

Theoretical Investigation of photoisomerization mechanisms of N-salicydenemethylfurylamine (SMFA)

Ai-Hua Gao, and Meishan Wang*

School of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, China

Received 1 April 2015; Accepted (in revised version) 10 May 2015

Published Online 6 June 2015

Abstract. Excited state reaction coordinates and the consequent energy profiles of a new Schiff base, N-salicydenemethylfurylamine (SMFA), have been investigated with the MP2 and CASSCF method. The potential energy profiles of the ground and the lowest excited singlet state are calculated. The excited state potential energy profile shows a small barrier in the LIIC pathway of dissociation along the O-H stretching coordinate. This work suggests that there are two pathways in the photochemical reaction of SMFA. In one pathway, the photochemical product is the enol-type minimum. In the other pathway, the ESIPT reaction is observed and an excited state stationary structure is reached. The trans-keto and cis-keto type structures will be obtained from photoexcitation of the enol isomer. Two conical intersections between the ground and excited states act as the gates for nonadiabatic decay to the ground state.

PACS: 34.70.+e; 42.70.-a

Key words: excited state reaction, ESIPT, photochromic effect, SMFA, photoisomerization mechanism.

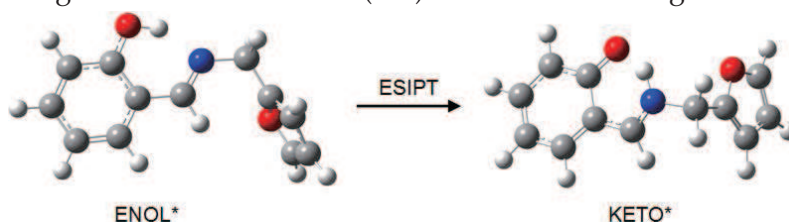
1 Introduction

Photochromism in organic molecules [1-2] is a kind of very important photochemical phenomenon and well-known to be among the ultrafast chemical reactions occurring in nature. Upon excitation, the stable form of a photochromic compound in the ground state tends to be a metastable form (excited-state minimum or conical intersection between two states). The molecule eventually reverts to original structure or converts to the other stable form in the ground state. The reversible cyclic nature of this process is the key feature of their importance in technical applications in the fields of photochemical area.

*Corresponding author. *Email address:* mswang1971@163.com (M. S. Wang)

Photochromism includes ultrafast processes such as cis-trans or trans-cis photoisomerization, [3-4] photochemical ring-closure-ring-opening reactions, [5-6] or excited-state intramolecular proton transfer (ESIPT). [7]

The photochromic processes of aromatic Schiff bases have been widely investigated since they play particularly important roles in the photochemistry area. These compounds can be used as logic devices, optical data processing, molecular motors, etc. [8-13] In aromatic Schiff bases, the mechanism and dynamics of ESIPT (from the original excited enol form to the keto form) and the creation of photochromic tautomer is concerned about in the investigations. These ultrafast dynamic reactions may be accompanied with other photochemical processes such as cis-trans or trans-cis photoisomerizations, internal conversion through conical intersections (CIs) or avoided crossing between two states.



Scheme 1: Molecular structures of enol (ENOL*) and keto (KETO*) tautomers of SMFA at the S_1 state.

Investigations should be done to understand the excited states of Schiff bases for the importance of photophysics of these compounds. However, very few studies has been done on the photophysics of Schiff bases yet. Jankowska and coworkers investigated the proton-transfer reaction in a model aromatic Schiff base, salicylidene methylamine (SMA), in the S_0 and S_1 states. There are two S_1/S_0 CIs between the S_0 and S_1 states which act as nonadiabatic gates for a radiationless decay to the S_0 state. Their calculations indicated that aromatic Schiff bases are potential candidates for optically driven molecular switches. [14] A theoretical study was reported on the photochemistry of salicylideneaniline in the gas phase using static electronic structure calculations and surface hopping dynamics simulations by Spörkel and coworkers. [15] Upon photoexcitation of the most stable cis-enol tautomer into the S_1 state, an ultrafast ESIPT was found in agreement with the work done by Ortiz-Sánchez. [16] The internal conversion is initiated by an out-of-plane motion around the C-C single bond. The molecule moves toward a CI providing an efficient deactivation channel to the S_0 state. Equal amounts of the S_0 cis-enol and trans-keto photoproducts were obtained by the dynamic simulations. Spörkel *et al.* demonstrated that the S_1 cis-keto form and the stable S_0 trans-keto one is responsible for fluorescence and photochromism, respectively. Recently, Moghadam *et al.* investigated the photophysics of a new Schiff base, N-salicyldenemethylfurylamine (SMFA), with the CC2 method. [17] The excited state potential energy profile shows a barrier-less dissociation pattern along the O-H stretching coordinate which verifies the proton transfer reaction at the first singlet excited (S_1) state (see scheme 1). The calculations indicate two CIs between the S_1 state and ground (S_0) state play important parts in nonadiabatic decay

