The Crystal Structure of Dihydrouracil: an Unusual Base of Transfer Ribonucleic Acid

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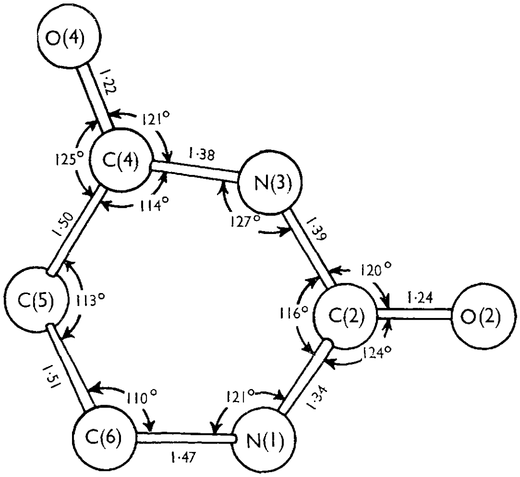
THE determination of the crystal structure of dihydrouracil was undertaken as part of the research on the stereochemistry of nucleic acid constituents. Dihydrouracil is one of the unusual heterocyclic bases present in transfer ribonucleic acid (t-RNA).[1] It is believed that the unusual constituents give t-RNAs their unique three-dimensional structures, making them suitable for their central role in the translational mechanism of protein synthesis.

Crystals of dihydrouracil were grown from dimethyl sulphoxide. The selection of a single-crystal for the present work was made difficult by the very pronounced cleavage exhibited by the crystals parallel to the (001) plane. Crystal data: $C_4H_6N_2O_2$, $M = 114$, monoclinic, $a = 4{\cdot}21 \pm 0{\cdot}01$, $b = 5{\cdot}81 \pm 0{\cdot}01$, $c = 19{\cdot}78 \pm 0{\cdot}01$ Å, $\beta = 95{\cdot}1 \pm 0{\cdot}1°$, $U = 482$, D_m (by flotation) $= 1{\cdot}58$, $D_c = 1{\cdot}58$, $Z = 4$, space group $P2_1/c$ (C^5_{2h}, No. 14), Cu-K_α ($\lambda = 1{\cdot}5418$ Å) radiation. Intensities of approximately 715 independent non-zero reflections were recorded on a Picker four-circle automatic diffractometer to a maximum 2θ value of 134°. The crystal structure was solved by a consideration of molecular packing and the application of the symbolic-addition method.[2] Refinement by isotropic and anisotropic full-matrix least-squares methods led to the present discrepancy index R of 0·10.

The bond lengths and bond angles are shown in the Figure. Many of the ring bonds show marked lengthening in comparison with uracil.[3] The greatest difference is in the C(5)–C(6) bond, which is 1·50 Å in dihydrouracil but only 1·34 Å in uracil. The variations in the bond distances indicate substantial change in the π-electron delocalization in the reduced pyrimidine system. A notable feature of the structure is the half-chair conformation of the six-membered ring, with atoms C(5) and C(6) displaced by about 0·3 Å on opposite sides of the ring plane. Thus, dihydrouracil is the only non-planar base in t-RNA. The ring puckering and the electronic changes accompanying hydrogenation are expected to influence its base-pairing and stacking characteristics in nucleic acids.



We thank Dr. S. T. Rao and Dr. J. Jackobs for computational help and the National Institutes of Health for support.

(*Received, May 6th,* 1968; *Com.* 554.)

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