UV/VIS SPECTRAL SIMULATION OF A SYMMETRICAL DISAZO DIRECT DYE BY THE HARTREE-FOCK APPROXIMATION

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Abstract
A disazo direct dye having a symmetrical structure, derived from the 4,4'-diaminostilbene-2,2'-disulfonic acid was previously synthesized and applied to water-based acrylic resins, in coatings. The dye structure was previously experimentally analyzed using the UV/VIS spectroscopy and theoretical Density Functional Theory (DFT) calculations were employed to compare the calculated with the experimental UV/VIS wavelengths. In this paper the molecular dye structure was modeled using the MMFF94 force field and the Hartree-Fock (HF) approach. The UV/VIS spectrum of the minimum energy optimized structure was simulated using the Configuration Interaction Singles (CIS), the Time-Dependent (TD) and the Zerner's Intermediate Neglect of Differential Overlap (ZINDO) methods to evaluate the electronic excitation spectra. The ZINDO approach gave better maximum absorption calculated values compared to the CIS and TD methods, as previously noticed in case of using the DFT approach. A generally good agreement between the experimental and theoretical computed absorption maxima was noticed.

Introduction
Azo dyes are known as the most important class of synthetic, colored organic compounds. They are almost invariably prepared by the diazotization of aromatic amines and by the coupling of the obtained diazonium compounds with phenols, naphthols, arylamines, pyrazolones [1]. They are widely used in textiles, food, pharmaceutical, cosmetic industries, medicine, high-performance technology, etc. [2-7].

The symmetrical disazo direct dye presented in this paper was previously synthesized using 4,4'-diaminostilbene-2,2'-disulphonic acid as middle component and 2,7-dihydroxynaphthalene as coupling component [8]. The objective of this study is to use the Hartree-Fock (HF) approximation to model the structure of this previously synthesized disazo direct dye (**1**) (Fig. 1) in ground state, and the CIS, TD and ZINDO methods for its UV/VIS spectrum simulation. The experimental absorption maxima were compared to the calculated ones.
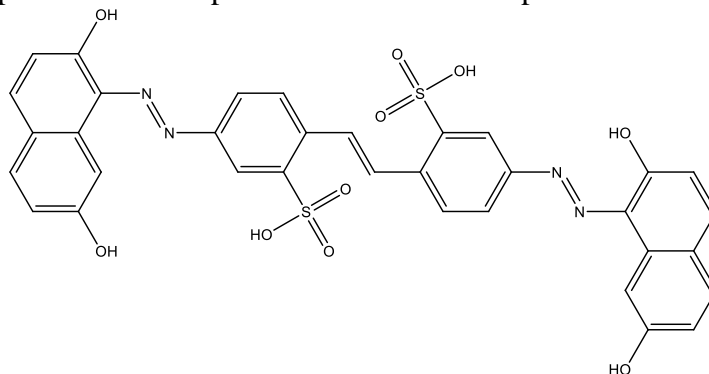

Figure 1. Structure of the disazo direct dye (**1**).

Theoretical structure investigation

The Marvin Sketch program, version 17.18.0, from ChemAxon (Marvin Sketch 17.18.0, 2017, ChemAxon Ltd., http://www.chemaxon.com.) was used to build the structure of the disazo diect dye (**1**). The conformational search was performed using the MMFF94 force field.

The minimum energy conformer thus derived was further geometry optimized in gas phase using the Hartree-Fock (HF) approach [9-11]. The ground state geometrical optimization of the title compound has been performed using the Gaussian 09 package [12]. All optimized structures were characterized as true minima by frequency calculations.

UV/VIS spectra simulation

Ultraviolet spectra analyses of the disazo direct dye (**1**), fully energy optimized in water, used as solvent, have been examined using the Configuration Interaction Singles (CIS) [13], Time-Dependent Systems (TD) [14] and Zerner's Intermediate Neglect of Differential Overlap (ZINDO) [15] methods. Eight singlet excited states were computed for the minimum energy dye conformer. The calculated wavelengths, which are a function of the molar absorption coefficients, were compared with the previously measured experimental data [8].

Results and discussion

The minimum energy conformer of the dye (**1**) derived from MMFF94 calculations was further optimized at the HF/3-21G level in ground state, using the Gaussian 09 program. The following data were obtained: the predicted SCF energy was of -3045.85701481 a.u., the unscaled zero-point correction (ZPE) = 0.575720 (Hartree/Particle); the thermal correction to the enthalpy (Hcorr) = 0.615792; the thermal correction to the Gibbs free energy (Gcorr) = 0.499944. To model the UV/VIS spectrum eight singlet excited states were considered.

