

Theoretical study on the photochemical cyclization and cycloreversion of a dithienylethene switch

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Abstract

In the last decades, the dithienylethene switches have been constituted as excellent candidates for developing molecular electronic devices. One of the reasons is that their photochromic properties, such that photochemical cyclization and cycloreversion, can be controlled using light. Although these properties have been widely investigated in different types of dithienylethene switches, and the results have helped to understand how they take place in photochemical reactions, it is not possible to generalize them for new dithienylethene switches. Here, we present a theoretical study of the photochemical cyclization and cycloreversion of a new dithienylethene switch using quantum chemical methods.

The absorption and emission were performed in the gas phase and solvent (toluene). The results obtained are in good agreement with the known experimental ones. Critical points on the ground- and excited-state potential energy surfaces were calculated using density functional theory; dynamics calculations were carried out using simulations of *ab initio* molecular dynamics. On the basis of the obtained potential energy profile, a general valid photochemical cyclization mechanism was identified.

Keywords: Cyclization, Cycloreversion, Excited States, Potential Energy Surfaces, *Ab Initio* Molecular Dynamics.

1 Introduction

In recent years, the study of dithienylethene switches has attracted the attention of many theoretical and experimental research groups. The reason lies in their good properties, thermal stability and fatigue resistance. In view of their properties, the dithienylethene switches seem as excellent candidates for developing molecular electronic devices [1-13].

A general scheme of a dithienylethene switch molecule in the open and closed form is presented in Figure 1. In a dithienylethene switch molecule, the light absorption in the range of UV induces a photocyclization (according to the Woodward-Hoffmann rules) from the open to closed ring and vice versa in the visible range [6, 14, 15].



Figure 1: Scheme of a reversible photocyclization reaction of a dithienylethene switch molecule. The left side represents the open ring and the right side represents the closed ring. The R_1 and R_2 are substituent, and the numbers 1 and 2 in the molecule mean the ring-closing carbon atoms, C_1 and C_2 , respectively.

In the open ring, the electronic interaction between the thiophene rings and the ethylene moiety is little, causing at the same time a poor electronic interaction between the substituents R_1 and R_2 . In the closed ring, after the photocyclization in the open ring, the thiophene rings lose their aromatic character and the ethylene moiety changes toward a single bond. Thus, the conjugation is extended over the whole molecule [1, 6, 16].

The photochemical cyclization and cycloreversion process of a dithienylethene switch has been widely studied [1–4, 6, 7, 11, 16, 52, 57–59]. It has been shown that this process is carried out under the absorption of a certain range of the light spectrum, both for the open and closed rings [6, 16]. The vast majority of theoretical works on this subject focuses on the computation of vertical excitation energies, the analysis of frontier orbitals and the analysis of potential energy surface scan along pre-determined coordinates, i.e., it is studied mostly from an electrostatic point of view. Complementary studies of the dynamics of the process would allow having a more

realistic idea of what happens [6]. However, a dynamic of photochemical processes can be computationally very expensive [17, 18]. In recent years the use of computational techniques such as simulations of *ab initio* molecular dynamics (AIMD) have allowed getting a more realistic idea of the photochemical process at a reasonable computational cost [6, 17, 18].

Following the path left in this field, the present work proposes a theoretical study of a dithienylethene switch using electrostatic calculations and simulations of *ab initio* molecular dynamics of the excited states. The dithienylethene switches investigated in this work are depicted in Figure 2. In order to do this, it is planned to use the Q-Chem program package which has shown great support for this type of calculations [19, 20]. This work is structured as follows. Section 2 contains a brief review of the theoretical approaches used during the research. In Section 3, we described the computational details. In Section 4 is described the results obtained and their analysis. Finally, in Section 5, we give conclusions and some future prospects of this work.



Figure 2: Chemical structure of the dithienylethene switch molecule. The left side represents the open ring and the right side represents the closed ring. The numbers 1 and 2 in the molecule mean the ring-closing carbon atoms, C_1 and C_2 , respectively.

2 Theoretical Framework

This section describes some concepts that were used or mentioned in the course of this thesis.

2.1 Excited States and Photocyclization Reactions

The photocyclization reaction of the dithienylethene switches takes place in the 1,3,5-hexatriene unit in a conrotatory fashion. It can be said that the 1,3,5-hexatriene is the simplest molecular framework of the dithienylethene switches. Understanding the photocyclization reaction in 1,3,5-hexatriene will help us to get a proper picture of the whole molecule. Therefore, in order to have a clear idea why the photocyclization reaction of the dithienylethene switches takes place in a conrotatory fashion and why not in a disrotatory fashion, i.e., in a thermal reaction, we describe below the Woodward-Hoffman rule based on the orbital symmetries in a 1,3,5-hexatriene.

As it is shown in Figure 3, a thermal reaction in a 1,3,5-hexatriene is allowed when the pair of electrons from the bonding orbitals in the ground state of the reactant are transferred to the bonding orbitals in the product. This results from the fact that the thermal reaction follows a disrotatory path which preserves the σ mirror plane for the bonding orbitals, more specifically, it preserves the orbital symmetry correlation between the reactant and the product. However, the reaction could be thermally forbidden, for example when there is a considerable activation energy between the ground state of the reactant and the ground state of the product [15, 21]. In this case, it can become photochemically allowed when the molecule is excited in such way that electrons are promoted to higher energy orbitals. This allows the molecule to have enough energy not only to overcome the activation energy but also to explore different reactions channels with the same Woodward-Hoffmann rules [22].

Now we focus on the photochemically allowed reaction. Figure 4 illustrates an orbital correlation diagram when the absorption of a photon leads the 1,3,5-hexatriene to the excitation of an electron from the bonding orbital 3π to the antibonding orbital 4π . The conrotatory path of the excited 1,3,5-hexatriene leads to the excited 1,3-cyclohexadiene keeping the same level of energy. In contrast, the disrotatory path involves a significant increase in energy [22, 23].

The orbital correlation diagram (Figure 4) shows that the excited 1,3-cyclohexadiene is formed via conrotatory path, but this is not true, it is generated in its ground state. Solving this discrepancy requires to consider the overall state of the molecule. We use the direct product between the symmetry of the orbitals of the two most external electrons, satisfying the following rules: $S \times S = S$; $S \times A = A$ and $A \times A = S$, where S means symmetric with character +1 and A means antisymmetric with character -1. In addition, we consider the conrotatory path through which the symmetry C₂ is preserved [22, 23].

Since 1,3,5-hexatriene $(1\pi,2\pi,3\pi)$ is correlated with the 1,3-cyclohexadiene $(1\sigma,1\pi,3\pi)$ (see



Figure 3: Scheme of the orbital correlation diagram for a 1,3,5-hexatriene in the ground state. Dashed lines relate empty orbitals with the same symmetry and solid lines relate occupied orbitals with the same symmetry.



Figure 4: Scheme of the orbital correlation diagram for a 1,3,5-hexatriene in the excited state. Dashed lines relate empty orbitals with the same symmetry and solid lines relate occupied orbitals with the same symmetry.

Figure 4), it follows that the 1,3,5-hexatriene $(1\pi^2 2\pi^2 3\pi^2, {}^1S)$ is correlated with 1,3-cyclohexadiene $(1\sigma^2 \ 1\pi^2 \ 3\pi^2, {}^1S)$, where 1S denotes the result of the direct product between the symmetry $S \times S = S$ and the superscript 1 means that the electrons are in a singlet configuration. Figure 5 shows a didactical scheme to represent the levels of energy of the results of the product of the symmetries. The dashed lines stand for the connections between the states with the same symmetry and multiplicity. Notice that it is not allowed to have crossings between the energy levels with the same symmetry (non-crossing rule), therefore the blue lines are used to remark what happens.

