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DFT Simulation for Properties Determination of Chelating Spironaphthoxazine Derivatives †

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Abstract

This work focus on investigation of ten newly synthesized spironaphthoxazines using DFT to elucidate how substituents control physicochemical behavior. Frontier-orbital analyses show substituent changes primarily shift the LUMO, controlling HOMO–LUMO gaps and electrophilicity; the open forms (MC) structures exhibit smaller gaps than closed spiro forms (SP) due to extended conjugation. Simulated IR/Raman spectra provide diagnostic markers for structural assignment. Thermodynamic parameters (S, Cp, H, G; 200–500 K) reveal higher S and Cp for MC forms and for longer alkyl chains, yielding lower G at elevated temperatures. Transition-state calculations indicate accessible SP↔MC isomerization barriers, confirming accessible switching. These results offer a predictive framework to position functional groups and tailor optical response, switching kinetics, and stability for responsive materials.

Keywords: spironaphthoxazines; DFT; simulation; reactivity indexes

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1. Introduction

Spironaphthoxazines belong to one of the most promising classes of organic photochromes. Their main applications include: optical data recording and storage and switches, smart materials, sensors, photocontrolled drug delivery, biosensors for diagnostics etc. Their applications, particularly in medical and related fields, stem from their high photostability, fast switching, and structural versatility [1]. Spironaphthoxazines exist in two primary forms: Closed Spiro (SP) form: colorless with lower dipole moment (~5 D) and Open Photomerocyanine (MC) form: colored and having a higher dipole moment. Upon UV irradiation, temperature, solvent or other stimuli exposure, the spironapthoxazines convert from SP to MC through the cleavage of spiro C-O bond [1,2]. This transformation dramatically changes their molecular properties, enabling specific interactions with other molecules. The general chemical formula of SP and MC forms of a spironaphthoxazine derivative in a ring-opening transformation reaction is presented in Figure 1.

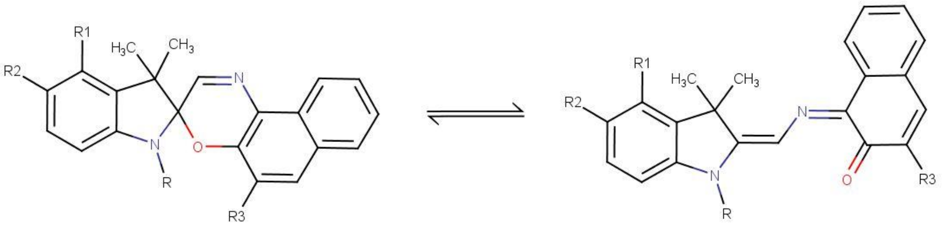


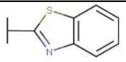
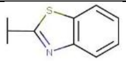
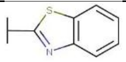
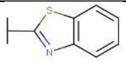
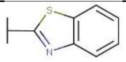
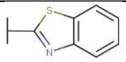
Figure 1. The general chemical formula of SP and MC forms of a spironaphthoxazine derivative in a ring-opening transformation reaction. R, R1, R2, R3 represent a different fragment.

A series of new spironaphthoxazines have been synthesized and the present work propose the investigation of ten of the new structures using Density Functional Theory (DFT) computations. Moreover, the goal of this work is to establish a foundation for future studies and identify new applications for these compounds. Property simulations enable us to assess the advantages of specific functional groups and optimize their placement within the molecular scaffold, thereby guiding the rational synthesis of targeted derivatives for desired applications.

2. Methods

DFT calculations was used and the molecules was described in PW91 and 6-311G(d,p) basis sets, in vacuum, for equilibrium geometry [3]. The optimized molecular structure and the energy of individual molecular orbitals were predicted for ten spironaphthoxazine derivatives with chemical structures constructed accordingly with data provided in Table 1 for base spironaphthoxazine presented in Figure 1. The calculations were made on the CTC conformer of the structures. HOMO-LUMO analysis with corresponding quantum global chemical reactivity descriptors of the studied molecules was obtained to predict molecular stability and reactivity of the molecules. Also, by DFT the vibrational frequencies, thermodynamic properties, NMR Chemical Shifts of molecules were predicted and the minimum energy pathway between the two geometries of the SP and MC forms with identification of the geometry of the transition state (TS) form was calculated. The results obtained based on computations were compared and discussed in order to establish the beneficial traits of possible future applications.

