LOW-LYING EXCITED-STATES OF BENZYLURACIL ISOMERS

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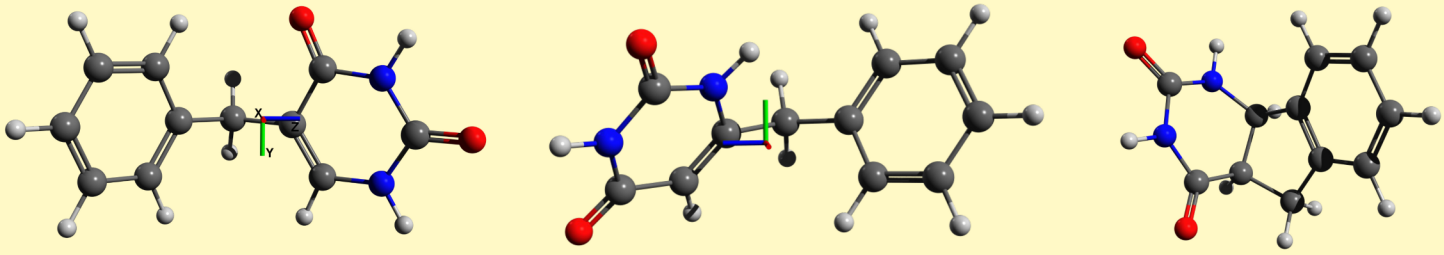
Abstract

A quantum chemical study is reported concerning the first and second singlet excited-states of 5-benzyluracil and 6-benzyluracil using the multireference self-consistent field (state-averaged CASSCF) method. The vertical excitation energies of low-lying excited-states were characterized considering the SA-CASSCF method, as well as using higher-level methods, such as CASPT2, MRCI and EOM-CCSD. 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 by comparing with the similar pathways found for the individual monomers of uracil and benzene. These molecules can be thought of as a model system for the study of crosslink reaction between DNA and proteins induced by UV light.

Molecular structures:



5-benzyluracil | 6-benzyluracil | 5-cyclo-benzyluracil

Vertical excitation energies:

Table 1. *Vertical excitation energies for the two lowest excited states of 5BU, 6BU, 5-cycBU and the isolated uracil and benzene molecules; Basis set: DZP; Methods: SA-CASSCF, MS-CASPT2, MRCI, EOM-CCSD, LT-DF-LCC2 implemented in the Molpro 2012.1 [1] program package.*

	S_1 (eV)	S_2 (eV)		S_1 (eV)	S_2 (eV)		S_1 (eV)	S_2 (eV)
5BU[2]			**6BU**			**Uracil**		
SA-CASSCF(20,14)	4.85	7.92				SA-CASSCF(14,10)	4.62	6.93
SA-CASSCF(18,14)	4.94	5.34	SA-CASSCF(18,14)	5.02	5.30		(0.0002)	(0.549)
SA-CASSCF(20,15)	5.02	7.02	SA-CASSCF(20,15)	4.85	7.90	MS-CASPT2(14,10)	4.87	5.83
	(0.003)	(0.571)		(0.000)	(0.0012)	EOM-CCSD	5.17	5.88
SA-CASSCF(18,15)	4.94	5.21	SA-CASSCF(18,15)	5.02	5.29	**Benzene**		
SA-CASSCF(20,16)	4.94	7.10				SA-CASSCF(6,6)	4.90	8.48
MS-CASPT2_*FC*(20,13)*	5.02	6.83					(0.001)	(0.000)
MS-CASPT2_*FC*(20,14)	4.93	6.28	MS-CASPT2_*FC*(20,14)	5.13	6.22	MS-CASPT2(6,6)	5.10	6.93
MRCI(20,14)	5.08	7.12				EOM-CCSD	5.30	6.86
MRCI (D) (20,14)	5.11	6.90	MRCI (D) (20,14)	5.38	6.32	**5-cycBU**		
EOM-CCSD	5.13	5.44	EOM-CCSD	5.19	5.42	SA-CASSCF(18,14)	4.90	6.82
LT-DF-LCC2	4.94	5.07	LT-DF-LCC2	4.89	5.15	EOM-CCSD	5.11	5.47