Now, let us look at the conrotatory ring closure in terms of the overall states of the molecule. If we start from the ground state of the 1,3,5-hexatriene, and considering the thermal reaction, then the ground state of the 1,3-cyclohexadiene can be reached without going through their excited states. However, this path presents a considerable activation energy barrier and therefore becomes energetically not feasible. Thus, in a photocyclization which involves 1,3,5-hexatriene units, there will exist a considerable activation energy barrier, as a result of the rise in energy in the orbital correlation and the peak generated by the non-crossing of the states of the same overall symmetry. The activation energy is overcome via conrotatory fashion through their excited states.



Figure 5: Scheme of the state correlation diagram for the photocyclization of 1,3,5-hexatriene to 1,3-cyclohexadiene. Dashed lines connect molecular orbitals with the same symmetry and same multiplicity, and solid blue lines connect molecular orbitals satisfying the non-crossing rule.

2.2 The Born-Oppenheimer (BO) Approximation

The problem of the three bodies in quantum mechanics is an example of the need to resort to approximate methods for solving the Schrödinger equation since it is not possible to solve it analytically. The complexity of the problem increases with the number of bodies in the system, like the molecular systems. An important feature in molecular systems is that nuclei are heavier than electrons, which means that the movement of electrons is much faster than nuclei and can adjust to the position of the nuclei simultaneously. Thus, taken into account the great difference of masses between the electrons and the nuclei, the position of the nuclei can be considered as fixed. This allows solving the Schrödinger equation for electrons with a static electronic potential. This approximation is known as the Born-Oppenheimer approximation or adiabatic approximation [22].

2.3 The Franck-Condon (FC) Principle

Photochemical reactions involve of absorption and emission of light, which at the same time generate electronic transitions between different states of energy. The absorption and emission of light are often described by the Franck-Condon principle. This principle states that the large difference between nuclear and electronic masses makes that an electronic transition to occur almost simultaneously, taking into account the timescale of the nuclear motions. From a quantum mechanical point of view, during an electronic transition the dynamic of nuclei does not change, i.e., the nuclear wavefunction remains unaltered [22].

Figure 6 illustrates a scheme of the Franck-Condon principle with two potential energy curves for two electronic states, S_0 and S_1 for a diatomic molecule. The transitions start from the lowest vibrational energy level of the ground electronic state at the equilibrium bond length Q_e (absorption, red line) and the first excited state at the equilibrium bond length Q'_e (emission, green line) toward the vibrational state with the most resembles wavefunction to the initial wavefunction, respectively. Notice that the transitions are represented as vertical lines since, in this way the transition preserves the nuclear locations, which it guarantees that the nuclear wavefunction remains unaltered during the transition.

This principle can be evaluated by computing the expectation value of the electronic transition dipole moment between the ground vibronic state and the upper vibronic state. For example, if we take the absorption described in Figure 6 and compute the electronic transition dipole moment, within the BO approximation, we can get the following factor

$$S(\nu',\nu) = \int d\tau \Phi_{\nu'}^*(Q_e) \Phi_{\nu}(Q_e).$$
 (1)

The overlap integral in Equation 1 is called Frank-Condon [22, 24]. Thus, if the overlap

between the two vibrational wavefunctions is large, then the overlap integral is large as well. The square of Equation 1 represents the relative intensities of the vibronic transition.



Internuclear distance

Figure 6: Illustration of the Franck-Condon principle.

2.4 Ab initio Molecular Dynamics (AIMD)

One of the most common algorithms for studying the behavior and dynamics of a molecular system is molecular dynamics (MD). This algorithm relies on solving Newton's equations of motions numerically for the system of interest. These equations allow to calculate the thermodynamics, kinetics, and dynamical properties of the system. In order to get the equations of motion, one requires to calculate the interatomic forces which are obtained from potential functions. In classical simulations, the potential functions are computed empirical, namely, they are parameterized with experimental data or they are fitted with *ab initio* data of small systems. This way of getting the potential functions limits their transferability to other systems [18, 25].

Unlike the classical simulations, the simulations based on methods of first principles do not present transferability problems. One of these methods is the *ab initio* molecular dynamics method (AIMD). In AIMD the forces are calculated *on-the-fly*, that is, during the course of the dynamics. The forces that act on the nuclei are generated from the electronic structure. Thus, contrary to the classical molecular dynamics, for AIMD the electronic parameters to calculate the forces of acting are not determined in advance. Therefore, the problem now is reduced to solve a system of many

electrons: solve the Schrödinger equation. For this purpose, methods such as Hartree-Fock (HF) and density function theory (DFT), among others, are used [25, 26].

In AIMD, the interatomic forces are calculated classically by $F = -\nabla_{\vec{R}} V(\vec{R})$, where $V(\vec{R})$ is a potential function and \vec{R} is nuclear coordinate. Through the BO approximation, $V(\vec{R})$ can be write as

$$V(\vec{R}) = \langle \Psi_0(\vec{r}) | H_e(\vec{r}_i; \vec{R}) | \Psi_0(\vec{r}) \rangle, \qquad (2)$$

where $H_e(\vec{r}_i; \vec{R})$ is the electronic Hamiltonian and $|\Psi_0(\vec{r})\rangle$ is the ground state wavefunction of the molecular system. Although AIMD is a very successful method to study chemical reactions, it has limitations in the timescales and the achievable length, as well as a high computational cost. These limitations, make the method applicable to small systems and chemical reactions in a timescale lower than 1 ns, the known limit [18, 25, 26].

2.5 Density Functional Theory (DFT)

One of the most important computational methods to study a molecular electronic structure is the Density Functional Theory (DFT). DFT is based on two theorems. The first theorem states that the total energy *E* of a molecular system can be represented as a unique functional of the electronic density $\rho(\vec{r})$ of the molecule. In other words, the external potential $v(\vec{r})$ that defines the Hamiltonian of the system has one to one relationship with $\rho(\vec{r})$, therefore this allows us to write

$$E_{v}[\rho(\vec{r})] = \int d\vec{r} v(\vec{r})\rho(\vec{r}) + F[\rho(\vec{r})], \qquad (3)$$

where

$$F[\rho(\vec{r})] = \langle \Psi[\rho(\vec{r})] | \hat{T} + \hat{U} | \Psi[\rho(\vec{r})] \rangle$$
(4)

is a universal functional, since the mathematical shape of the kinetic energy \hat{T} and the repulsive Coulombic interaction potential \hat{U} are the same in any molecular system [27, 28].

The second theorem states that the density which minimizes the total energy is the density of the ground state. Thus, by the minimal principle:

$$E_v[\rho(\vec{r})] \ge E_v[\rho_0(\vec{r})] = E,$$
 (5)

where $\rho_0(\vec{r})$ and *E* are the density and the energy of the ground state, respectively.

Notice that in a system of *N* electrons, the electronic density is understood as the probability to find an electron in a position \vec{r} where the other electrons (N - 1) are anywhere in the molecular space [29, 30].

While it is true that these theorems guarantees the existence and the unicity of a functional of the energy in terms of the density, they can not describe the form of this functional. However, it is possible to express the energy as

$$E_{v}[\rho(\vec{r})] = \int d\vec{r}v(\vec{r})\rho(\vec{r}) + \frac{1}{2} \int \int d\vec{r}d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + G[\rho(\vec{r})],$$
(6)

 $G[\rho(\vec{r})]$ is a universal functional

$$G[\rho(\vec{r})] = T_s[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})],$$
(7)

where $T_s[\rho(\vec{r})] = -\frac{1}{2} \sum_{i=1}^N \int d\vec{r} \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r})$ is the kinetic energy functional of a non-interacting electrons system and $\phi_i(\vec{r})$ is the *i*-th monoelectronic orbital. $E_{xc}[\rho(\vec{r})]$ is the exchange correlation (xc) energy functional of an interacting electrons system which mathematical form is not known. From here and using the method of Lagrange multipliers we can arrive to a set of self-consistent equations:

$$\left(-\frac{1}{2}\nabla^{2} + v(\vec{r}) + \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{xc}(\vec{r}) - \epsilon_{j}\right)\phi(\vec{r}) = 0,$$
(8)

$$\rho(\vec{r}) = \sum_{j=1}^{N} |\phi_j(\vec{r})|^2,$$
(9)

and

$$v_{xc} = \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta \rho(\vec{r})}.$$
(10)

They are called Kohn-Sham (KS) equations, where $\phi_j(\vec{r})$ and ϵ_j are the KS single-particle orbital and the KS energies of a fictitious system. To use this theory in the praxis, it is necessary to approximate E_{xc} . There are several works about approximations of the E_{xc} such that local density approximation (LDA), general gradient approximation (GGA), hybrid functionals, etc [28, 30]. Nowadays, there are not only sophisticated functionals to approach E_{xc} but even to approach the kinetic energy functional, with the purpose of obtaining a DFT that depends only on the density in an explicit way [31, 32]. In this thesis, we focus in giving a brief explanation about DFT and the functionals we have used. We describe them in the next section.

