LOW-LYING EXCITED-STATES OF 5-BENZYLURACIL

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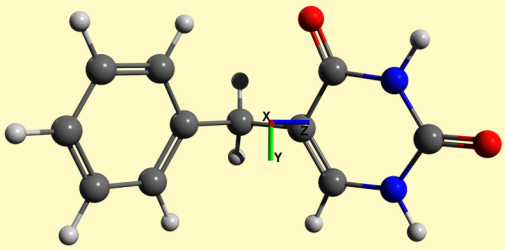
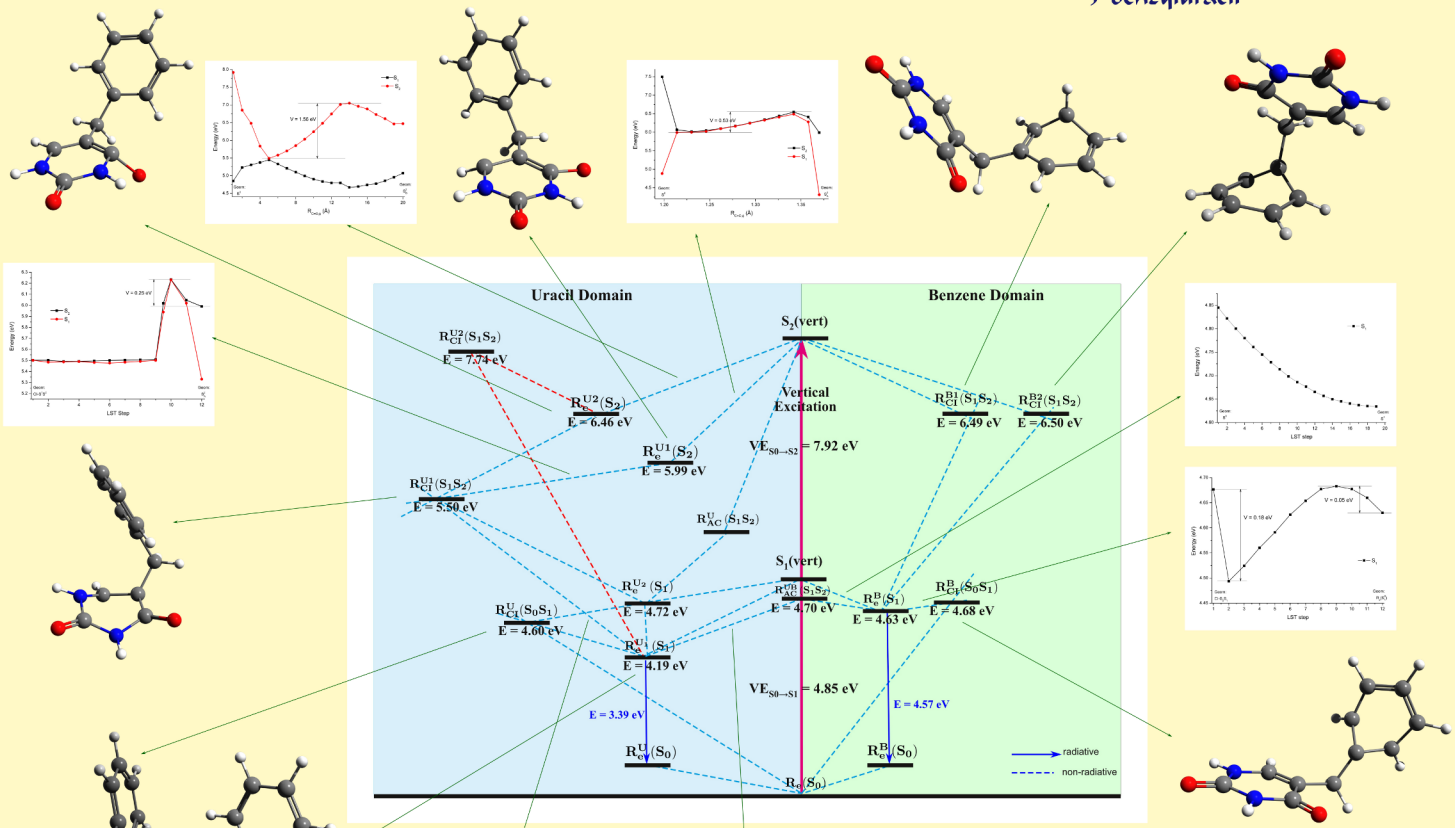
Abstract

