

Excited-State Parameters of One Intramolecular Cyclization by TD-DFT, CIS and ZINDO Methods

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ABSTRACT

Using a time-dependent-density functional theory (TD-DFT), Configuration Interaction Singles (CIS) and Zerner's Intermediate Neglect of Differential Overlap (ZINDO) methods, we have investigated the UV-Visible spectra of one new intramolecular cyclization at before and after intramolecular attack. All structures were optimized at the B3LYP/6-311++G** level while UV-Visible parameters were calculated via different basis sets; 6-31++G**, 6-31+G* and 6-31G*. In the all compounds, with the presence of donors substituted λ_{\max} values are greater, when acceptors substituted are smaller, in the TD-DFT and CIS methods. In the CIS and TD-DFT methods, after the cyclization oscillator strength is low i.e. possibility of transmission and transmission intensity is low, because between two aromatic rings, carbonyl groups does not exist. The 3D-surfaces diagrams showed changes of the λ_{\max} and energy gap compared with Hammett Para-effect number in the CIS and TD-DFT methods, clearly. The calculations were performed using GAUSSIAN 09W suite of programs.

Keywords: Excited-state, UV-Visible, TD-DFT, CIS, Hammett equation, Intramolecular cyclization

INTRODUCTION

Many researchers focused on chemistry and biological behaviors of 9H-pyrrolo (1, 2-a) indol-9-one (fluorazone) and its derivatives [1, 2]. This important interest occurs from the fact that fluorazone shows the direct chemical precursor of 9H-pyrrolo (1, 2-a) indole (fluorazene). Very recently, organic chemists have found that some 9H-pyrrolo (1, 2-a) indole, directly obtained from 9H-pyrrolo (1, 2-a) indol-9-one [3, 4]. In recent years, there has been an increasing interest in excited-state properties [5-7]. The excited-state behavior of the binary and trio aromatic compounds has attracted much attention [8-10]. The development of correlation between UV-visible absorption

and Hammett substituent constants is one of the major achievements of physical chemistry [11]. Hammett substituent coefficients (ρ) are used to evaluate the effect of the substituents upon the rate of a chemical reaction for which mechanism is known. Several studies were reported the correlation between UV absorption frequencies with substituent parameters [12-14].

The present work, we wish investigate excited-state parameters of before and after fluorazone cyclization (Figure1.). We focus on Time-Dependent Density Functional Theory (TD-DFT), which is presently the most popular method to treat

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excited states in a DFT framework. Extensive reviews on TDDFT exist [15, 16]; most of them emphasize formal aspects of the theory. Also has been used Zerner's Intermediate Neglect of Differential Overlap (ZINDO) method [17] and Configuration Interaction Singles (CIS).

Generally, TD-DFT works quite well for low-lying valence excited states, but fails to account for excitations to Rydberg states. The accuracy of TD-DFT excitation energies is largely dependent on the quality of both occupied and virtual Kohn-Sham orbitals and eigenvalues, and the failure of TD-DFT to treat Rydberg states is related to the fact that the incorrect asymptotic behaviour of the exchange-correlation potential of conventional functionals leads to a rather poor description of virtual orbitals. Apart from pure Rydberg states, problems with TD-DFT might also occur when valence and Rydberg states are strongly interacting, or when transitions involving extensive charge transfer are studied [18].

THEORETICAL

At first, all primary structures has been optimized by DFT method (B3LYP) [19] and the 6-311++G** standard large basis set as implemented in the GAUSSIAN 09 suite of programs [20]. Then, UV-Visible spectrum has been simulated by TD-DFT, CIS and ZINDO methods at these three series basis sets:

- A. 6-31++G** for "3a" and "3b", also "a" and "b" molecules.
- B. 6-31+G* for "3c" and "3d", also "c" and "d" molecules.
- C. 6-31G* for "3e" and "e" molecules.

The computational limitations were reason of use three basis set for UV-Visible spectrum. The output of Gaussian, i.e., orbital energies and coefficients was analyzed and visualized with Chemcraft 1.6 [21] and GaussView 5.0.8 [22]. Note, in all excited-state calculations is considered the new states equal to 100. This computational detail is very important and effective in the final output results.