2.6 Time Dependent Density Functional Theory (TD-DFT)

Even though DFT is a powerful tool to study the molecular structure of molecular systems, it is not able to describe problems that involve molecular optics and electronic spectroscopy, i.e., problems related to electronically excited states [33, 34]. It was not, however, until 1984 with the Runge-Gross theorem that the time-dependent density functional theory (TD-DFT) started

[35]. The theorem states that when a system in its ground state is under a time-dependent (TD) perturbation, then the TD electronic density determines the TD external potential plus a TD scalar function [33–35]. TD-DFT like DFT, despite being also a formally exact theory, must be approximated. Thus, through linear-response (LR) theory, it is possible to access the information of the excited states of the system. The LR-TD-DFT can be used if the TD perturbation is small in the sense that the perturbation does not change completely the ground state of the system.

One of the most widely used LR-TD-DFT was developed by Casida [33] and it has been implemented in many computational chemistry software. For further information on the subject, see the following references [33–35]. We would like to highlight certain characteristics of this theory. The conventional TD-DFT is based on the adiabatic approach which implies that it is not possible to calculate conical intersections with TD-DFT[34, 36, 37]. Asymptotically corrected hybrid functionals with a HF exchange between 20% and 25% achieve better results for systems that are in singly excited states [34]. TD-DFT demands low computational effort, however, in cost to the methods based on the wavefunction (for example CASPT2 or LR-CC), it is not accurate when computing the excited state energies. This lack of accuracy is related to the Coulomb self-interaction of the electrons, also called self-interaction-error, caused by the approximation of the xc energy functional [38, 39].

2.7 Scaled Opposite-Spin with the Configuration-Interaction Singles plus perturbative Doubles (SOS-CIS(D))

As it was mentioned in the last section, there is not an exact xc energy functional in DFT and TD-DFT. Therefore, It is natural to look into the methods that do not present this problem. The methods based on the wavefunction have been shown to be a good alternative to study excited states, however, in general to a high computational cost [40, 41].

A good candidate for the study of the excited states of a molecular system is the scaled opposite-spin with the configuration-interaction singles plus perturbative doubles (SOS-CIS(D)), since it presents a reasonable computational cost and high accuracy in the calculation of excited state energies [40, 41]. This method is an improvement to the perturbative doubles correction to configuration interaction with single substitutions (CIS(D)) method, which in turn is based on the traditional configuration interaction with single substitutions (CIS) method. Recall that in a CIS method, the wavefunction of the system is a linear combination of the ground state wavefunction plus the sum of all possible wavefunctions in which an electron of an occupied ground state orbital is promoted to a virtual orbital. The correction of the energy of the double excitation to the CIS method, CIS(D), is done through the second-order perturbative theory. Finally, an improvement to the CIS(D) method is implemented mainly by the use of a separate scaling of the same-spin and opposite-spin contributions. The scale factor is 0 and 1.3, respectively [40, 42].

Additionally, it is important to mention the limitations that SOS-CIS(D) has showed. This method may be inappropriate to describe a molecular system when the ground state wavefunction has a strong multicofigurational character, i.e., it fails when the system presents a near-degeneracy in the excited states. Also, the method fails when its excited states have doubly excited character [40, 41].

3 Computational Details

We compute the excited state energies of the dithienylethene photo-switches for the open and closed ring (see Figure 2), their potential energy surfaces (PESs) restricted to one reaction coordinate and the *ab initio* molecular dynamics of these molecules when they go from the open ring to the closed ring and vice-versa. All the calculations were performed using Q-Chem04 [20].

3.1 Ground- and Excited- State Geometry Optimization

Geometry optimization of the ground state and the first excited state for the open and closed ring were performed at the DFT level of theory, using an ω B97X-D functional and a cc-pVDZ basis set [43]. We briefly describe the ω B97X-D functional and a cc-pVDZ basis set.

The ω B97X-D functional is a long-range correlated (LC) hybrid density functional that includes atom-atom dispersion corrections, expressly it includes a fitted function of interatomic distances that contains adjusted parameters that control the dispersion for atom pairs and the strength of dispersion corrections. Furthermore, this functional is improved with a 100% of long-range exact exchange and a 22% of short-range exact exchange, i.e., a 100% HF exchange for longrange electron-electron interactions and a 22% HF exchange for short-range electron-electron interactions. It is important to mention that this functional is free of self-interaction problem for a long-range, but it is not free of self-interaction for short-range [44].

The correction consistent polarized valence double-zeta (cc-pVDZ) is one of the most useful basis set for correlated molecular calculations [43]. This kind of basis set was designed to recover the energy correlation of the valence electrons through the addition of a set of higher angular momentum functions (also called polarization functions) with the similar amount of correlation energy. As "VDZ" means doubling the number of valence orbitals, the basis set has one contracted function for each core atomic orbital, two contracted functions for each valence atomic orbital and one set of polarization functions. Therefore, for the atoms we are interested in we have: 5 basis functions for a Hydrogen, 14 and 18 basis functions for the elements from the first and second row of the periodic table, respectively [43, 45].

3.2 Vertical Excitation Energies

After having reached the minimum of the ground state for the open and closed ring, a set of first ten excited states calculations were performed. The methods used were SOS-CIS(D) and TD-DFT. Table 1 shows the functionals used and a description of the contribution to the exchange and correlation parts.

All the functionals used are hybrid functionals, with exception of BLYP. A hybrid functional approximates the xc energy part with a percentage of the exact exchange contribution from HF

and the remainder with the contribution of the others *ab initio* or empirical sources. Once the excited states were computed, an optimization of the first excited state was carried out. After that, a set of ten excited states calculations was performed on the first excited state optimized structure on the ground state, i.e. emission. The level of theory used was the same used for the ground state optimized structure.

The	ory		Description	References
	חעום	Exchange:	B88(GGA)	[40, 47]
	BLYP	Correlation:	LYP (GGA)	[46, 47]
	B3I VD	Exchange:	20% HF + 8% Slater (LSDA) + 72 % B88 (GGA)	[49, 40]
	DOLIT	Correlation:	19% VWN1RPA (LSDA) + 81% LYP (GGA)	[40, 49]
	<u>ВНІ V Р</u>	Exchange:	50% HF + 50% B88 (GGA)	[50]
	DIILII	Correlation:	LYP (GGA)	[00]

Table 1: Description of functionals used for TD-DFT calculations.

3.3 Solvent Effect

For the vertical excited state calculations we carry out two scenarios. One in gas phase and the second one in a solvent. Based on a preliminar experimental work [51], we used toluene as solvent. The solvent medium was created using a polarizable continuum model (PCM). The theory selected in this method was "integral equation formalism" (IEF-PCM) since it works well with lower dielectric constants [20].