A numerical study is reported concerning the first and second singlet excited-states of 5-benzyluracil using the multireference self-consistent field (state-averaged CASSCF) method. The vertical excitation energies of low-lying excited-states were characterized using higher-level methods, such as CASPT2, MRCI, EOM-CCSD, and TDDFT using the Molpro program package. The local minima and conical intersections found on the potential energy surfaces (PESs) were characterized in terms of molecular geometry and natural population analysis. Different relaxation pathways on the PESs are identified and discussed. The molecule can be thought of as a model system for the study of crosslink reaction between DNA and proteins induced by UV light.

Molecular structure:



5-benzyluracil



Mol./Method	S_1 (eV)	S_2 (eV)	Mol./Method	S_1 (eV)	S_2 (eV)
5BU			**Uracil**		
SA-CASSCF(20,14)	4.85	7.92	SA-CASSCF(14,10)	4.62	6.93
SA-CASSCF(20,15)	5.02	6.22	MS-CASPT2(14,10)	4.90	6.45
MS-CASPT2(20,13)	5.02	6.83	MRCI (D) (14,10)	4.99	6.64
MS-CASPT2(20,14)	4.93	6.28			
MRCI(20,14)	5.08	7.12	**Benzene**		
MRCI (D) (20,14)	5.11	6.90	SA-CASSCF(6,6)	4.90	8.48
EOM-CCSD	5.13	5.44	MS-CASPT2(6,6)	4.93	8.10
LT-DF-LCC2	4.94	5.07	MRCI (D) (6,6)	4.97	8.05
TDDFT (B3LYP)	4.72	4.91			

Table 1. *Vertical excitation energies for the two lowest excited states of 5BU and the isolated uracil and benzene molecules.*

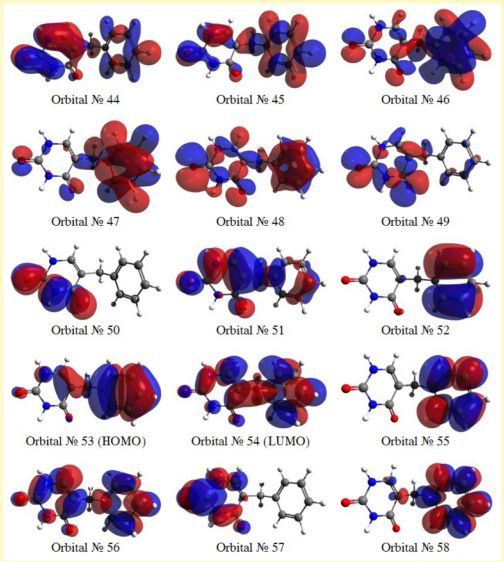


Figure 1. *The spatial shapes of orbitals involved in the Complete Active Space for 5BU.*

Conclusions

- The structures found for the benzene and uracil fragments in 5BU, are close to the ones already obtained for the isolated compounds.
- The CH2 bridge behaves just as a small perturbation giving rise to minor changes in molecular structure, and this supports the idea that 5BU can be actually used as model system for the photo-crosslink reaction.
- We have found three conical intersections that could play a crucial role in the 5BU decay pathways: as for the single isolated fragments - benzene and uracil -, they represent ultrafast non-radiative decay channels leading to lower energy electronic states.
- This work represents a first step in the characterization of the nucleic acid-proteins crosslink reaction at the molecular level using ab initio methods. A natural extension of the static knowledge about the 5BU molecular system provided with the present theoretical investigation, will include solvent (for a condensed phase simulation) and thermal effects.

Acknowledgement

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