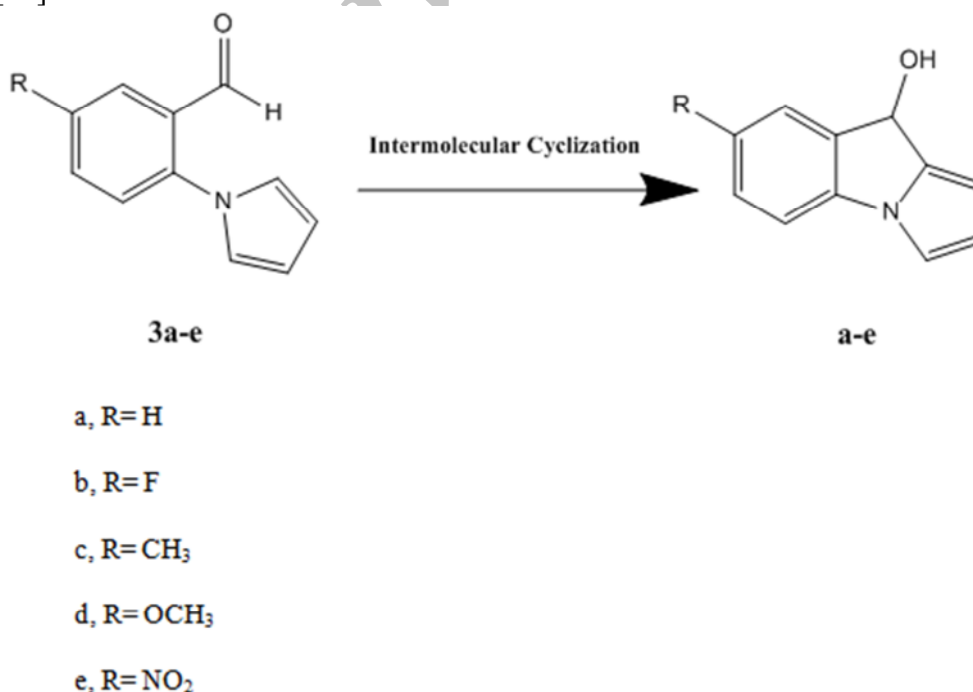


Fig. 1. Schematic of cyclization reaction.

RESULTS AND DISCUSSIONS

The results from the calculations on 3a-3e (before cyclization) and a-e (after cyclization) are presented in Table 1. When comparing the wavelengths of maximum absorption calculated by the different methods, it should be kept in mind that, the data values depending on the number of aromatic rings or conjugated system. In the all compounds, λ_{\max} values of ZINDO method are bigger than CIS and TD-DFT methods. In all cases, CIS and TD-DFT results are approximately in agreement with each others. In the 3a-3e, with the presence of donors substituted λ_{\max} values are bigger, when acceptors substituted are smaller, in the TD-DFT and CIS methods. The reason of last result is entrance and exit of electrons (by resonance or inductive) into the conjugated system. About a-e (after cyclization) this result is not true, because after cyclization is generated a new ring and the conjugated systems are changed.

The Values of λ_{\max} for 3a, 3b and 3e became greater after cyclization; reason of deviation for 3c and 3d (donor substituted) is Basis Set limitation. We were forced to use of comparatively small basis sets (6-31+G*) for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, this limitation caused to obtained unreasonable results for 3c and 3d. In the years away, Pople and co-workers [23] have calculated vertical excitation energies for pyridine using CIS in combination with the 6-31G(d) and 6-31+G(d) basis sets. They indicates that the 6-31+G(d) basis set does not improve the description of such states. Later, Bauernschmitt and Ahlrichs [24] performed CIS calculations on the same system using the very large basis set due to Sadlej [25]. This basis set, which

includes diffuse functions of each angular momentum type on each atom, gave energies that, for the eight lowest excited states. The calculated oscillator strength can be equivalent to possibility of transmission in the selection rules. In the CIS and TD-DFT methods, after the cyclization oscillator strength is low i.e. possibility of transmission and transmission intensity is low, because between two aromatic rings, carbonyl groups does not exist. It is very self-explaining that between absorption wavelength and Energy Gap is inverse relationship.

In Figure 2, simulated spectra with the TDDFT, CIS and ZINDO methods, both with the "New States=100". Many interesting similarities between CIS and TD-DFT methods spectra can be found. In the all cases, CIS and TD-DFT spectrum have very similar spectra Models, also always absorption values for TD-DFT is under the CIS.