3.4 Potential Energy Surfaces

Relaxed and unrelaxed potential energy surface (PES) scans for both open and closed ring were performed in the ground state and the first excited state. The level of theory used for the PES scans was ω B97X-D/cc-pVDZ. The relaxed PES scans are performed with partial optimization for the ground state. For each step, the distance between the two reactive carbon atoms (C₁ and C₂ in Figures 1 and 2), i.e., the reaction coordinate, was kept fix while all the other geometry parameters were relaxed. Due to the high computational cost that implies to compute the ground state optimization for each step, the reaction coordinate is varied from 1.5 to 3.5 Å with a step of 0.4 Å. The unrelaxed PES scans are performed with the vertical excitations for ground state geometries.

3.5 Dynamics

The AIMD trajectories for the first excited as well as for the third excited state for the open and closed ring were computed in the BO approximation with TD-DFT using the functional B3LYP and $6-31+G^*$ as the basis set in the gas phase. The $6-31+G^*$ is a kind of Pople style basis set where the core orbitals are a contraction of six primitives of the Gaussian Type Orbitals (PGTOs) and the valence orbitals are split. The inner part of the valence orbitals is a contraction of three PGTOs and the outer part is represented by one PGTOs. Additionally, this basis set has a set of sp diffuse functions on heavy atoms (denoted by "+" before G) and a single d-type polarization function on heavy atom (denoted by "*" after G) [45].

The time-step used for all AIMD trajectories was 20 a.u. which is around 0.5 fs (1 a.u. = 0.0242 fs). The number of molecular dynamics steps, AIMD-steps, were 1500. This means a total simulation time of around 726 fs. The initial velocities were determined via random sampling of nuclear velocities from a Maxwell-Boltzmann distribution using a temperature of 298 K. It is worth pointing out that the simulations run at a constant energy and not at a constant temperature, so the mean nuclear kinetic energy will fluctuate during the course of the simulation [20].

4 Results and Discussions

4.1 Ground State Geometry and Frontier Orbitals

The dithienylethene switch considered for the present research is depicted in Figure 2. This molecule has 43 atoms and 243 electrons and they were optimized in their ground state using DFT theory, with the functional ω B97X-D and a cc-pVDZ basis set. Thus, for the open and closed ring, 497 basis functions were employed (5 for each H, 14 for each C and each F, and 18 for each S and each Cl). After the optimization, the distance between the two reactive carbon atoms for the closed ring was around 1.5 Å and for the open was around 3.5 Å. These results are in good agreement with previous works of similar molecular structures and different substituents [10, 52–54]. Furthermore, a frequency analysis was performed for the optimized ground state open and closed ring. The frequency analysis does not present imaginary frequencies for both isomers. This means that the geometries optimized are at a minimum on the ground state potential energy surface.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the optimized ground state open and closed ring are shown in Figure 7. Here, it is observed that the frontier orbitals are highly delocalized over the entire conjugated system for the open and closed ring. In the open ring, the delocalization of the LUMO is more concentrated over all the hexatriene unit and less concentrated on the benzene ring unit. This form of delocalization

of the frontier orbitals has been reported in previous works with variants of the dithienylethene open and closed ring [53, 55].



Figure 7: Frontier orbitals for the dithienylethene, open ring (left) and closed ring (right).

4.2 Absorption and Emission: Open and Closed Ring

The first ten vertical excited states of the open and closed ring were calculated at the level of TD-DFT in combination with the BLYP, B3LYP, and BHLYP xc functionals, as well as with SOS-CIS(D). These results are given in the Appendix in Tables 6 to 13. The values of the vertical excitation energies reported in Tables 2 to 5 predict the first bright transition for the absorption and emission for the lowest bright state with significant oscillator strength.

A recent experimental absorption spectrum of the open and closed ring [51] in toluene shows that the photocyclization occurs around 312 nm, corresponding to an excitation energy of 3.974 eV and for the photocycloreversion occurs around 540 nm, corresponding to an excitation energy of 2.296. These values are in good agreement with the computed TD-DFT/B3LYP values reported

in Table 3 and Table 5. We concluded that the bright transition of $S_{0min} \rightarrow S_3$ at 4.404 eV for the open ring and $S_{0min} \rightarrow S_1$ at 2.385 eV for the closed ring are responsible for the initial excitation in the UV region and the visible region, respectively.

At the level of TD-DFT (see Tables 4 and 5), one observes that the excitation energies rise when the amount of HF exchange is increased in the xc-functional (see Table 1). Thus, all the energies reported in the tables in the Appendix show the systematically increasing blueshift of the whole states with growing amounts of HF exchange. For example, in Table 6, the excitation energy of the S₁ state exhibits values of 3.062, 3.643 and 4.096 eV, when the BLYP (0% HF), B3LYP (20% HF) and BHLYP (50% HF) xc-functionals are employed. Notice that as well as the HF exchange increases, the values of the oscillator strengths also increase.

Table 2: Vertical excitation energies of the open ring calculated at different levels of theory using the cc-pVDZ basis set in the gas phase for the lowest bright state with significant oscillator strength. The vertical excitation energies (VEE) are given in eV and nm, the oscillator strengths (f) and the major orbital change(s) contributing to the transition (Tran.) are also given. HOMO is denoted by H and LUMO is denoted by L.

Theory	Exc. States		Absorp	tion			Emissio	n	
meory		VEE (eV)	VEE (nm)	f	Tran.	VEE (eV)	VEE (nm)	f	Tran.
	$S_{0min} \rightarrow S_6$	4.040	307	0.164	$H-2 \rightarrow L$				
DLTP	$S_{1min} \rightarrow S_0$					1.799	689	0.383	$L\toH$
	$S_{0min} \rightarrow S_3$	4.483	277	0.412	$H \to L\text{+}1$				
BJLIP	$S_{1min} \rightarrow S_0$					1.869	663	0.400	$L\toH$
	$S_{0min} \rightarrow S_2$	4.679	265	0.111	$\text{H-1} \rightarrow \text{L}$				
BHLYP	$S_{1min} \rightarrow S_0$					2.146	578	0.440	$L\toH$
	$S_{0min} \rightarrow S_1$	4.970	249	0.253	$H\toL$				
303-013(D)	$S_{1min} \rightarrow S_0$					1.780	696	0.397	$L\toH$

Table 3: Vertical excitation energies of the open ring calculated at different levels of theory using the cc-pVDZ basis set in toluene for the lowest bright state with significant oscillator strength. The vertical excitation energies (VEE) are given in eV and nm, the oscillator strengths (f) and the major orbital change(s) contributing to the transition (Tran.) are also given. HOMO is denoted by H and LUMO is denoted by L.

Theory	Exc. States		Absorp	otion			Emissio	n	
Theory	Ext. Oldios	VEE (eV)	VEE (nm)	f	Tran.	VEE (eV)	VEE (nm)	f	Tran.
	$S_{0min} \rightarrow S_3$	3.705	335	0.091	$\text{H-1} \rightarrow \text{L+1}$				
DLTF	$S_{1min} \rightarrow S_0$					1.666	744	0.465	$L\toH$
	$S_{0min} \rightarrow S_3$	4.404	282	0.735	$H \to L{\text{+}1}$				
DOLTF	$S_{1min} \rightarrow S_0$					1.738	713	0.465	$L\toH$
	$S_{0min} \rightarrow S_2$	4.607	269	0.163	$\text{H-1} \rightarrow \text{L}$				
DHLTF	$S_{1min} \rightarrow S_0$					2.018	614	0.488	$L\toH$
	$S_{0min} \rightarrow S_1$	4.909	253	0.351	$H\toL$				
303-013(D)	$S_{1min} \rightarrow S_0$					1.648	752	0.440	$L\toH$
Exp. ^a	$S_{0min} \rightarrow S_1$	3.974	312						

^aFrom Refs.[1]

Table 4: Vertical excitation energies of the closed ring calculated at different levels of theory using the cc-pVDZ basis set in the gas phase for the lowest bright state with significant oscillator strength. The vertical excitation energies (VEE) are given in eV and nm, the oscillator strengths (f) and the major orbital change(s) contributing to the transition (Tran.) are also given. HOMO is denoted by H and LUMO is denoted by L.

