

## Reactivity of the triplet excited state of thymine and its derivatives

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Thymine (Thy) triplet excited state, populated either directly or through photosensitization, is an essential species in the processes involved in DNA damage. Its photochemistry has been related to the formation of dimeric lesions like the well-known cyclobutane dimers (CPD). By contrast, and according to the generally accepted paradigm, the (6-4) photoproducts (6-4PP) formation only occurs upon direct irradiation from a singlet excited state. First, the attention will be centered on the CPD photosensitization by exogenous and endogenous photosensitizers. Indeed, the triplet energy of thymine in DNA is a critical parameter as the feasibility of triplet-triplet energy transfer is linked to the excited state energies of the donor (photosensitizer) and acceptor (thymine) compounds. Its precise value has been established through combination of laser flash photolysis experiments and agarose gel electrophoresis.[1] Next, the ability of 64PP to play the role of an intrinsic UVA-photosensitizer will be addressed through the study of their 5-methyl-2-pyrimidone chromophore.[2] The overall results reveal that 64PP can act as a Trojan horse promoting DNA lesions in its neighbourhood. This result is of particular importance in relation with clustered DNA damages, which are hardly repaired and are responsible for critical biological events. Finally, the photochemistry of Thy from upper triplet excited states will be explored by considering the Norrish–Yang photocyclization as typical  $n\pi^*$  photoreaction. From the obtained results, it is proposed that part of the assumed “singlet” Thy photoreactivity, like the Paternò-Büchi photoreaction leading to 64PP formation, can proceed instead from an upper triplet excited state with the appropriate electronic configuration.[3]

### References

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