to the S_0 state in SMFA. Two barrier-less reaction coordinates direct the excited system to the ground state of enol-type structure. A trans-keto type structure was obtained from photoexcitation of the enol form and can be responsible for the photochromic effect of this molecule. In particular, no cis-keto tautomer was found in the ground state.

In the present work, the potential energy profiles of the ground and the lowest excited singlet state were calculated in order to understand the photochromic dynamics processes of SMFA. In the optimization of the ground state, three form of isomers were obtained, including enol, cis-keto and trans-keto isomers. Two CIs provide gates for nonadiabatic decay to the ground state. The trans-keto and cis-keto type structures will be produced after photoexcitation of the enol form and the keto isomers can be responsible for the photochromic effect of SMFA.

2 Computational details

To explore the landscape of the ground state of SMFA, the MP2 method were employed. All stationary points of SMFA in the ground state were optimized at the MP2 level with 6-311G(d) basis set. The excited-state minima were determined by two-state-averaged CASSCF method. The full p-orbitals active space is computationally limited. Thus, we adopted CASSCF(14,12) with 6-31G(d) basis set, where (14,12) represents 14 electrons in 12 orbitals in active space. To confirm the presence of the S_1/S_0 CIs, optimization of the CI geometry was performed with the aid of the CASSCF/6-31G(d) method. The active space consists of 14 electrons distributed over 12 orbitals.

To elucidate the mechanisms of the ultrafast ESIPT and photoisomerization of SMFA, linearly interpolated internal coordinate (LIIC) [18] pathways were constructed in the ground and excited states using CCSD/6-31G(d) level. The *ab initio* calculations were performed with the Molpro 2010.1 quantum chemistry package. [19]

3 Results and Discussion

3.1 Photophysically Relevant Isomers and Conical Intersections of SMFA

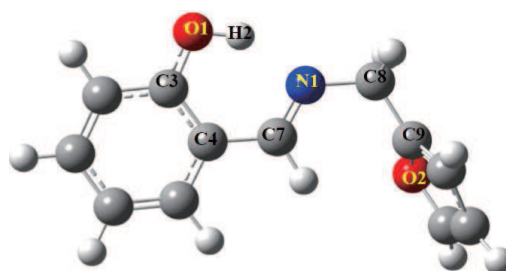


Figure 1: Atom numbering used in SMFA.

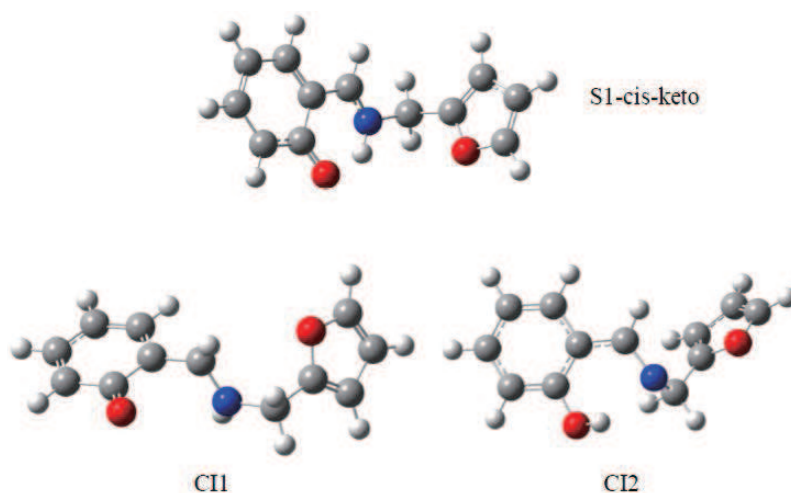


Figure 2: Optimized structures for minimum in the S_1 state (S1-cis-keto) and conical intersections between S_0 and S_1 states (CI1 and CI2) using the CASSCF(14, 12)/6-31G(d) level of theory.

