Structure of the *cis–syn*-Photodimer of Uracil: A Puckered Cyclobutane

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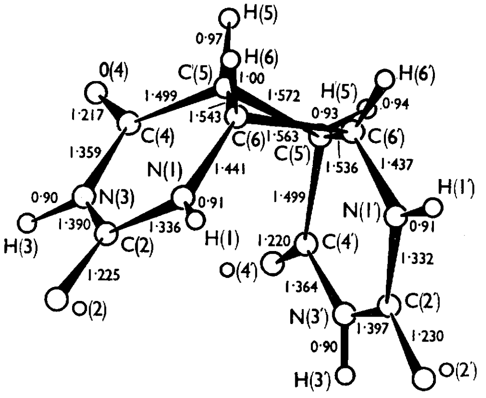
URACIL DIMERS have been isolated from irradiated frozen solutions of the monomer[1] and from irradiated TMV-RNA.[2] Although the biological significance still remains unknown, the occurrence of uracil photodimers has led to the elucidation of the structure of one of four possible isomers. The structure of the ice dimer has been shown by n.m.r. methods[3] and by chemical methods[4] to be the *cis-syn*-dimer. We report the determination of the structure by *X*-ray diffraction: the ice dimer is indeed the *cis-syn*-isomer, and the cyclobutane ring is puckered in the solid state.

Uracil dimer was made by irradiation of a frozen uracil solution (500 mg./l.), 125 ml. at a time[5] and recrystallized from water. The dimer has an R_F of 0·20 in isopropyl alcohol–water (3 : 1, v/v) and 0·30 in n-propanol–water (7 : 3, v/v), on t.l.c., corresponding to UU_4 of Greenstock and Johns.[6] (Uracil R_F's are 0·58 and 0·66 respectively.) The crystals are monoclinic, space group $P2_1/n$ (a = 13·249 ± 0·001, b = 11·191 ± 0·001, c = 6·279 ± 0·0002 Å, β = 94·751 ± 0·004°).

The structure was solved by direct methods from the phases of 264 of the 2135 independent reflections (including 507 "unobserved") collected on a diffractometer. The final R, after refinement by full-matrix least-squares, is 0·045. Non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen with isotropic thermal parameters. Standard deviations in non-hydrogen atom bond-lengths are 0·0025 Å, and in bonds involving hydrogen, 0·026 Å.



FIGURE

The molecule and the bond lengths are shown in the Figure. Hydrogen-bonding to six neighbouring molecules, with an average bond-length of 2·869 Å, forms a strong three-dimensional network in the crystal. The heterocyclic rings are not planar: C(5) and C(6) in each ring are $-0{\cdot}13$ Å and $+0{\cdot}15$ Å out of a "best" plane through each ring. The cyclobutane ring is puckered, with a dihedral angle of 155° comparable to other puckered cyclobutane rings.[7] The heterocyclic rings are "twisted" relative to one another: the dihedral angles looking along the C(5)–C(5′) and C(6)–C(6′) bonds are 23° and 25° respectively. The bond lengths in both heterocyclic rings, with the exception of the C(5)–C(6) bonds, agree very well with those found in the *trans-anti*-thymine dimer,[8] which has a planar cyclobutane ring. Thus, the conformation of the cyclobutane ring appears to have no effect on the conformation of each heterocyclic ring. However, the relative twist resulting from the puckered cyclobutane ring in the *cis-syn*-dimer may be advantageous in the formation and/or stabilization of the dimer in polymer structures such as RNA.

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