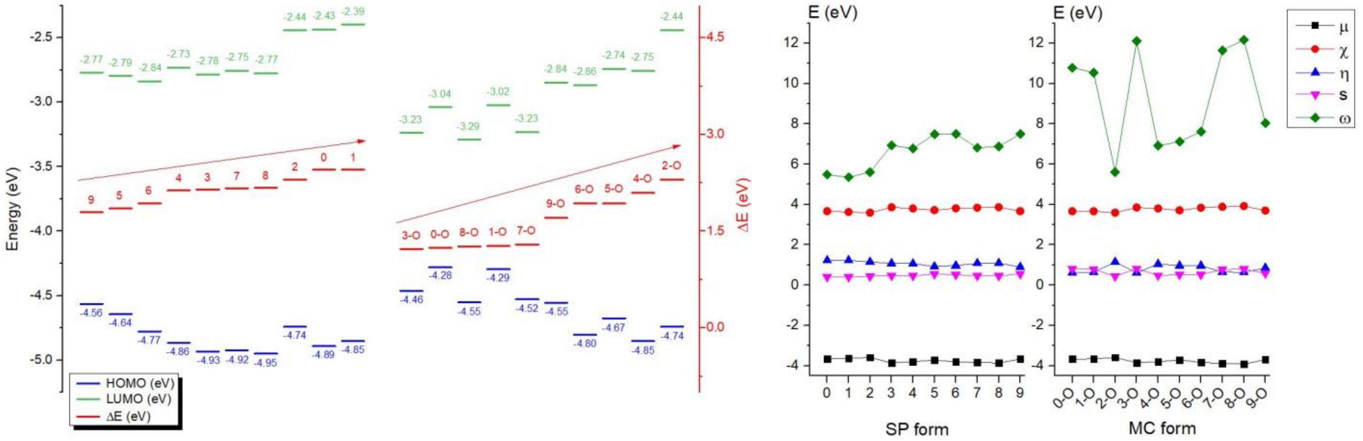
Table 1. The chemical formula of the series 0–9 of the spironaphthoxazines with corresponding substituents and the abbreviation of SP and MC forms used in this work accordingly with [1].

Molecular Formula	R	R1	R2	R3	SP form abb.	MC form abb.
C22 H20 N2 O	CH_3	H	H	H	0	0-O
C22 H20 N2 O2	CH_3	H	H	OH	1	1-O
C25 H26 N2 O2	C_4H_9	H	H	OH	2	2-O
C29 H23 N3 O S	CH_3	H	H		3	3-O
C32 H29 N3 O S	C_4H_9	H	H		4	4-O
C37 H31 N3 O S	CH_3	$(CH{=}CH_2)_2$	$(CH{=}CH_2)_2$		5	5-O
C40 H37 N3 O4 S2	C_4H_9	$(CH{=}CH_2)_2$	$(CH{=}CH_2)_2$		6	6-O
C33 H29 N3 O3 S	$C_3H_6COOCH_3$	H	H		7	7-O
C32 H27 N3 O3 S	C_3H_6COOH	H	H		8	8-O

