

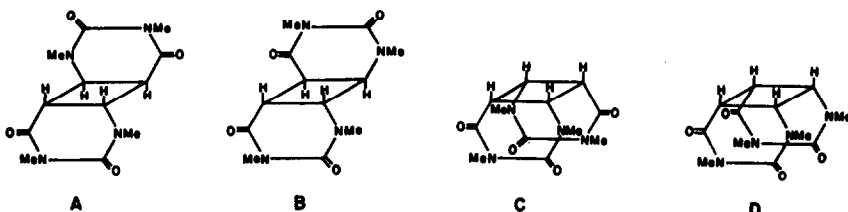
STRUCTURES AND STEREOCHEMISTRY OF THE
FOUR 1,3-DIMETHYLURACIL PHOTODIMERS

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The formation of four photodimers of 1,3-dimethyluracil (DMU) by irradiation of its solution in acetone or in frozen aqueous solution has been described recently^{1,2,3}. The dimers have been named by us A, B, C and D, enumerated according to increasing polarity on the thin-layer chromatogram, the least polar being A. The structure and stereochemistry of dimer A have been derived from crystallographic data, and being centrosymmetric, it has been given the trans-anti formula¹. We wish to report now the structures and stereochemistry of dimers B, C, and D which are trans-syn, cis-anti and cis-syn, respectively.



Evidence for the proposed structures and stereochemistry is given in the following data. The dimers show the appropriate molecular peaks in the mass spectra⁴. They can be monomerized to 1,3-dimethyluracil by irradiation of their solutions with short ultra-violet light ($\lambda \sim 240 \text{ nm}$)¹ or by the employment of light of longer wavelength ($\lambda > 300 \text{ nm}$) with photosensitizers, such as quinones⁵. The n. m. r. spectra of all four dimers show bands at τ 5.5-6.5 region, typical of cyclobutane protons⁶, and do not show any absorption of vinylic protons. The ultraviolet spectra of the dimers indicate the absence of a $-\text{C}=\text{C}-\text{CO}-$ system. These data exclude the possibility of other structures for the dimers, such as through one single C-C bond formation or an oxetane. Further information concerning both structure and stereochemistry of the dimers can be derived from their

dipole moments. The measured dipole moments (in dioxan) of the four dimers have been found to be as follows: A-1.19, B-3.35, C-6.07, and D-6.33 Debye. Dimer A, which is centrosymmetric, possesses the smallest dipole moment. The expected dipole moment of this dimer would be 0, and the deviation may result from conformational distortions of the molecule in solution. The dipole moments of the other dimers seem to be in accord with the proposed structures and stereochemistry based on vector addition of the dipoles of the individual pairs of atoms for the different dimeric structures⁷. It is noteworthy that the rate of migration of the various dimers on chromatographic columns is in agreement with the measured dipole moments⁸. Dimer B or D gives 5,5'-bis-1,3-dimethyluracil (I) when irradiated with ultraviolet light in the presence of quinones, indicating that these dimers are of the syn type (head to head). I showed m.p. 290-292° (from chloroform-acetone), m.wt. 278 (mass spectrum), λ_{\max} (ethanol) 282 nm, ϵ 14000, and was found to be identical with 5,5'-bis-1,3-dimethyluracil prepared according to Ishihara and Wang⁹.

Irradiation of a frozen aqueous solution of uracil has been reported to yield the cis-syn dimer^{10,11}. We have methylated the ice-dimer of uracil using Ag₂O and methyl iodide¹², and the methylated product was found to be identical with our dimer D, indicating that this is the cis-syn DMU-dimer. The uracil ice-dimer was contaminated with another dimer which gave dimer C upon methylation by the same procedure.

Prof. E. Fahr informed us that he has reached similar conclusions about the structure and stereochemistry of the four DMU photodimers. We are indebted to Prof. Fahr for disclosing the information prior to its publication.

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