

03.2-5 CRYSTAL TRANSFORMATION AND CONFORMATIONAL CHANGE OF DISODIUM ADENOSINE 5'-TRIPHOSPHATE AND THE STRUCTURE OF $\text{ATPNa}_2 \cdot 2\text{H}_2\text{O}$. By Yoko Sugayara and Hitoshi Iwasaki, The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan.

Single crystals (I) of ATPNa_2 , presumably trihydrate, grown from the water - 1-propanol solution ($P2_12_12_1$, $a = 29$, $b = 21$, $c = 7.0 \text{ \AA}$) were unstable and transformed into another form (II, $a = 30.35$, $b = 20.83$, $c = 7.027 \text{ \AA}$) within a month. They further changed gradually into dihydrate (III, $a = 27.57$, $b = 21.07$, $c = 7.085 \text{ \AA}$) within next nine months. The space group remained unchanged during these crystal transformations.

The cell parameters of II coincided with those of the trihydrate (Kennard et al., Proc. Roy. Soc. London (1971) A325, 401; Larson, Acta Cryst. (1978) B34, 3601; hereafter KL). Refinement starting from the Larson's parameters based on our own intensity data confirmed general features of the KL structure, except that the assignment of O(W4) and Na(4) in KL should be interchanged.

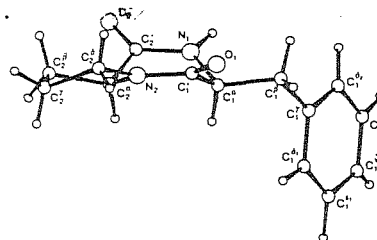
The structure of III, $\text{ATPNa}_2 \cdot 2\text{H}_2\text{O}$, was solved by the direct methods and refined to $R = 0.096$ for 2509 reflections ($|F_o| \geq 3\sigma(F_o)$). All interatomic distances and bond angles could be refined to chemically reasonable values without any constraints. Of the two symmetry-independent ATP molecules A and B, the structure of A is similar to that of KL, but the conformation of B is unique: the ribose ring takes the 4E ($C(4')$ -endo) form and $O(4')-C(4')-C(5')-O(5')$ is trans. The bridging P-O bond lengths range from 1.54 to 1.64 \AA with an average of 1.60 \AA . The crystal structure is closely related to that of II. III is lacking in the water molecules corresponding to O(W1) and O(W4) (originally assigned to Na(4)) of KL. Hydrogen bond network involving the hydroxyl oxygen atoms of the ribose groups is quite different from that in II.

03.2-6 CYCLIC DIPEPTIDES CONTAINING PROLINE. THE CRYSTAL STRUCTURE AND CONFORMATION OF CYCLO(-L-PHE-L-PRO-). By F. Mazza, Istituto di Strutturistica Chimica "G. Giacomello" CNR, C.P. n. 10, 00016 Monterotondo Stazione, Roma and by F. Pinnen, G. Zanotti and G. Lucente, Istituto di Chimica Farmaceutica, Facoltà di Farmacia, Università di Roma "La Sapienza", 00185 Roma (Italy).

Cyclic oligopeptides, both in the solid state and in solution, represent simple and valuable models to gain information on peptides and proteins. A large number of data have been obtained by studying cyclic systems containing amino acids with aromatic side-chains and/or cyclic imino acids. The constraint imposed by the presence of an additional ring and the possible interaction between the aromatic side chain with the peptide bonds have focused the attention on these models. As continuation of our studies in this field (S. Cerrini, W. Fedeli, G. Lucente, F. Mazza, F. Pinnen and G. Zanotti, Int. J. Peptide Protein Res., 1983, 22) we here report the crystal and molecular structure of cyclo(-L-Phe-L-Pro-): $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$, monoclinic, s.g. $P2_1$, $a = 10.789(2)$, $b = 10.061(2)$, $c = 5.668(3) \text{ \AA}$, $\beta = 92.70(3)^\circ$, $V = 614.5(5) \text{ \AA}^3$, $Z = 2$. The structure has been solved by MULTAN and refined to a final R and R_w respectively of 0.038 and 0.054 for 1895 independent reflec-

tions with $I > 2.0\sigma(I)$. The conformation of the molecule is shown in the Figure.

The diketopiperazine (DKP) ring assumes a boat conformation with equatorial β -carbon atoms. The ω_1 and ω_2 torsion angles are -4.5 and -0.5° respectively. The DKP-ring is folded along the line joining the α -carbon atoms with a β value of 51° . This degree of folding is the largest so far observed for such ring systems (I.L. Karle: The Peptides Gross-Meienhofer eds., Ac. Press(1981), 4,6). The C_1^α and C_2^α atoms lie 0.603 and 0.551 \AA respectively above the mean plane of the other four ring atoms. The pyrrolidine ring assumes the $C_2-C_2^\beta-C_2^\gamma$ -endo- C_2^γ -exo half-chair conformation and the benzylic side-chain is in an extended conformation toward the nitrogen. An hydrogen bond of 2.988 \AA between the phenylalanine NH and CO groups of screw related molecules characterizes the crystal packing. Conformational comparisons with other cyclic dipeptides containing proline will be discussed.



03.2-7 OBSERVATION OF A HIGHLY EXTENDED PARALLEL CHAIN PLEATED SHEET ARRANGEMENT: THE CRYSTAL STRUCTURE OF L-VALYL-GLYCYL-GLYCINE. By V. Lalitha, R. Murali and E. Subramanian, Department of Crystallography and Biophysics, University of Madras, Madras-600 025, India.

The tripeptide, L-valyl-glycyl-glycine, crystallizes from water in the monoclinic space group $C2$, with $a = 24.058(3)$, $b = 4.801(1)$, $c = 10.623(2) \text{ \AA}$, $\beta = 110.02(1)^\circ$, $Z = 4$. $\text{CuK}\alpha$ intensity data for 813 reflections ($\sin\theta/\lambda < 0.53 \text{ \AA}^{-1}$) from a diffractometer were used to solve the structure by direct methods using SHELX84 computer program and to refine the structure anisotropically to a final R -index of 0.045.

The peptide chain has an extended all trans conformation, with $\psi_1 = 123.1^\circ$, $\omega_1 = -179.5^\circ$, $\beta_2 = -155.1^\circ$, $\psi_2 = 154.7^\circ$, $\omega_2 = 170.7^\circ$, $\beta_3 = -146.6^\circ$, and $\psi_3 = 180.0^\circ$. The peptide chain repeat distance ($1C^\alpha - 3C^\alpha$) is 7.25 \AA . The conformation of the valyl side chain is given by $\gamma_{11} = -52.5^\circ$, $\gamma_{12} = -174.2^\circ$.

Two interpeptide hydrogen bonds (3.05 \AA , 3.05) between adjacent molecules related by the b -translation of the lattice gives rise to the familiar extended parallel chain pleated β -sheet arrangement, with angles at hydrogen atoms of 148° and 151° . The conformation adopted by the molecule in forming the parallel chain arrangement appears to be the most extended in comparison to all previous observations.