C40 H37 N3 O S	$C_4H_8SO_3H$	$(CH{=}CH_2)_2$	$(CH{=}CH_2)_2$	H	9	9-O

3. Results

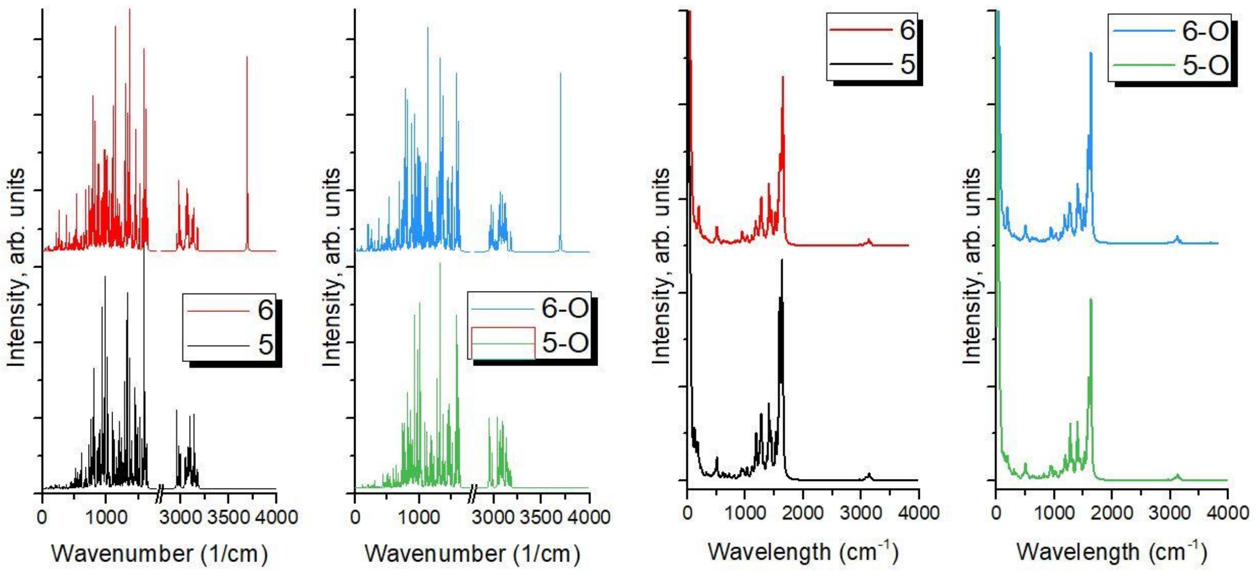
The analysis of the frontier orbitals, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), indicates the shapes and distributions of these orbitals, showing where the electron density is concentrated in the considered molecules. The global reactivity descriptors as chemical potential (μ), electronegativity (χ), global hardness (η), global softness (s) and electrophilicity (ω), were resulted from HOMO-LUMO analysis [4], by considering the energies determined with the GGA/PW91 density functional. The calculated values for all the considered structures are summarized in graphs presented in Figure 2.



(**a**) (**b**)

Figure 2. (**a**)—The HOMO (blue horizontal lines and values) and LUMO (green horizontal lines and values) energies, energy gap values in ascending order from left to right (red horizontal lines with structures abbreviations); (**b**)—left panel for SP forms and right panel for MC forms represent Chemical potential (μ)—black color, Electronegativity (χ)—red color, Global Hardness (η)—blue color, Global Softness (s)—magenta color and Electrophilicity (ω)—green color. The presented values are in eV.