SMFA (see Fig. 1) contains a planar structure of salicylaldehyde and the methyl-furyl part. It was reported that the planar structure of salicylaldehyde is due to intramolecular hydrogen bonding (OH...NC). [20-24] It can be predicted that there are several possibilities for various orientations taken by the methyl-furyl part of the molecule. In Ref. 17, using the calculations at the MP2/cc-pVDZ level of theory, sixteen minima in the enol form were found in the ground state of SMFA. The MP2 calculation indicated that the trans-keto form is stable at the ground state. The energetic level of trans-keto form is about 0.83 eV, which is significantly higher than the original minimum of the most stable enol configuration. While no minimum was found for the cis-keto tautomer of this molecule.

In our work, the stationary structures of SMFA were optimized in the ground state using MP2 level with 6-311G(d) basis set and CASSCF(14, 12) level with 6-31G(d) basis set, in order to understand the features of the ground state of this molecule. The performed calculations located thirty-five stationary structures on the ground state potential energy surface of SMFA. Twenty minima correspond to various conformers of the enol form. The other fifteen minima belong to the conformers of the keto form, eight of which belong to the cis-keto tautomer and the other seven to the trans-keto tautomer. The MP2/6-311G(d) and CASSCF(14, 12)/6-31G(d) calculations may lead to poor results. Therefore, the MP2 calculation with cc-pVTZ basis set were also performed in the optimization for the ground state. The optimized geometries (enol, cis-keto and trans-keto tautomers) are in good agreement with those obtained with MP2/6-311G(d) and CASSCF(14, 12)/6-31G(d) calculations. The optimized structures of enol tautomers at the MP2/6-311G(d) level of theory are presented in Table 1 and the optimized structures of cis-keto and trans-keto ones are shown in Table 2.

It can be seen that there are several tautomers in the ground state for various orien-

Table 1: Optimized geometries of several isomers of SMFA in the ground state at the MP2/6-311G(d) level of theory.

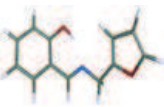
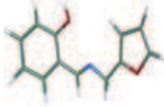
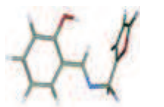
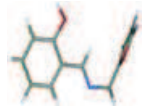
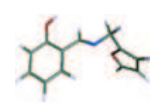
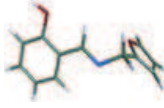
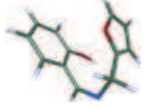
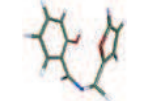
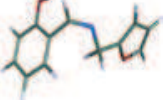
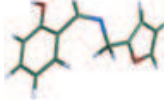
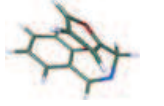
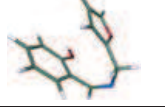
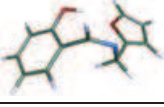
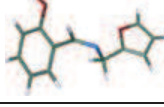
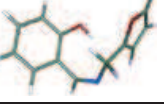
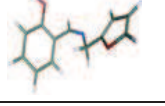
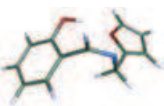
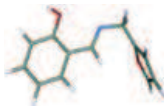
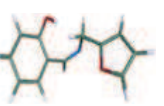
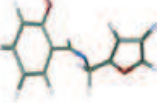
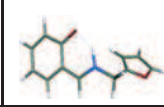
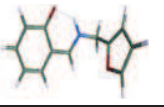
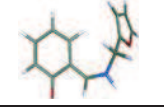
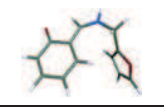
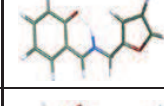
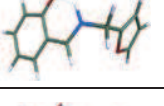
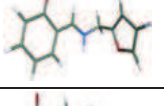
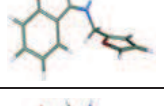
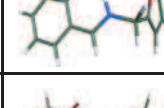
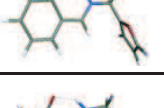
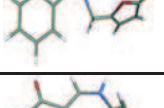
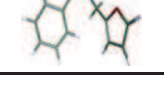
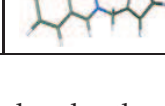
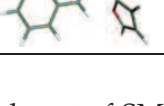
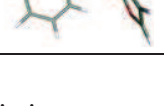
Structure	Optimized geometry	Structure	Optimized geometry	Structure	Optimized geometry	Structure	Optimized geometry
S0-enol-1a		S0-enol-1b		S0-enol-6a		S0-enol-6b	
S0-enol-2a		S0-enol-2b		S0-enol-7a		S0-enol-7b	
S0-enol-3a		S0-enol-3b		S0-enol-8a		S0-enol-8b	
S0-enol-4a		S0-enol-4b		S0-enol-9a		S0-enol-9b	
S0-enol-5a		S0-enol-5b		S0-enol-10a		S0-enol-10b	

Table 2: Optimized geometries of several isomers of SMFA in the ground state at the MP2/6-311G(d) level of theory.