The previously reported experimental UV/VIS spectrum in water of the dye (**1**) is characterized by two electronic absorption bands located at 329 nm and 560 nm [8].

The CIS/IEF-PCM(WATER)/3-21G, TD/IEF-PCM(WATER)/3-21G and ZINDO calculations were performed at the HF/3-21G level to simulate the UV/VIS spectrum of the minimum energy conformer of the direct azo dye (**1**) in water. The theoretical UV/VIS transitions were presented by visible absorption maxima and oscillator strengths in Table 1.

Table 1. Calculated CIS, TD and ZINDO absorption maxima and the oscillator strengths of dye (**1**).

Excited state	CIS		TD		ZINDO	
	Wavelength (nm)	Oscillator strength	Wavelength (nm)	Oscillator strength	Wavelength (nm)	Oscillator strength
S1	414	0.000	443	0.000	576	0.000
S2	407	0.000	435	0.000	570	0.000
S3	284	2.539	293	2.301	416	1.593
S4	279	0.079	286	0.026	403	0.012
S5	238	0.284	244	0.176	349	0.072
S6	232	0.261	239	0.164	347	0.069
S7	216	0.354	223	0.314	297	0.342
S8	211	0.008	219	0.014	292	0.057

The simulated UV/VIS spectra of the minimum energy conformer at the HF/3-21G level are presented in Figures 2 to 4. The visible maximum absorption (λ_{max}) value obtained at the HF/3-21G level in the water phase with the ZINDO approach is bigger than the CIS and TD

ones, for the third excited state: λ_{max} (ZINDO) = 416 nm; λ_{max} (TD) = 293 nm; λ_{max} (CIS) = 284 nm. For the seventh excited state, a closer maximum absorption value is noticed for the ZINDO approach, having λ_{max} = 297 nm, compared to the other methods: λ_{max} (TD) = 223 nm and λ_{max} (CIS) = 216 nm. Only the dominant configuration with the oscillator strength value > 0.30 for each excited state was considered. Two distinct low absorption peaks were observed in the CIS and TD simulated spectra, corresponding to lower oscillator strength values. Their presence was not noticed in the experimental UV/VIS spectrum. ZINDO method is considered to have the nearest results to the UV/VIS experimental spectrum.
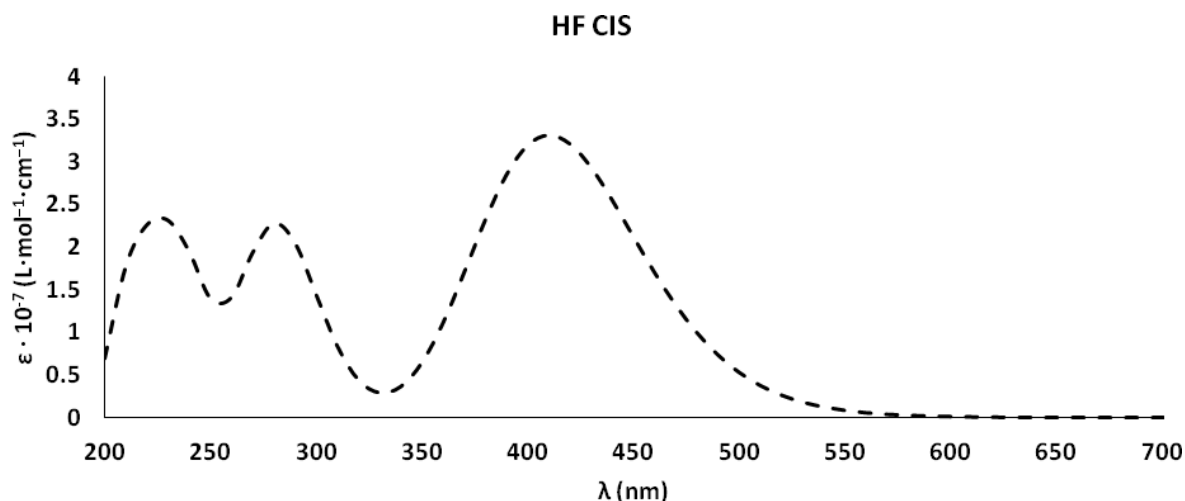
HF CIS