*FC – The closed orbitals were considered frozen

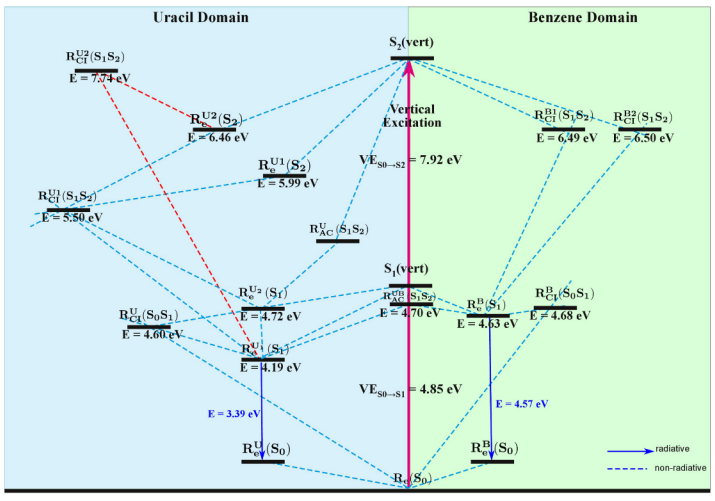


Figure 1. *The global energy diagram of different local minima and conical intersection points on the PES for different excited state levels for 5BU, obtained using the (20,14) active space CASSCF method.*

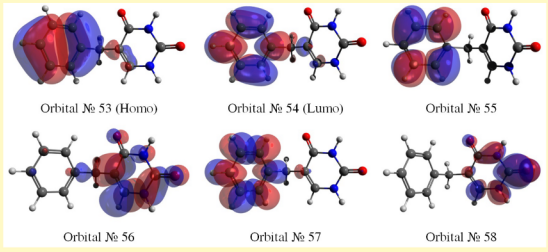


Figure 2. *The spatial shapes of the Homo and five virtual orbitals involved in the Complete Active Space for 5BU at $R_e^B(S_1)$ geometry.*

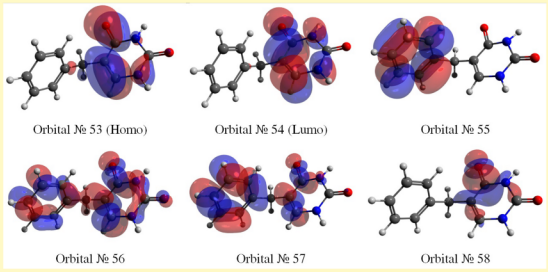
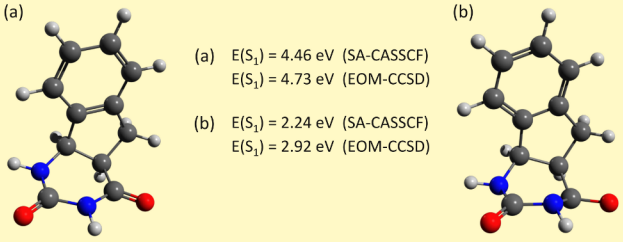


Figure 3. *The spatial shapes of the Homo and five virtual orbitals involved in the Complete Active Space for 5BU at $R_e^U(S_1)$ geometry.*



(a) $E(S_1)$ = 4.46 eV (SA-CASSCF)
$E(S_1)$ = 4.73 eV (EOM-CCSD)

(b) $E(S_1)$ = 2.24 eV (SA-CASSCF)
$E(S_1)$ = 2.92 eV (EOM-CCSD)

Figure 4. *The optimized equilibrium geometries of 5-cycBU first excited state: (a) benzene branch; (b) uracil branch.*

Conclusions

- The vertical excitation energies found for the benzene and uracil fragments in 5BU, 6BU and 5cycBU, 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 or 6BU can be actually used as model system for the photo-crosslink reaction (5-cycBU or 6-cycBU).
- 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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REFERENCES

[1] MOLPRO, version 2012.1, A package of *ab initio* H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushenkov, G. Rauhut, T. B. Adler, *et al.* see http://www.molpro.net.

[2] M. Micciarelli, C. Altucci, B. Della Ventura, R. Velotta, V. Toşa, A. B. Gónzalez Pérez, M. Pérez Rodríguez, Á. R. de Lera, and A. Bende: "Low-lying excited-states of 5-benzyluracil", Physical Chemistry Chemical Physics, **15**, 7161 - 7173 (**2013**).