Structure	Optimized geometry	Structure	Optimized geometry	Structure	Optimized geometry	Structure	Optimized geometry
S0-cis-keto1		S0-cis-keto5		S0-trans-keto1		S0-trans-keto5	
S0-cis-keto2		S0-cis-keto6		S0-trans-keto2		S0-trans-keto6	
S0-cis-keto3		S0-cis-keto7		S0-trans-keto3		S0-trans-keto7	
S0-cis-keto4		S0-cis-keto8		S0-trans-keto4			

tations taken by the methyl-furyl part of SMFA, which is in agreement with our prediction. In addition, the planar structure of salicylaldimine in the enol isomers is due to intramolecular hydrogen bonding (O1H2...N1C8) and intramolecular hydrogen bonding (C3O1...H2N1) is also been found in the cis-keto isomers. In our calculations, atom numbering was set and considered as shown in Fig. 1. The optimization of the molecule indicates that the conformer of 5a is the most stable in the ground state, consistent with

Table 3: Selected bond lengths (Å) and dihedral angles (deg) of optimized structures in the ground state obtained at the MP2/6-311G(d) level.

Geometry						
Structure	O1-H2	H2-N1	C3-C4-C7-N1	C4-C7-N1-C8	C7-N1-C8-C9	N1-C8-C9-O2
S0-enol-5a	0.98	1.80	0.3	179.8	1.9	80.4
S0-cis-keto1	1.72	1.04	4.4	-172.8	111.0	177.5
S0-cis-keto2	1.71	1.04	-4.8	171.7	-109.6	179.5
S0-cis-keto3	1.73	1.04	0.5	-176.8	109.2	70.5
S0-cis-keto4	1.75	1.03	-0.4	175.9	-100.2	-68.6
S0-cis-keto5	1.73	1.03	-1.29	174.6	-93.9	71.0
S0-cis-keto6	1.73	1.03	1.32	-174.6	93.9	-71.1
S0-cis-keto7	1.71	1.04	1.61	-177.2	-24.6	-71.4
S0-cis-keto8	1.71	1.04	-1.65	177.1	25.2	71.2
S0-trans-keto1	4.74	1.01	176.8	168.7	-96.9	68.5
S0-trans-keto2	4.74	1.01	-177.3	-168.7	93.6	71.4
S0-trans-keto3	4.44	1.01	-179.2	-1.0	179.7	71.1
S0-trans-keto4	4.42	1.01	-176.1	3.7	-76.0	164.6
S0-trans-keto5	4.42	1.01	176.2	-3.4	75.5	-163.9
S0-trans-keto6	4.43	1.01	-170.2	9.3	-104.9	65.0
S0-trans-keto7	4.45	1.01	-170.6	10.4	-94.9	-52.6

Table 4: Relative energies (eV) with respect to the conformer of S0-enol-5a at the MP2/6-311G(d) level.

Structure	Relative energy	Structure	Relative energy	Structure	Relative energy	Structure	Relative energy
S0-enol-1a	0.03	S0-enol-6a	0.44	S0-cis-keto1	0.37	S0-trans-keto1	0.78
S0-enol-1b	0.59	S0-enol-6b	0.39	S0-cis-keto2	0.37	S0-trans-keto2	0.88
S0-enol-2a	0.47	S0-enol-7a	0.53	S0-cis-keto3	0.37	S0-trans-keto3	0.78
S0-enol-2b	0.39	S0-enol-7b	0.58	S0-cis-keto4	0.37	S0-trans-keto4	0.88
S0-enol-3a	0.63	S0-enol-8a	0.53	S0-cis-keto5	0.35	S0-trans-keto5	0.88
S0-enol-3b	0.64	S0-enol-8b	0.59	S0-cis-keto6	0.35	S0-trans-keto6	0.91
S0-enol-4a	0.49	S0-enol-9a	0.49	S0-cis-keto7	0.35	S0-trans-keto7	0.90
S0-enol-4b	0.65	S0-enol-9b	0.69	S0-cis-keto8	0.35		
S0-enol-5a	0.0	S0-enol-10a	0.55				
S0-enol-5b	0.59	S0-enol-10b	0.65				

the result of Ref 17. In this work, we investigated the photochemical processes of the conformer of 5a. In Table 3, we presented the selected geometric parameters in the optimized structures of 5a and the keto isomers obtained by MP2/6-311G(d) calculations in the ground state. The cis-keto or trans-keto isomers could be obtained by rotation of N1-C8 bond or by rotation of C8-C9 bond.

