameters of the remaining atoms were refined assuming anisotropic temperature factors. The view of the molecule along [010] is shown in the picture. The X–ray study revealed one molecule of crystallizing water, which forms two hydrogen bonds O···O with the peptide molecules. Their lengths are 2.763 and 2.801 Å. The hydrogen bonds connect the peptide molecules into chains parallel to [201]. The torsion angles in Ac–Deg–NHMe are: $\omega_0 = 171.2(6)$, $\varphi_1 = 68.9(8)$, $\psi_1 = 19.5(9)$, $\omega_1 = 178.5(7)^\circ$. Comparison of the torsion angles values with those for α–helical and 3_{10}–helical conformations indicates that in the crystal of Ac–Deg–NHMe the Deg residues exist in a conformation more close to 3_{10}– than to α–Helix. On the basis of the atomic parameters from X–ray study the INDO and IEHT calculations were carried out using the programs QCPE141 and FORTICON. The results of the calculations will be discussed.

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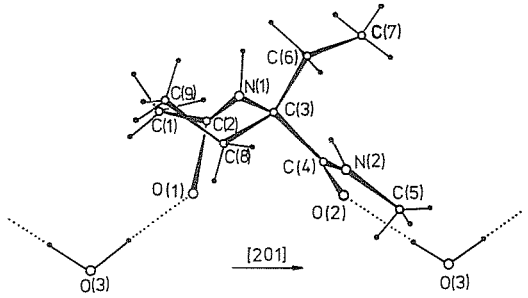

03.2–18 STRUCTURAL STUDY OF $[CoPO_8C_{10}N_4H_{11} \cdot (H_2O)_4] \cdot 3H_2O$. By E. Molins, A. Caubet, C. Miravitlles, X. Tejada and V. Moreno. Facultat de Física and Facultat de Química, Universidad de Barcelona. Fac. de Química, Tarragona. Instituto "Jaime Almera", C.S.I.C., Apartado 30102, Barcelona. Spain.

In our departments we are working on metal complexes of purine and pyrimidine nucleotides (V. Moreno et al. Inorg. Chem. to be published). In order to make a decisive confirmation of Co–5'IMP etablished by means of spectral and chemical techniques, it was undertaken its study by X–ray diffraction methods. The crystals are pale violet with a = 6.877(3), b = 10.909(6), c = 26.102 (9) A, $P2_12_12_1$ and Z = 4. The Co and P atoms were located by direct methods (MULTAN 11/82) and the remaining atoms by succesive Fourier synthesis. At this stage the structural model doesn't correspond with the expected one. Full matrix least–squares refinement was carried out with the SHELX–76 program. The final R–value is 0.080. The final structural model shows that, during the synthesis, the ribose ring is broken and the fragment C3P–O3P is caught by the Co–atom and used for connect it to the phosphate group. Similar processes can occur in biological reactions.