Theory	Exc. States		Absorptio	on			Emissio	n	
meory		VEE (eV)	VEE (nm)	f	Tran.	VEE (eV)	VEE (nm)	f	Tran.
	$S_{0min} \rightarrow S_1$	2.250	551	0.358	$H\toL$				
	$S_{1min} \rightarrow S_0$					1.801	688	0.384	$L\toH$
	$S_{0min} \rightarrow S_1$	2.485	499	0.400	$H\toL$				
DOLTE	$S_{1min} \rightarrow S_0$					1.871	663	0.401	$L\toH$
	$S_{0min} \rightarrow S_1$	2.990	415	0.489	$H\toL$				
DILTE	$S_{1min} \rightarrow S_0$					2.147	577	0.441	$L\toH$
	$S_{0min} \rightarrow S_1$	2.820	440	0.488	$H\toL$				
303-015(D)	$S_{1min} \rightarrow S_0$					1.782	696	0.397	$L\toH$

Table 5: Vertical excitation energies of the closed ring calculated at different levels of theory using the cc-pVDZ basis set in toluene for the lowest bright state with significant oscillator strength. The vertical excitation energies (VEE) are given in eV and nm, the oscillator strengths (f) and the major orbital change(s) contributing to the transition (Tran.) are also given. HOMO is denoted by H and LUMO is denoted by L.

Theory	Evo States		Absorptio	on			Emissio	n	
Theory		VEE (eV)	VEE (nm)	f	Tran.	VEE (eV)	VEE (nm)	f	Tran.
	$S_{0min} \rightarrow S_1$	2.154	576	0.444	$H\toL$				
	$S_{1min} \rightarrow S_0$					1.668	743	0.467	$L\toH$
	$S_{0min} \rightarrow S_1$	2.385	520	0.478	$H\toL$				
DOLTE	$S_{1min} \rightarrow S_0$					1.740	713	0.466	$L\toH$
	$S_{0min} \rightarrow S_1$	2.875	431	0.554	$H\toL$				
DULLE	$S_{1min} \rightarrow S_0$					2.018	614	0.489	$L\toH$
	$S_{0min} \rightarrow S_1$	2.715	457	0.554	$H\toL$				
303-013(D)	$S_{1min} \rightarrow S_0$					1.650	752	0.441	$L\toH$
Exp. ^a	$S_{0min} \rightarrow S_1$	2.296	540						

^aFrom Refs.[1]

4.3 Potential Energy Surface (PES)

In this section, the PES of the ground state and first excited state is investigated in detail to shed further light on the possible switching mechanisms. The PESs were performed at the ω B97X-D/cc-pVDZ theory level.

One observes in Figure 8 that the ground state (S₀) PES has two minima corresponding to the open ring (OR) located around 3.5 Å distance between the two reactive carbon atoms and the closed ring (CR) located around 1.5 Å between the two reactive carbon atoms, i.e., the reaction coordinate. These minima are separated by an energy barrier of 60.1 kcal mol⁻¹ for the cyclization reaction located at 1.9 Å and 65 kcal mol⁻¹ for the cycloreversion reaction located at 2.3 Å. The presence of energy barriers in the ground state is important for the thermal stability of the open and closed ring [21, 54], how was explained in Subsection 2.1.

The TD-DFT calculations of the first-excited state (S_1) PES give information of the cyclization reaction. This process starts with a photoexcitation from the OR S₀ optimized geometry to the Franck-Condon (FC) on S_1 with an energy of 66.2 kcal mol⁻¹. A relaxation process takes place from the FC on S_1 to a minimum on S_1 . In this relaxation path on S_1 , there are two intermediate energy barriers located at 2.1 Å and 1.9 Å, of 49.7 kcal mol⁻¹ and 43.7 kcal mol⁻¹, relative to the OR, respectively. By superimposing the PESs of S₀ and S₁, it is observed that they intersect in two points, Cl₁ and Cl₂ (see Figure 8). Based on earlier computational studies of photocyclization processes of similar molecules, the decay processes from S₁ to S₀ that precede the formation of the CR are expected to be mediated by conical intersections at high geometric changes of the molecule, for example in the vicinity of transition states or in the minimum on S₁ [8, 13, 52, 54]. Although these points seem CIs, the method used (TD-DFT/\u03c6B97X-D) to locate them is a singlereference method and as such is not suitable for the explicit location of a conical intersection and the need for multi-reference methods is obvious. However, it is well known that multi-reference methods are computationally expensive for large conjugated systems [56]. The minimum on S_1 surface (represented by OPT) is located at 1.6 Å with an energy of 30.0 kcal mol $^{-1}$ relative to the OR. The geometry of the minimum on S₁ surface is closed to the geometry of the CR. From the minimum on S₁ surface may occur a photon emission in accord with the FC principle to the CR S₀. Another chance to reach the CR S_0 is from the CI_2 , then the system decays radiationlessly to the S_0 . The relative energy between the minimum on S_1 and the CR minimum is 18.8 kcal mol⁻¹.

Unlike the cyclization reaction, the information of the cycloreversion reaction is limited. After the photoexcitation from the CR S₀ state optimized geometry to the Franck-Condon (FC) on S₁ with an energy of 39.1 kcal mol⁻¹ relative to the OR (see Figure 8), the relaxation path achieves the same minimum on S₁ that the cyclization reaction.



Figure 8: Potential energy perfile of the dithienylethene switch molecule in the open and closed form at the ground state (S_0) and the first excited state (S_1) as a function of the distance between the two reactive carbon atoms, $r(C_1-C_2)$ (see Figure 2). The letters "FC" "CI" "OR" "CR" and "OPT" refer to Franck-Condon states, conical intersections, the open ring form, the closed ring form and the optimized molecular structure, respectively. The solid blue line represents the S_0 and the solid red line represents the S_1 . Energies [kcal mol⁻¹] are given relative to the OR form.

4.4 Ab initio Molecular Dynamics (AIMD)

In order to obtain deeper information of the dynamic of the photochemical cyclization and cycloreversion of the dithienylethene switch in Figure 2, the AIMD in the first singlet excited state of the open and closed ring were performed at the TD-DFT level of theory, using a B3LYP functional and a 6-31+G* basis set in the gas phase.

4.4.1 AIMD in the First Singlet Excited State: Open Ring

TD-DFT/B3LYP calculations in Table 2 show that the first singlet excited state of the open ring is $H \rightarrow L+1$ corresponding to a photon energy of 4.483 eV in the third excited state. This value is also observed in Figure 9 (a) when the dynamic was starting. Due to wall time (10 days) in high-performance computing (HPC) cluster, the dynamic achieved a time scale around 60 fs. In this time scale, it is observed that the excitation energy decreases from 4.45 eV to approximately 3.9 eV. From Table 2, the emission energy from the S₁ minimum is around 1,9 eV. Additionally, at the time limit of 60 fs, the excitation energy has decreased, but the molecular system has not yet reached the minimum on S₁, there is an energy difference of almost 2 eV. However, this decrement is a good signal that shows a trend of the dynamic of the system toward the minimum on S₁.

The changes in the distance between the reactive carbon atoms C_1 and C_2 of the open ring during the dynamic are shown in Figure 9 (b). The dynamic start with the distance value of the optimized open ring, i.e, around 3.5 Å, reaching a minimum of 3.44 Å around 25 fs and a maximum of 3.52 Å around 60 fs. Based on these values and trajectory of the dynamics up to the time limit of the simulation, it can not be said that there was a significant change in the distance of the reactive atoms, nor a decreasing trend towards a close value to the distance in the closed ring (≈ 1.5 Å), simply a slow fluctuation of the distance around the start value is observed.

The difference between the energy in each AIMD step and the initial energy (Δ Energy) during the dynamic is illustrated in Figure 9 (c). The fluctuation showed during the dynamic is related with the fluctuation of the mean nuclear kinetic energy during the course of the simulation [20]. The maximum difference reached during the time scale of 60 fs is 0.11 kcal mol⁻¹ around 20 fs.