A good example to understand is absorption spectrum for "e" that value of λ_{\max} is 168.46 nm at CIS method; while this value is 177.86 nm respects TD-DFT method with lower than absorption. Unfortunately ZINDO method in all cases, only the shows one of the main peak and also could not follow the patterns of the other two methods. The interesting thing is presence of three sharp and intense peaks at "3e" and "e" spectrum in the CIS and TD-DFT methods, in fact these sharp and intense peaks is observed same tiny peak in other substitutions. For all compounds, before cyclization there is one small shoulder that after cyclization, this shoulder to become bigger and stronger, in the three methods.

M. H. Ghorbani *et al.* /J. Phys. Theor. Chem. IAU Iran, 9(2): 53-60, Summer 2012**Table 1.** Calculated wavelengths of maximum absorption (nm), oscillator strength and energy gap (e.V.)

Molecule	Hammett Number	Excited-State Parameters	Methods		
			TD-DFT	CIS	ZINDO
3a	0	λ_{\max} (nm)	176.47	166.85	218.79
		Oscillator Strength	0.6045	0.8578	0.8400
		Energy Gap (ev)	7.0258	7.4307	5.6668
a	0	λ_{\max} (nm)	193.20	170.74	216.30
		Oscillator Strength	0.4760	0.3529	0.9514
		Energy Gap (ev)	6.4173	7.2614	5.7321
3b	0.062	λ_{\max} (nm)	172.82	164.69	222.03
		Oscillator Strength	0.4785	0.7191	0.9007
		Energy Gap (ev)	7.1741	7.5282	5.5841
b	0.062	λ_{\max} (nm)	179.35	168.99	216.52
		Oscillator Strength	0.3434	0.3150	0.5957
		Energy Gap (ev)	6.9130	7.3367	5.7261
3c	-0.17	λ_{\max} (nm)	180.55	170.15	225.48
		Oscillator Strength	0.9159	1.0320	0.8744
		Energy Gap (ev)	6.8669	7.2867	5.4988
c	-0.17	λ_{\max} (nm)	179.03	176.64	216.51
		Oscillator Strength	0.3837	0.4346	0.9366
		Energy Gap (ev)	6.9255	7.0192	5.7266
3d	-0.268	λ_{\max} (nm)	186.08	178.08	231.63
		Oscillator Strength	0.6825	1.0359	0.4680
		Energy Gap (ev)	6.6628	6.9621	5.3528
d	-0.268	λ_{\max} (nm)	178.67	176.60	216.73
		Oscillator Strength	0.3542	0.3844	0.9607
		Energy Gap (ev)	6.9394	7.0208	5.7207
3e	0.778	λ_{\max} (nm)	169.09	160.00	222.84
		Oscillator Strength	1.3804	1.3445	0.6898
		Energy Gap (ev)	7.3324	7.7492	5.5763
e	0.778	λ_{\max} (nm)	177.86	168.46	210.04
		Oscillator Strength	0.8706	1.0937	0.6847
		Energy Gap (ev)	6.9709	7.3597	5.9029