In order to evaluate the energetic levels of all isomers associated with this molecule in the ground state, their energetic levels with respect to the conformer of S0-enol-5a were presented in Table 4. S0-enol-1a is only 0.03 eV less stable than S0-enol-5a. The energetic level of other rotamers is at least 0.35 eV higher than that of S0-enol-5a. It should be noted that both the cis-keto and trans-keto isomers are stable at the ground state in our calculations. The energetic levels of the cis-keto and trans-keto isomers are higher than the most stable enol form S0-enol-5a at least 0.35 eV and 0.78 eV, respectively.

We also did the geometry optimization of the S_1 state at the CASSCF(14,12)/6-31G(d) level of theory and the minimum (S_1 -cis-keto) obtained in geometry optimization were presented in Fig. 2. It can be seen that the geometry optimization of S_0 -enol-5a at the S_1 state shows an excited state proton transfer from the hydroxyl group to the imine of SMFA. This is in agreement with the result of CC2 method.[17] It may indicate that ESIPT reaction occurs after the S_0 -enol-5a isomer is excited to the S_1 state.

The characterization of conical intersections is essential to understand mechanisms of a wide range of photochemical reactions. We optimized conical intersections between the ground and excited states of SMFA with CASSCF(14,12)/6-31G(d). Two conical intersections were found (see Fig. 2). One is in keto form and the other is in enol form, which is consistent with the results of Ref 17.

3.2 Potential Energy Profiles

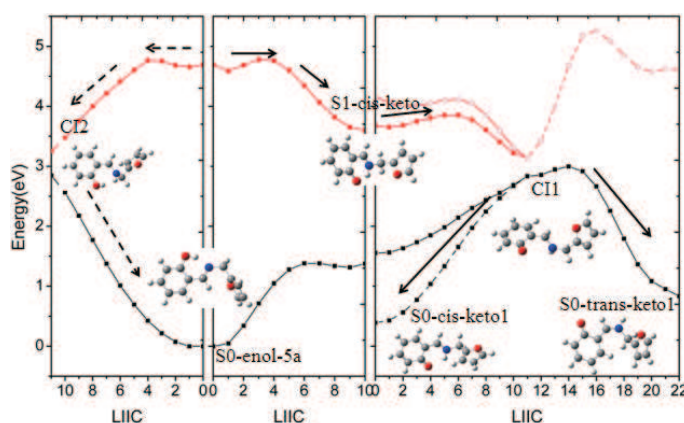


Figure 3: Computed potential energy curves of SMFA in the S_0 state (squares) and S_1 state (circles) along the LIIC pathways using at the CCSD/6-31G(d) level. Pathways are constructed among the optimized S_0 -enol-5a, S_1 -cis-keto, CI1, S_0 -cis-keto1, S_0 -trans-keto1 geometries and among the optimized S_0 -enol-5a and CI2 geometries. All energies are relative to S_0 -enol-5a.

In Fig. 3, the LIIC pathways were obtained in the ground and excited states by using CCSD/6-31G(d) level. The hydrogen transfer reaction path obtained by Moghadam is barrierless. It illustrates that the enol form of SMFA, S_0 -enol-5a, is a typical ESIPT system. However, the middle panel of Fig. 3 shows the pathway of the ESIPT process in the molecule and there is a small barrier (0.2 eV) in the excited state. It may be caused by the LIIC method we used in the calculations. Upon the enol form of S_0 -enol-5a excited to the S_1 state, there are two pathways for the photochemical reactions. The left panel of Fig. 3 shows the pathway in which the photochemical product is the enol-type minimum, S_0 -enol-5a. The conical intersection, CI2, acts as the nonadiabatic gate for radiation-less decay from the excited state to the ground state. The middle and right panels of Fig. 3 indicate the photoisomerization process of SMFA. Upon excitation, the ESIPT reaction

occurs and a stationary structure, S1-cis-keto is reached. The molecule approached to a conical intersection, CI1, by the twisting of bonds in the methyl-furyl part of the molecule. Then, the molecule decays to the ground state. In our calculation, two kinds of chemical products can be produced, the trans-keto and cis-keto isomers.

