Solution-phase Photodimerization of Dimethylthymine[1]

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The photodimerization reactions of thymine and its *N*-methyl derivatives are of importance in the understanding of the photodeactivation of DNA.[2] Due to efficient dimerization in frozen media,[3] and the usage of concentrations (*ca.* 10^{-4}M) which could be expected to limit solution-phase dimerization, little is known concerning the non-sensitized photochemistry of thymine and its derivatives in solution.[4,5] Photodimerization[6,7] of 1,3-dimethylthymine (DMT) in ice leads to the formation of two dimers (m.p.s 256 and 229°), with the higher-melting isomer identified[8,9] as the *syn* head-to-head (*syn* h-h) structure (I), and the lower melting dimer unassigned.

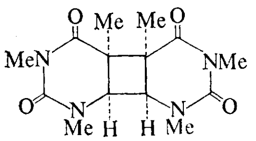
We now report that the photolysis of DMT in aqueous solution (0·1M, λ >280 mμ) gives rise to the formation of four dimers, the two "ice dimers", a third (m.p. 261—262°) which has been isolated, and a fourth, detected chromatographically. The structures of all four dimers can now be assigned.

The high-melting ice dimer has been identified as the *syn* h-h structure, (I). The lower melting (229°) isomer, made by the tetramethylation of an optically active thymine dimer,[10] must be either (II) or (IV). The singlet cyclobutane ^{13}C–H satellite peak in the n.m.r. spectrum[9] is consistent only with the head–to–tail structure, (II).†

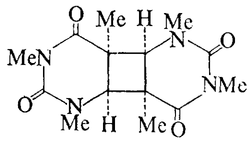
The analytical and spectral data‡ require that the new dimer (m.p. 261—262°) be one of the remaining cyclobutanes, (III) or (IV). The n.m.r. spectrum, measured with the aid of a computer of average transients, contains the expected ^{13}C–H satellite peak for the cyclobutane hydrogens [J 158 ± 2 c./sec.; values for (I) and (II) are 151 and 155 ± 2][9] and, as with the second dimer, the peak is observed to be a singlet. This compound must therefore be the remaining h–t structure, (III). The fourth dimer, though not isolated, is assigned the remaining structure (IV), and has, in fact, been shown by chromatography to be identical with an authentic sample of (IV) (m.p. 258°) prepared by tetramethylation of the appropriate thymine dimer.§

The relative efficiency of the photodimerization in concentrated solution, first suggested by preparative runs (94% conversion of a 0·28M solution, 24 hr.), is confirmed by quantum-yield measurements using a monochromator set to emit light at 300 ± 11 mμ. The overall quantum yield for dimerisation is $5 \cdot 0 \times 10^{-2}$ [(I), 38%; (II), 36%; (III), 19%; (IV), 7%]. By contrast, the dinucleotide thymidylyl-3′,5′-thymidine (TpT) is reported[11] to photodimerize in solution with a quantum yield of 1×10^{-2}.

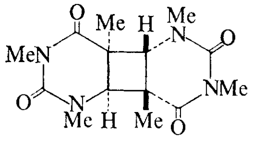
Finally, irradiation of DMT (0·1M) in acetonitrile containing a triplet quencher (*cis*-piperylene, 0·1M) leads to a small (*ca.* 12%) reduction in dimer formation compared to similar runs made in the absence of quencher. A predominantly singlet pathway for photodimerization in concentrated solution is thus indicated, similar to that observed for TpT in aqueous solution,[12] but contrasting with the complete quenching of thymine dimerization in dilute (acetonitrile) solution.[5] The possibility of a singlet excimer intermediate is being considered; the intervention of excimers in solution-phase photodimeriation has been suggested[13] and was recently proposed for the TpT system.[12]



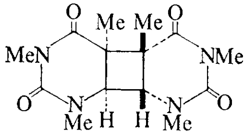
(I) (*syn* h-h)



(II) (*syn* h-t)



(III) (*anti* h-t)



(IV) (*anti* h-h)

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† Dr. D. Weinblum has reached the same conclusion on the basis of dipole moment data; N. Camerman, private communication.

‡ Elemental analysis satisfactory for a DMT dimer; λ_{max} (KBr) 5·90, 6·00 μ; λ_{max} (H_2O) 230 mμ (ϵ 5,900); n.m.r. (CF_3CO_2H): 1·57(3), 3·18(3), 3·38(3), 3·99(1) δ (relative areas), all singlets. Irradiation at 254 mμ regenerates the u.v. spectrum of DMT.

§ We are grateful to Dr. D. Weinblum for this sample.

[1] Considered as part of the series, "Organic Photochemistry"; for previous part see H. Morrison and R. Peifier, *J. Amer. Chem. Soc.*, 1968, in the press.

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