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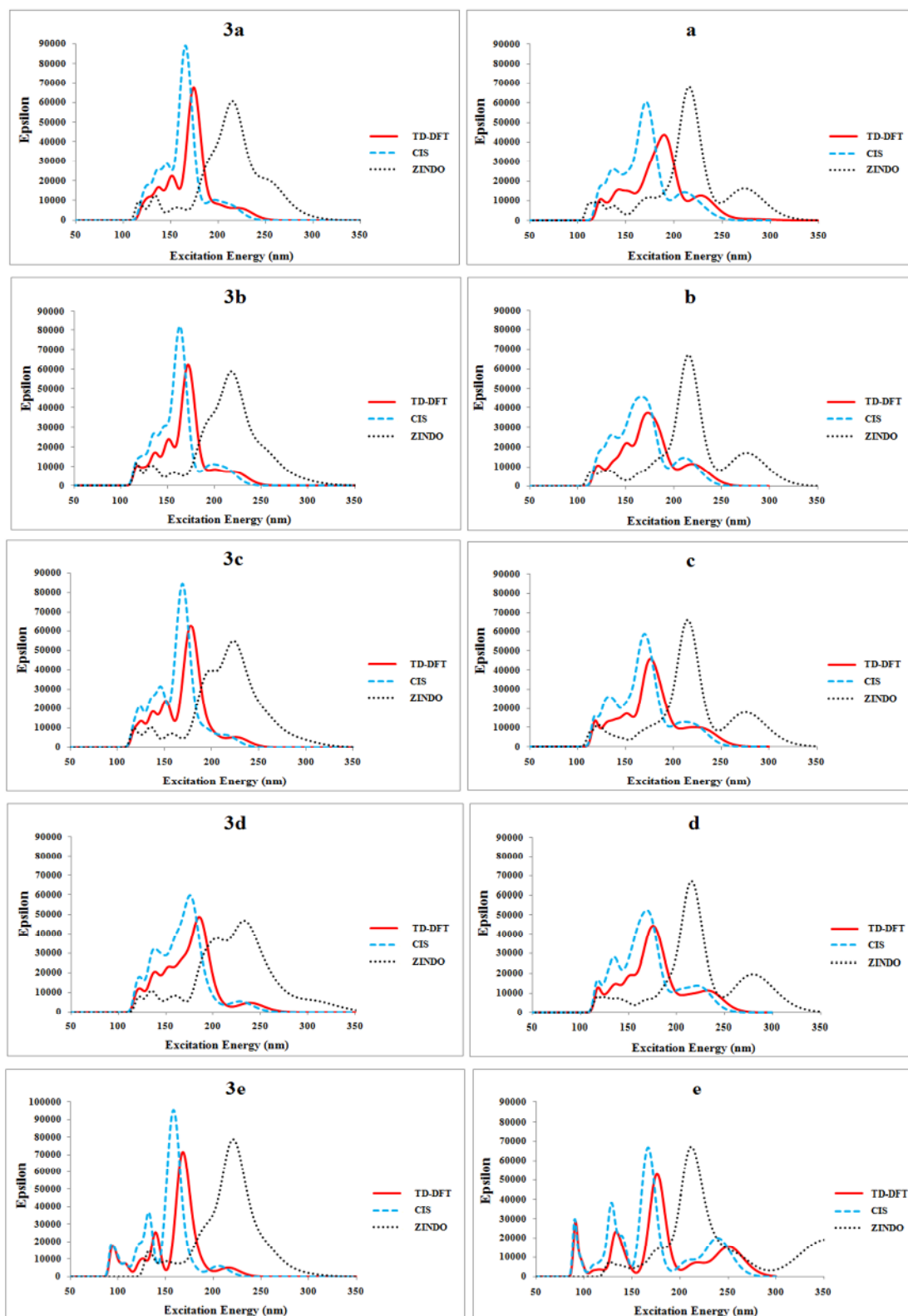


Fig. 2. The calculated UV-Vis spectrum for all compounds by three methods.