4 Conclusions

In this work, we studied the photochromic processes of aromatic Schiff bases, SMFA. We carried out the optimization in the ground state and found there are several stationary structures for various orientations taken by the methyl-furyl part of the molecule. The obtained stationary structures are enol, cis-keto and trans-keto forms. Upon the enol form of S0-enol-5a excited to the S1 state, there are two pathways for the photochemical reactions. In one pathway, a conical intersection (CI2) acts as the nonadiabatic gate for radiation-less decay to the ground state and the photochemical product is the enol-type minimum. In the other pathway, the ESIPT reaction is observed and a stationary structure is reached in the excited state. The optimized conical intersection (CI1) plays an important part in nonadiabatic dynamic process in SMFA. Then, two kinds of chemical products will be produced, the trans-keto and cis-keto isomers.

References

- [1] H. Bouas-Laurent, H. Durr, *Pure Appl. Chem.*, 2001, 73, 639-646.
- [2] A. Senior, F. G. Shephard, *J. Chem. Soc.*, 1909, 95, 1943-1952.
- [3] R. Siewertsen, H. Neumann, B. Buchheim-Stehn, R. Herges, C. Näher, F. Renth, F. Temps, *J. Am. Chem. Soc.*, 2009, 131, 15594-15595.
- [4] A.-H. Gao, B. Li, P.-Y. Zhang, K.-L. Han, *J. Chem. Phys.*, 2012, 137 204305.
- [5] S. Prager, I. Burghardt, A. Dreuw, *J. Phys. Chem. A*, 2014, 118, 1339-1349.
- [6] F. Liu, K. Morokuma, *J. Am. Chem. Soc.*, 2013, 135, 10693-10702.
- [7] S. Yamazaki, A. L. Sobolewskic, W. Domcke, *Phys. Chem. Chem. Phys.*, 2011, 13, 1618-1628.
- [8] J. M. Tour, *J. Am. Chem. Soc.*, 1996, 118, 2309-2310.
- [9] H. Dürr, H. Bouas-Laurent, Access Online via Elsevier, 2003.
- [10] S. Pu, Z. Tong, G. Liu, R. Wang, *J. Mater. Chem. C*, 2013, 1, 4726-4739.
- [11] L. Zhao, D. Sui, J. Chai, Y. Wang, S. Jiang, *J. Phys. Chem. B*, 2006, 110, 24299-24304.
- [12] C.-M. Che, C.-C. Kwok, S.-W. Lai, A. F. Rausch, W. J. Finkenzeller, N. Zhu, H. Yersin, *Chem. -Eur. J.*, 2010, 16, 233-247.
- [13] G.-D. Tang, J.-Y. Zhao, R.-Q. Li, C. Yuan, Z.-C. Zhang, *Spectrochim. Acta., Part A* 2011, 78, 449-457.
- [14] J. Jankowska, M. F. Rode, J. Sadlej, A. L. Sobolewski, *Chem. Phys. Chem.*, 2012, 13, 4287-4294.
- [15] L. Spörkel, G. Cui, W. Thiel, *J. Phys. Chem. A*, 2013, 117, 4574-4583.
- [16] J. M. Ortiz-Sánchez, R. Gelabert, M. Moreno, J. M. Lluch, *J. Chem. Phys.*, 2008, 129, 214308.
- [17] A. J. Moghadam, R. Omidyan, V. Mirkhani, *Phys. Chem. Chem. Phys.*, 2014, 16, 2417-2424.
- [18] P. Zhou, J. Liu, K. Han, G. He, *J. Comput. Chem.* 2014, 35, 109-120.
- [19] H. J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schutz, *et al.* MOLPRO, version.

- [20] J. M. Fernández-G, F. del Rio-Portilla, B. Quiroz-García, R. A. Toscano, R. Salcedo, J. Mol. Struct., 2001, 561, 197-207.
- [21] A. Filarowski, T. Glowiake, A. Koll, J. Mol. Struct., 1999, 484, 75-89.
- [22] H. Fukuda, K. Amimoto, H. Koyama, T. Kawato, Org. Biomol. Chem., 2003, 1, 1578-1583.
- [23] H. Tanak, J. Phys. Chem. A, 2011, 115, 13865-13876.
- [24] A. J. Moghadam, R. Omidyan, V. Mirkhani, Phys. Chem. Chem. Phys., 2014, 16, 2417-2424.