Figure 9: AIMD in the first singlet excited state of the open ring. (a) Excitation energy in eV vs. Time in fs. (b) Distance C1-C2 in Å vs. Time in fs. (c) Δ Energy in kcal mol⁻¹ vs. Time in fs, where Δ Energy means the difference between the energy in each AIMD step and the initial energy.

4.4.2 AIMD in the First Singlet Excited State: Closed Ring

TD-DFT/B3LYP calculations in Table 4 show that the first singlet excited state of the close ring is $H \rightarrow L$ corresponding to a photon energy of 2.485 eV in the first excited state. This value is also observed in Figure 10 (a) when the dynamic was starting. Due to wall time (10 days) in high-performance computing (HPC) cluster, the dynamic achieved a time scale around 54 fs. In this time scale, it is observed that the excitation energy decreases from 2.45 eV to approximately 1.8 eV. From Table 4, the emission energy from the S₁ minimum is around 1,9 eV which is observed around 45 fs in the time scale in the dynamic. Additionally, at the time limit of 54 fs, the excitation energy has decreased. This information suggests that the closed ring has energetically reached the minimum on S₁.

The changes in the distance between the reactive carbon atoms C_1 and C_2 of the closed ring during the dynamic are shown in Figure 10 (b). The dynamic start with the distance value of the optimized closed ring, i.e, around 1.5 Å, reaching a maximum of 1.66 Å around 54 fs. At 45 fs, the closed ring achieved a distance the reactive carbon atoms of 1.6 Å which is the distance value on the S_1 minimum for the closed ring. Thus, like the excitation energy, the distance corresponding to the S_1 minimum is reached at 45 fs.

The difference between the energy in each AIMD step and the initial energy (Δ Energy) during the dynamic is illustrated in Figure 10 (c). The fluctuation showed during the dynamic is related with the fluctuation of the mean nuclear kinetic energy during the course of the simulation [20]. The maximum difference reached during the time scale of 54 fs is 0.16 kcal mol⁻¹ around 8 fs.



Figure 10: AIMD in the first singlet excited state of the closed ring. (a) Excitation energy in eV vs. Time in fs. (b) Distance C1-C2 in Å vs. Time in fs. (c) Δ Energy in kcal mol⁻¹ vs. Time in fs, where Δ Energy means the difference between the energy in each AIMD step and the initial energy.

5 Conclusions and Outlook

A theoretical study on the photochemical cyclization and cycloreversion of a dithienylethene switch was performed using electrostatic calculations and simulations of *ab initio* molecular dynamics of the excited states.

From the electrostatic calculations, it can be concluded that the dithienylethene switch in Figure 2 presents a distance between the reactive carbon atoms C_1 and C_2 of 1.5 Å for the ground state optimized open ring and of 3.5 Å for the ground state optimized closed ring. These distances are in good agreement with previous works.

Based on the vertical excitation energies computed, the bright transitions of $S_{0min} \rightarrow S_3$ at 4.404 eV for the open ring and $S_{0min} \rightarrow S_1$ at 2.385 eV for the closed ring are responsible for the initial excitation in the UV region and the visible region, respectively.

The results from the PES allow to conclude that the thermal stability of the open and closed ring is due to the presence of a high-energy barriers in the S_0 . Additionally, the photocyclization processes from S_1 to S_0 is mediated by conical intersections at high geometric changes of the molecule, for example in the vicinity of transition states or in the minimum on S_1 . However, the method used to locate them is a single-reference method and as such is not suitable for the explicit location of a conical intersection.

From the excited state dynamics, it can be concluded that a time scale of 60 fs is not enough to observe relevant changes in the geometry of the dithienylethene switches, however it is enough to observe that the excitation energy tends to decrease after the FC on S_1 for both OR and CR. Beside, in a time scale of 45 fs, the CR reaches the minimum on S_1 .

We consider that there is an extensive path of research that could be carried out to understand deeper the photochemical cyclization and cycloreversion of the dithienylethene switches studied. The first and simplest step would be to extend the wall time since, in particular, the AIMD demands more time to be able to observe relevant changes in the geometry of the dithienylethene switches. From the theoretical point of view, one could study dithienylethene switch with different electron-withdrawing and donating substituents, to observe how the substituents affect the frontier orbitals and excited state energies. This would be useful to accelerate or delay the cyclization and cycloreversion process. Furthermore, multi-reference methods could help us to locate the conical intersections accurately. The new results can be then compared with the ones obtained with TD-DFT, and see whether it is worth to use a computationally expensive multi-referential method versus a cheap TD-DFT. Finally, it would be interesting to perform a relaxed PES of the S₁ with two reaction coordinates (bound distance and dihedral angle), with the aim of obtaining a more precise idea of the cyclization process obtained.

energies	(VEE) are	given in e	V and	nm, the	oscillator (strengths (f) and t	the amp	olitude (Arr	np.) are als	o giver	n. The lo	owest brig	tht states w	vith sigr	iificant
oscillator	strength a	tre remark∉	∋d in y∈	jllow.												
		ВГҮР				ВЗЦҮР				BHLYP				SOS-CIS(I	Ô	
	VEE (eV)	VEE (nm)	f	Amp.	VEE (eV)	VEE (nm)	f	Amp.	VEE (eV)	VEE (nm)	f	Amp.	VEE (eV)	VEE (nm)	f	Amp.
-	3.062	405	0.027	0.937	3.643	340	0.048	0.968	4.096	303	0.077	0.936	4.970	249	0.253	<mark>0.692</mark>
N	3.441	360	0.014	0.872	4.074	304	0.031	0.948	4.679	265	0.111	0.940	5.082	244	0.447	0.662
ო	3.706	335	0.050	0.739	4.483	277	0.412	0.882	4.914	252	0.670	0.940	4.811	258	0.005	0.601
4	3.918	316	0.027	0.567	4.554	272	0.221	0.924	5.183	239	0.174	0.954	5.521	225	0.299	0.424
Ŋ	3.946	314	0.001	0.763	4.754	261	0.016	0.563	5.278	235	0.001	0.654	5.534	224	0.528	0.544
9	4.040	307	0.164	0.772	4.769	260	0.055	0.597	5.603	221	0.107	0.849	6.094	203	0.106	0.469
7	4.178	297	0.002	0.918	4.803	258	0.241	0.673	5.716	217	0.261	0.628	5.859	212	0.101	0.440
80	4.211	294	0.376	0.588	4.919	252	0.005	0.938	5.814	213	0.001	0.986	6.034	205	0.184	0.514
6	4.288	289	0.039	0.771	4.988	249	0.068	0.841	5.938	209	0.029	0.484	6.516	190	0.132	0.292
10	4.449	279	0.001	0.915	5.272	235	0.097	0.868	6.129	202	0.054	0.575	6.559	189	0.010	0.404

6 Appendix

Table 6: Absorption of the open ring calculated at different levels of theory using the cc-pVDZ basis set in the gas phase. The vertical excitation

Table 7:	: Emission of the open r	ring calculated at different levels of theory	y using the cc-pVI	DZ basis set in	the gas phase.	The vertical excit	itatior
energies	s (VEE) are given in eV a	ind nm, the oscillator strengths (f) and the	amplitude (Amp.)	are also given.	The lowest bright	t states with signi	ifican
oscillator	or strength are remarked in	n yellow.					