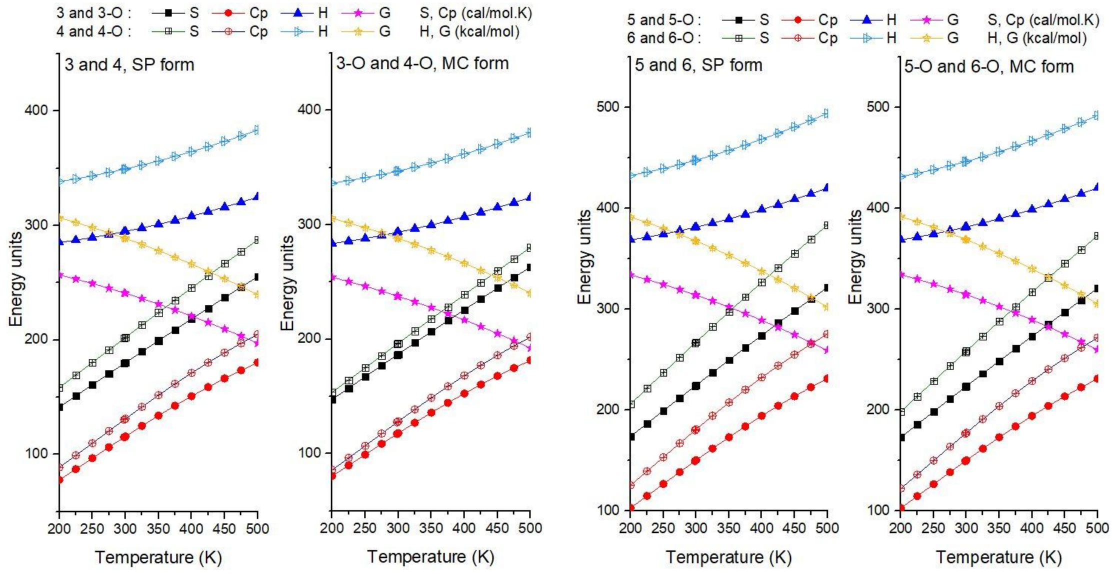
It can be observed in Figure 2, that tuning substituents affects the acceptor part, where electron-withdrawing groups stabilize the LUMO, and electron-donating groups destabilize it. Left structures (considering the ascending order from left to right) have lower excitation energies leading to longer wavelength absorption and increased electrophilicity, while right structures show the opposite. If these relate to closed versus open forms, MC structures generally have smaller gaps due to extended conjugation. From the results obtained, the simulated IR (Figure 3a)) and Raman (Figure 3b)) spectra of compounds 5, 6, 5--O, and 6--O were selected for illustration and comparison.



(**a**) (**b**)

Figure 3. (**a**)—IR frequencies of 5 and 6 structures (left panel) and 5-O and 6-O structures (right panel); (**b**)—Raman spectra at temperature of 298.0 K for 5 and 6 structures (left panel) and 5-O and 6-O structures (right panel) with Lorentzian smearing: 20 cm^{-1} and Incident light: 514.5 nm.

Figure 4a,b shows the comparative influence of the length of the hydrocarbon radical in the R position (Figure 1) on the thermodynamic behavior of structures 3, 4, 5 and 6 and their MC forms. For this purpose, pairs of similar structures differing only in the R fragment (Table 1) were used.



(**a**) (**b**)

Figure 4. The standard thermodynamic quantities (Entropy (S), Heat Capacity (Cp), Enthalpy (H), Free Energy (G)) for temperature domain of 200 K to 500 K, with Zero-Point Vibrational Energy included. The calculated values are graphically presented in (**a**)—for 3 and 4 SP forms (left panel) and 3-O and 4-O MC forms (right panel) and in (**b**)—for 5 and 6 SP forms (left panel) and 5-O and 6-O MC forms (right panel).

Considering Figure 4a,b it was observed that, MC forms (3--O, 4--O, 5-O and 6-O) show higher heat capacity (Cp) and entropy (S) compared to spiro structures (3, 4, 5 and 6) probably due to greater flexibility/delocalization in the open form (more degrees of freedom in the -C4H9 chain). Enthalpy (H) changes little with fragment R length. MC forms has slightly higher H, but the entropy gain means its Free energy (G) drops faster with temperature; thus the open form is increasingly favored at higher temperatures, while spiro form may be preferred at lower temperatures. Because T·S factor (here, T·S is change in entropy with temperature in Gibbs law) is larger for 4 and 6, the G values become relatively lower at higher temperature, so 4 and 6 is slightly more thermodynamically favored than 3 and 5 as temperature rises. Table 2 are given the computed values for the transition state energy and the isomerization reaction parameters from the SP form to the MC form, for some of the studied structures. Therefore, Figure 5 presents the frontier orbitals HOMO and LUMO obtained after the transition state optimization and calculated energy gap.

Table 2. This is a table. Tables should be placed in the main text near to the first time they are cited.