Figure 2. The calculated molar absorption coefficient (ε) versus the wavenumber (λ) of the dye (**1**), using the CIS approach at the HF/3-21G level.
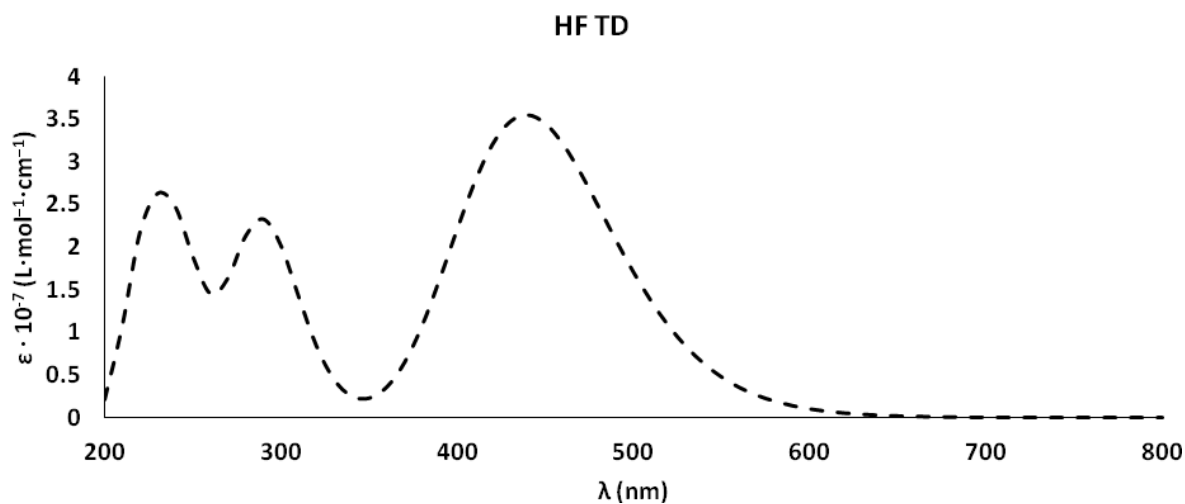
HF TD

Figure 3. The calculated molar absorption coefficient (ε) versus the wavenumber (λ) of the dye (**1**), using the TD approach at the HF/3-21G level.
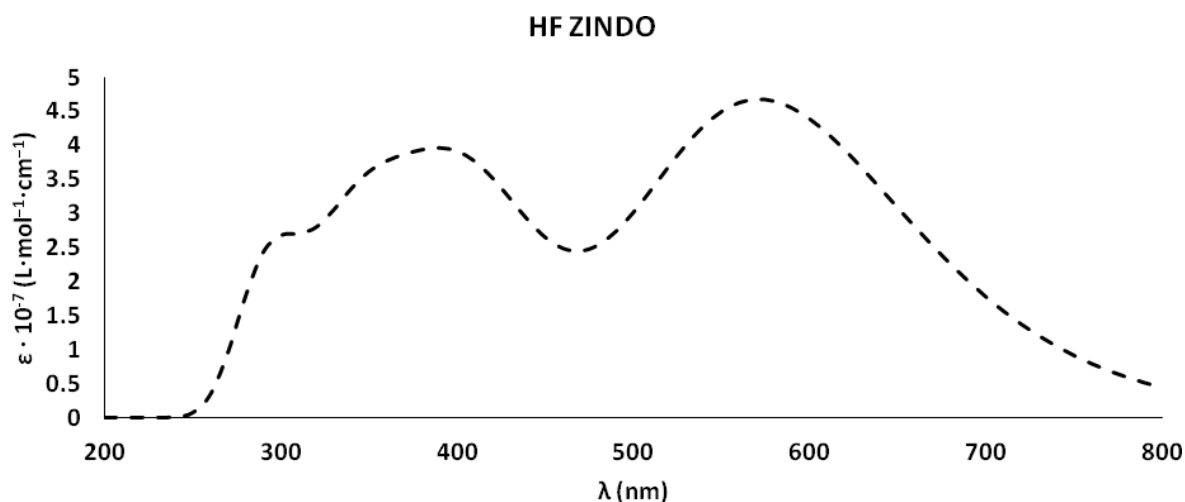
HF ZINDO

Figure 4. The calculated molar absorption coefficient (ε) versus the wavenumber (λ) of the dye (**1**), using the ZINDO approach at the HF/3-21G level.

Conclusion

The UV/VIS electronic spectrum was simulated for a disazo direct dye structure optimized using the Hartree-Fock approach and the 3-21G basis set. Good agreement between the experimental and ZINDO calculated wavelengths (λ_{max}) values was observed. Better UV/VIS simulation results were achieved using the ZINDO approach and comparable results with the experiment were noticed, compared to the TD and CIS methods, as previously reported for dye structure simulation using the DFT approach [8].

Acknowledgements

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