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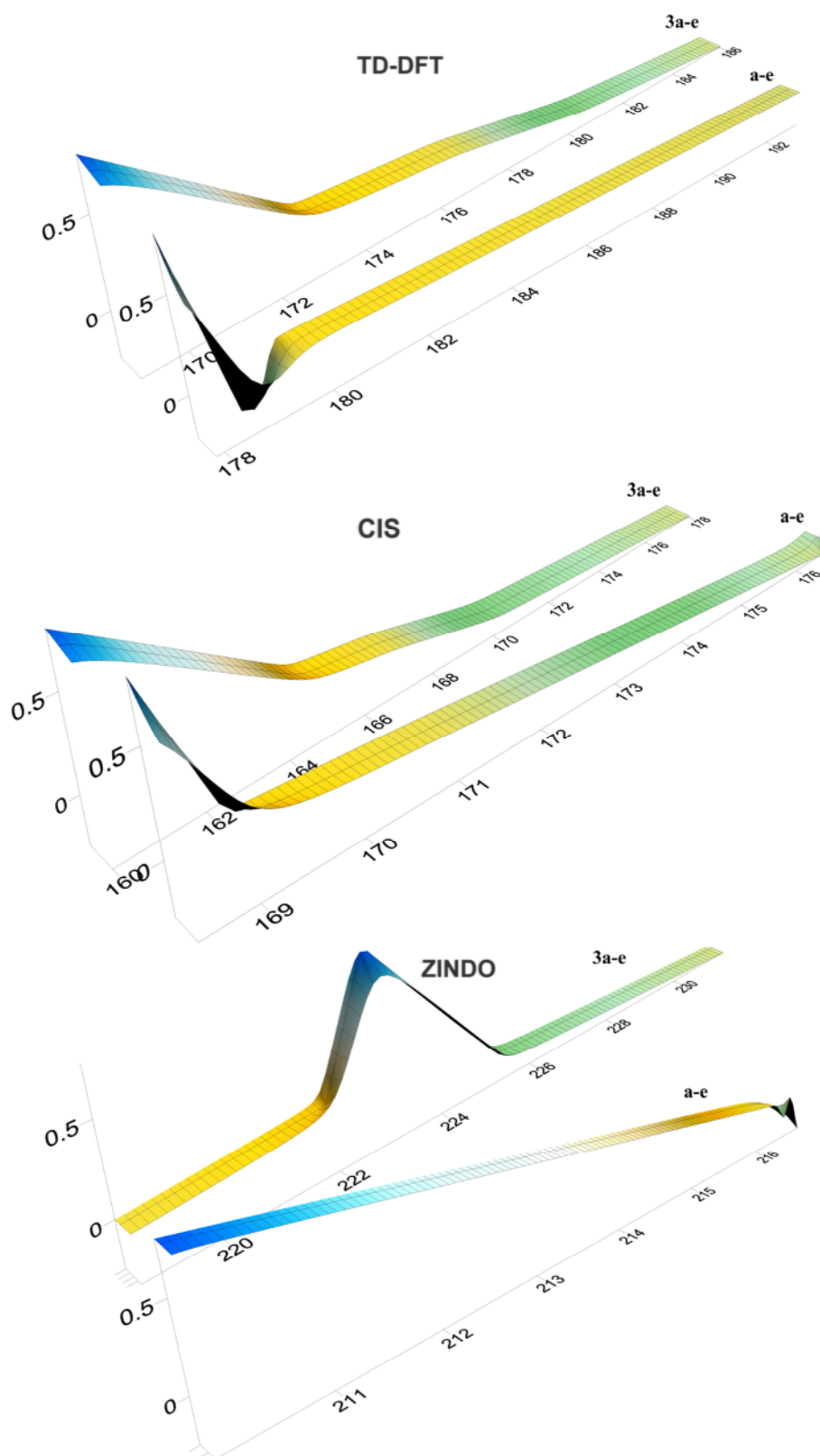


Fig. 3. The 3D surfaces of all compounds by three methods. X-axis: λ_{\max} (nm), Y-axis: energy gap (e.V.), Z-axis: Hammett number.

In the Fig. 3 shows three-dimension surface maps of all aromatic molecules by three methods, after and before cyclization. On the x-axis is the observed λ_{\max} (nm), the y-axis is based on energy gap (e.v.) of the λ_{\max} and z-axis is the observed Hammett para- effect number. The main data of this 3D surface exist in Table 1. As usual TD-DFT and CIS are similar results, have been formation of the ring the Hammett number is very effective in certain range of wavelengths. ZINDO method shows completely different and uncertain results. These changes in TD-DFT method is very intense, we can understand this sensitivity by 3D-surface compare to CIS method.

CONCLUSION

In this work we present the results of excited-state parameters for new intramolecular cyclization by three famous methodology; TD-DFT, CIS and ZINDO. First, electronic absorption spectra of two different states of reactant were calculated using three different quantum chemical methods. In the all computational calculations, TD-DFT method is in very close agreement with CIS output data, and ZINDO method has low accuracy. We were forced to use of comparatively small basis sets (6-31+G*) that this limitation caused to our results have a little deviations. Before cyclization, with the presence of donors substituted λ_{\max} values are bigger, when acceptors substituted are smaller, in the TD-DFT and CIS methods. CIS and TD-DFT spectrum have very similar spectra Models, also always absorption values for TD-DFT is smaller the CIS. ZINDO method in all cases, only shows one of the main peak and also could not follow the patterns of the other two methods. In the 3D-surfaces, TD-DFT and CIS are similar results, have been formation of the ring the Hammett number

is very effective in certain range of wavelengths. ZINDO method shows completely different and uncertain results.

Overall, have been investigated before and after intramolecular cyclization by UV-Visible spectrum tools, it is seem the results of TD-DFT method is more logical than other methods, because in the CIS method is only singly excited configurations with reference to a single-determinantal ground-state wave function, also ZINDO method has a simple methodology.

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