Molecular Formula	TS Name	ΔE (SP-MC) [eV]	Energy of Reaction [kJ/mol]	Energy of Barrier [kJ/mol]
C22 H20 N2 O	(0-TS)	−28,170.682760	9.992	13.679
C22 H20 N2 O2	(1-TS)	−30,213.788084	9.133	13.268
C29 H23 N3 O S	(3-TS)	−47,807.757338	10.696	20.898
C33 H29 N3 O3 S	(7-TS)	−56,150.123369	10.878	15.119
C32 H27 N3 O3 S	(8-TS)	−55,080.590484	11.475	15.509

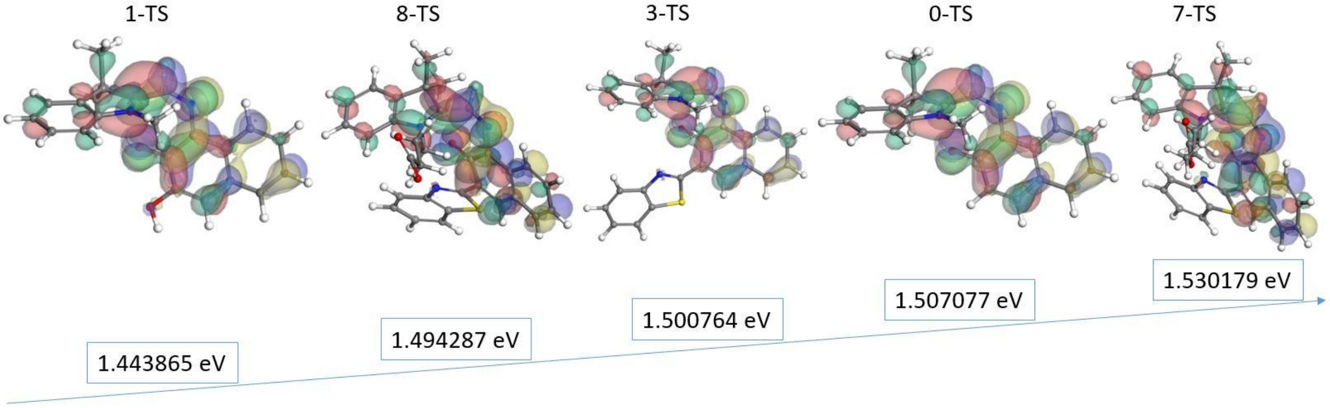


Figure 5. The plot of energy gap (the ascending values on the blue arrow) and the frontier orbitals HOMO and LUMO (for an isovalue of 0.03) of the chemical structure of the transition state. The surfaces are drawn by yellow/blue and green/red colors for HOMO and LUMO, respectively, where the negative/positive blobs are represented by light and dark colors. The grey, red, blue, yellow and white spheres represent the carbon, oxygen, nitrogen, sulfur and hydrogen atoms, respectively.

4. Conclusions

In this contribution DFT study was used to set up structure–property relationships for a new series of spironaphthoxazines. Substituent engineering primarily modulates the acceptor part of the molecules, stabilizing or destabilizing the LUMO and thus tuning the HOMO–LUMO gap, electrophilicity, and expected absorption wavelengths. The obtained results have shown that MC forms generally display smaller gaps than the closed spiro forms, consistent with extended conjugation. Thermodynamic analyses show higher entropy and heat capacity for MC versus SP, and for longer R chains (-C4H9 > -CH3), reflecting increased flexibility; consequently, free energy for longer-chain analogs decreases more steeply with temperature, making 4 and 6 slightly more favored than 3 and 5 at elevated temperatures. Simulated IR and Raman spectra provide diagnostic fingerprints for structures 5, 6 and their MC isomers, supporting experimental assignment. Transition-state calculations confirm feasible SP→MC isomerization with modest barriers (13–21 kJ/mol) and small reaction energies (9–11 kJ/mol), indicating thermally and photochemically accessible switching.

Author Contributions: Conceptualization, A.N. and V.C.; methodology, A.N. and V.C.; software, V.C. and V.A.; validation, A.N. and S.M.; formal analysis, A.N.; investigation, A.N.; resources, V.C. and A.V.; data curation, A.N. and S.M.; writing—original draft preparation, A.N.; writing—review and editing, A.N.; visualization, S.M. and A.V.; supervision, A.N.; project administration, A.N. All authors have read and agreed to the published version of the manuscript.

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