

Crystal and Molecular Structure of a 6-Methyluracil Photodimer

IRRADIATION of a frozen aqueous solution of thymine with 254 nm light resulted in the formation of a cyclobutyl dimer of thymine (T=T)¹⁻³. An analogous uracil dimer (U=U) is formed when uracil is irradiated under similar conditions^{4,5}. These results are of great importance in understanding the photochemistry and photobiology of nucleic acids (reviews, refs. 2, 5, 6). Thus much work has been carried out on the mechanistic study of the photodimerization of pyrimidines⁷. The photodimerization of α,β -unsaturated ketones may be examined similarly. As part of these studies the four dimers of 6-methyluracil (6 MU), for example, *cis-syn*, *cis-anti*, *trans-syn* and *trans-anti*, have been isolated in a pure state from 6 MU under a variety of conditions. The stereoconfigurations of these dimers of 6 MU=6 MU have been assigned (unpublished work) using techniques such as NMR, IR and chemical reactivities; however, the complete three-dimensional structure can only be determined by X-ray diffraction analysis. The crystal and molecular structure of a *cis-syn* type of 6 MU=6 MU has recently been reported⁸. In this communication we report the X-ray diffraction study of the *cis-anti* isomer.

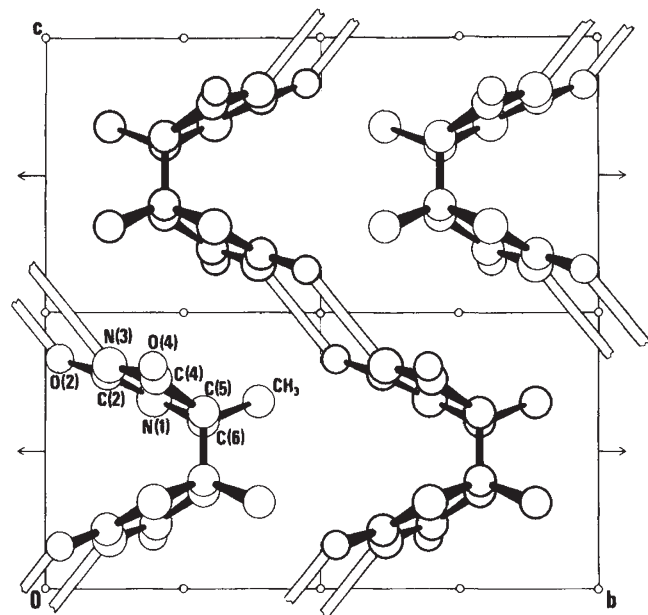


Fig. 1 Projection of the structure on (100). Double lines indicate hydrogen bonds. The two-fold axis of rotation shown in the figure will generate C'(6) from C(6), and so on.

A single crystal of this dimer (see ref. 8 for isolation procedure) measuring $0.5 \times 0.6 \times 0.2$ mm was used. It was found to be monoclinic with a , 6.84 ± 0.02 Å; b , 12.70 ± 0.04 Å; c , 12.58 ± 0.04 Å; β , $96.56^\circ \pm 0.20^\circ$ and space group $C 2/c$ with four molecules per unit cell. X-ray intensities were measured using a Hilger and Watts linear diffractometer with MoK_α radiation. Of the 960 independent reflexions observed, 890 showed significant differences between peak and background counts. Three strong reference reflexions were monitored periodically and showed no significant changes during the course of the X-ray measurements. The structure was determined using the symbolic addition procedure¹⁰. All the non-hydrogen atoms were located on a Fourier map computed with the most probable sign combination. The positional and thermal parameters of the C, N and O atoms were refined by a least squares procedure. The index of agreement (R_1) between observed and calculated structure factors for the 890

reflexions used in the calculations is 11%. Although our results clearly establish the molecular structure, further work of refinement is being continued.

The main features of the molecular and crystal structures are shown in Fig. 1. Bond distances and angles are similar to those found in the other photodimers studied thus far^{9,11-17}. The principal features of the molecular structure are, first, the molecule is a *cis-anti* isomer and has a two-fold axis of symmetry perpendicular to the cyclobutyl ring; second, the cyclobutyl ring is nearly planar, with a dihedral angle of 178° ; third, the eight atoms of the uracil moiety are practically coplanar: the maximum deviation of one of the atoms of the pyrimidine ring from the "best" plane passing through the atoms of the nucleus corresponds to C(5) and has a value of 0.005 Å; fourth, atoms of the pyrimidine nuclei nearly overlap when projected on a plane perpendicular to the C(6)-C(5), C(5)-C(6) bonds, the angular displacement being 6° ; and fifth, the angle between the "best" planes passing through the cyclobutane and pyrimidine rings has a value of 115.8° . The molecules are held together in the crystal by hydrogen bonds and by van der Waals contacts. The hydrogen bonds are (1) those connecting O(4) and N(1) of one dimer with N(1) and O(4), respectively, of the dimer located one a unit cell translation above the first (not shown in Fig. 1); (2) those connecting O(2) and N(3) of one dimer with N(3) and O(2), respectively, of another dimer (Fig. 1). The hydrogen bonds give rise to a two-dimensional network nearly perpendicular to the b axis. The van der Waals contacts involve the methyl groups and connect the hydrogen bonded networks in the third dimension, nearly parallel to the b axis (Fig. 1).

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