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ВГҮР	ВLYP				ВЗГУР				внгур				SOS-CIS((O	
VEE (eV) VEE (nm) f Amp. VEE (eV)	VEE (nm) f Amp. VEE (eV)	f Amp. VEE (eV)	Amp. VEE (eV)	VEE (eV)	VEE (nm)	+	Amp.	VEE (eV)	VEE (nm)	-	Amp.	VEE (eV)	VEE (nm)	-	Amp.
1.799 689 0.383 0.953 1.869	689 0.383 0.953 1.869	0.383 0.953 1.869	0.953 1.869	1.869	663	0.400	0.967	2.146	578	<mark>0.440</mark>	0.970	1.780	969	0.397	0.952
2.464 503 0.001 0.708 2.924	503 0.001 0.708 2.924	0.001 0.708 2.924	0.708 2.924	2.924	424	0.002	0.763	3.771	329	0.043	0.839	3.869	320	0.649	0.814
2.952 420 0.003 0.923 3.495	420 0.003 0.923 3.495	0.003 0.923 3.495	0.923 3.495	3.495	355	0.110	0.620	4.338	286	0.272	0.764	3.930	315	0.074	0.713
3.034 409 0.067 0.505 3.675	409 0.067 0.505 3.675	0.067 0.505 3.675	0.505 3.675	3.675	337	0.031	0.820	4.441	279	0.635	0.657	4.644	267	0.034	0.598
3.311 374 0.014 0.85 3.793	374 0.014 0.85 3.793	0.014 0.85 3.793	0.85 3.793	3.793	327	0.074	0.765	4.497	276	0.165	0.748	4.485	276	0.219	0.655
3.331 372 0.003 0.857 3.932	372 0.003 0.857 3.932	0.003 0.857 3.932	0.857 3.932	3.932	315	0.603	0.641	4.905	253	0.019	0.797	4.515	275	0.149	0.647
3.461 358 0.622 0.759 3.990	358 0.622 0.759 3.990	0.622 0.759 3.990	0.759 3.990	3.990	311	0.104	0.699	5.074	244	0.035	0.859	5.365	231	0.018	0.399
3.635 341 0.016 0.887 4.250	341 0.016 0.887 4.250	0.016 0.887 4.250	0.887 4.250	4.250	292	0.148	0.715	5.268	235	0.056	0.739	5.208	238	0.120	0.665
3.729 332 0.071 0.697 4.378	332 0.071 0.697 4.378	0.071 0.697 4.378	0.697 4.378	4.378	283	0.018	0.827	5.438	228	0.024	0.714	5.097	243	0.096	0.550
3.803 326 0.053 0.585 4.563	326 0.053 0.585 4.563	0.053 0.585 4.563	0.585 4.563	4.563	272	0.005	0.932	5.494	226	0.006	0.848	5.910	210	0.005	0.705

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Table 8:	: Absorption of the closed ring calculated at different levels of theory using the cc-pVDZ basis set in the gas phase. The vertical excitation
energies	s (VEE) are given in eV and nm, the oscillator strengths (f) and the amplitude (Amp.) are also given. The lowest bright states with significan
oscillator	or strength are remarked in yellow.

		ВLYP				ВЗЦҮР				ВНГҮР				SOS-CIS((C	
	VEE (eV)	VEE (nm)	f	Amp.	VEE (eV)	VEE (nm)	f	Amp.	VEE (eV)	VEE (nm)	f	Amp.	VEE (eV)	VEE (nm)	ţ	Amp.
-	2.250	551	0.358	0.954	2.485	499	0.400	<mark>0.974</mark>	2.990	415	<mark>0.489</mark>	0.971	2.820	440	<mark>0.488</mark>	<mark>0.944</mark>
Q	2.761	449	0.011	0.804	3.322	373	0.020	0.869	4.294	289	0.137	0.894	4.432	280	0.601	0.785
ო	3.242	382	0.015	0.877	3.825	324	0.075	0.648	4.790	259	0.110	0.791	4.865	255	0.000	0.612
4	3.317	374	0.058	0.546	3.989	311	0.049	0.649	4.831	257	0.320	0.743	5.170	240	0.018	0.417
£	3.499	354	0.093	0.738	4.107	302	0.271	0.671	4.903	253	0.264	0.809	4.725	262	0.047	0.589
9	3.575	347	0.016	0.898	4.198	295	0.267	0.628	5.116	242	0.044	0.699	5.098	243	0.110	0.642
7	3.623	342	0.330	0.659	4.319	287	0.013	0.613	5.352	232	0.052	0.443	4.948	251	0.124	0.693
8	3.906	317	0.029	0.656	4.565	272	0.118	0.808	5.573	222	0.056	0.878	5.627	220	0.206	0.664
6	3.976	312	0.021	0.847	4.729	262	0.056	0.867	5.797	214	0.036	0.465	6.299	197	0.419	0.495
10	4.120	301	0.066	0.491	4.879	254	0.042	0.734	5.862	212	0.008	0.492	6.052	205	0.207	0.485

Table 9:	9: Emission of the closed ring calculated at different levels of theory using the cc-pVDZ basis set in the gas phase. The vertical excitation	Ы
energies	es (VEE) are given in eV and nm, the oscillator strengths (f) and the amplitude (Amp.) are also given. The lowest bright states with significa	Int
oscillator	tor strength are remarked in yellow.	

		ВГҮР				ВЗГҮР				внгур				SOS-CIS(I	Ô	
N_EXC.	VEE (eV)	VEE (nm)	_	Amp.	VEE (eV)	VEE (nm)	f	Amp.	VEE (eV)	VEE (nm)	f	Amp.	VEE (eV)	VEE (nm)	f	Amp.
-	1.801	688	0.384	0.953	1.871	663	0.401	0.967	2.147	577	0.441	0.970	1.782	969	0.397	0.952
N	2.465	503	0.001	0.708	2.924	424	0.002	0.763	3.771	329	0.043	0.838	3.870	320	0.649	0.814
ო	2.952	420	0.003	0.923	3.496	355	0.11	0.619	4.339	286	0.272	0.763	3.930	315	0.074	0.713
4	3.035	408	0.067	0.505	3.676	337	0.032	0.819	4.441	279	0.634	0.658	4.643	267	0.033	0.601
5	3.312	374	0.014	0.841	3.792	327	0.072	0.768	4.498	276	0.166	0.749	4.484	277	0.217	0.656
9	3.330	372	0.003	0.851	3.932	315	0.602	0.640	4.904	253	0.019	0.797	4.516	275	0.150	0.648
7	3.461	358	0.621	0.758	3.990	311	0.105	0.699	5.073	244	0.035	0.859	5.364	231	0.018	0.398
80	3.636	341	0.017	0.887	4.250	292	0.149	0.716	5.268	235	0.056	0.737	5.208	238	0.120	0.665
6	how to	332	0.070	0.698	4.378	283	0.018	0.827	5.438	228	0.025	0.717	5.096	243	0.097	0.551
10	3.804	326	0.053	0.585	4.563	272	0.005	0.932	5.495	226	0.005	0.850	5.910	210	0.005	0.706

Table 10): Absorpti	on of the c	open rii	ng calc	ulated at o	lifferent lev	els of 1	theory ı	using the c	c-pVDZ b	asis se	t in tolu	lene. The	vertical e	xcitatior	ener-
gies (VE	E) are giv∉	eV a	nd nm,	the os	scillator stre	engths (f) s	and the	e amplit	tude (Amp.	.) are alsc	o given.	The lo	owest brigh	ht states v	vith sigr	nificant
oscillator	r strength a	ure remark«	ed in ye	jlow.												
		BLYP				ВЗЦҮР				BHLYP				SOS-CIS(
N EXC.	VEE (eV)	VEE (nm)		Amp.	VEE (eV)	VEE (nm)		Amp.	VEE (eV)	VEE (nm)		Amp.	VEE (eV)	VEE (nm)		Amp.
-	3.026	410	0.036	0.947	3.601	344	0.063	0.973	4.020	308	0.097	0.931	4.909	253	0.351	<mark>0.655</mark>
C		000	000 0			000	010		100	000	0010	0000		C L C		

	f Amp.	5 <mark>1 0.655</mark>	01 0.616	3 0.418	0.609	50 0.509	15 0.559	58 0.507	15 0.545	33 0.359	11 0.402	
(D)		0.35	0.50	0.40	0.0	0.55	0.12	0.05	0.34	0.13	0.01	
SOS-CIS	VEE (nm)	253	250	225	258	226	199	222	211	189	190	312
	VEE (eV)	4.909	4.952	5.507	4.802	5.491	6.226	5.592	5.873	6.577	6.542	3.974
	Amp.	0.931	0.926	0.937	0.952	0.660	0.859	0.684	0.988	0.484	0.600	
	f	0.097	0.163	0.764	0.181	0.001	0.139	0.301	0.002	0.025	0.064	
внгур	VEE (nm)	308	269	258	242	235	224	219	215	210	204	312
	VEE (eV)	4.020	4.607	4.809	5.116	5.280	5.540	5.659	5.764	5.915	6.086	3.974
	Amp.	0.973	0.959	0.93	0.938	0.645	0.599	0.592	0.927	0.855	0.882	
	f	0.063	0.046	0.735	0.141	0.021	0.092	0.131	0.009	0.098	0.114	
ВЗЦҮР	VEE (nm)	344	306	282	275	262	260	259	253	250	236	312
	VEE (eV)	3.601	4.047	4.404	4.511	4.736	4.761	4.778	4.896	4.957	5.257	3.974
	Amp.	0.947	0.895	0.729	0.583	0.76	0.732	0.617	0.922	0.791	0.664	
	f	0.036	0.022	0.091	0.057	0.004	0.227	0.464	0.003	0.034	0.046	
ВГҮР	VEE (nm)	410	362	335	319	316	310	299	296	290	278	312
	VEE (eV)	3.026	3.427	3.705	3.893	3.925	3.995	4.144	4.183	4.275	4.456	3.974
		-	N	ო	4	5	9	7	8	6	10	Exp.

Table 11: Emission of the open ring calculated at different levels of theory using the cc-pVDZ basis set in toluene. The vertical excitation energies (VEE)
are given in eV and nm, the oscillator strengths (f) and the amplitude (Amp.) are also given. The lowest bright states with significant oscillator strength
are remarked in yellow.

	ВLYP				ВЗГУР				внгур				SOS-CIS((C	
VEE (nm) f		1	Amp.	VEE (eV)	VEE (nm)	ب	Amp.	VEE (eV)	VEE (nm)	<u>ب</u>	Amp.	VEE (eV)	VEE (nm)	-	Amp.
744 0.465	0.465		0.967	1.738	713	0.465	0.977	2.018	614	<mark>0.488</mark>	0.975	1.648	752	<mark>0.440</mark>	0.956
502 0.001	0.001		0.718	2.930	423	0.003	0.778	3.757	330	0.096	0.867	3.793	327	0.853	0.779
415 0.046	0.046		0.663	3.461	358	0.166	0.644	4.244	292	0.662	0.890	3.862	321	0.055	0.664
411 0.062	0.062		0.643	3.688	336	0.247	0.645	4.293	289	0.435	0.692	4.625	268	0.127	0.552
380 0.014	0.014		0.922	3.768	329	0.364	0.555	4.393	282	0.119	0.692	4.434	280	0.244	0.460
372 0.353 (0.353 (0	0.565	3.838	323	0.245	0.722	4.923	252	0.028	0.753	4.413	281	0.137	0.529
368 0.406 (0.406 (0	0.779	3.974	312	0.092	0.662	5.054	245	0.032	0.862	5.355	232	0.025	0.437
335 0.133 (0.133 (0	0.703	4.220	294	0.160	0.732	5.238	237	0.075	0.729	5.166	240	0.127	0.653
331 0.007	0.007		0.691	4.366	284	0.009	0.840	5.468	227	0.006	0.698	5.101	243	0.132	0.560
324 0.013	0.013		0.739	4.565	272	0.004	0.950	5.501	225	0.019	0.607	5.896	210	0.006	0.489

able 12: Absorption of the closed ring calculated at different levels of theory using the cc-pVDZ basis set in toluene. The vertical excitation en
rgies (VEE) are given in eV and nm, the oscillator strengths (f) and the amplitude (Amp.) are also given. The lowest bright states with significan
scillator strength are remarked in yellow.

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		ВГҮР				ВЗЦҮР				ВНГУР				SOS-CIS(I	Ô	
	VEE (eV)	VEE (nm)	Ŧ	Amp.	VEE (eV)	VEE (nm)	f	Amp.	VEE (eV)	VEE (nm)	f	Amp.	VEE (eV)	VEE (nm)	f	Amp.
-	2.154	576	0.444	<mark>0.968</mark>	2.385	520	<mark>0.478</mark>	<mark>0.981</mark>	2.875	431	<mark>0.554</mark>	0.975	2.715	457	<mark>0.554</mark>	<mark>0.947</mark>
N	2.760	449	0.013	0.819	3.315	374	0.033	0.889	4.234	293	0.236	0.901	4.321	287	0.785	0.774
ო	3.258	381	0.074	0.554	3.813	325	0.123	0.701	4.689	264	0.392	0.707	4.878	254	0.001	0.596
4	3.331	372	0.044	0.786	3.979	312	0.207	0.672	4.738	262	0.074	0.715	5.103	243	0.050	0.368
Ŋ	3.459	358	0.231	0.656	4.050	306	0.382	0.557	4.847	256	0.343	0.864	4.770	260	0.062	0.559
9	3.513	353	0.123	0.834	4.138	300	0.091	0.846	5.124	242	0.025	0.700	5.031	246	0.118	0.584
7	3.596	345	0.139	0.854	4.334	286	0.014	0.660	5.346	232	0.049	0.405	4.893	253	0.148	0.690
80	3.903	318	0.045	0.717	4.542	273	0.140	0.830	5.532	224	0.066	0.857	5.566	223	0.238	0.654
6	4.034	307	0.091	0.677	4.710	263	0.074	0.893	5.777	215	0.038	0.470	6.421	193	0.641	0.625
10	4.165	298	0.027	0.819	4.886	254	0.050	0.784	5.842	212	0.014	0.503	5.889	211	0.230	0.502
Exp.	2.296	540			2.296	540			2.296	540			2.296	540		

Table 13	13: Emission of the closed ring calculated at different levels of theory using the cc-pVDZ basis set in toluene. The vertical excitation ener-
gies (VEI	EE) are given in eV and nm, the oscillator strengths (f) and the amplitude (Amp.) are also given. The lowest bright states with significant
oscillator	or strength are remarked in yellow.

SOS-CIS(D)		VEE (eV) VEE (nm) f Amp.	VEE (eV) VEE (nm) f Amp. 1.650 752 0.441 0.956	VEE (eV) VEE (nm) f Amp. 1.650 752 0.441 0.956 3.795 327 0.853 0.779	VEE (eV) VEE (nm) f Amp. 1.650 752 0.441 0.956 3.795 327 0.853 0.779 3.862 321 0.055 0.663	VEE (eV) VEE (nm) f Amp. 1.650 752 0.441 0.956 3.795 327 0.853 0.779 3.862 321 0.055 0.663 4.627 268 0.122 0.557	VEE (eV) VEE (nm) f Amp. 1.650 752 0.441 0.956 3.795 327 0.853 0.779 3.862 321 0.055 0.663 4.627 268 0.122 0.557 4.432 280 0.247 0.464	VEE (eV) VEE (nm) f Amp. 1.650 752 0.441 0.956 3.795 327 0.853 0.779 3.795 321 0.853 0.779 3.862 321 0.055 0.663 4.627 268 0.122 0.557 4.432 280 0.247 0.464 4.415 281 0.137 0.53	VEE (eV) VEE (nm) f Amp. 1.650 752 0.441 0.956 3.795 327 0.853 0.779 3.795 321 0.853 0.779 3.862 321 0.055 0.663 4.627 268 0.122 0.557 4.432 280 0.247 0.464 4.415 281 0.137 0.53 5.355 232 0.0247 0.464	VEE (eV) VEE (nm) f Amp. 1.650 752 0.441 0.956 3.795 327 0.853 0.779 3.862 321 0.055 0.663 3.862 321 0.055 0.663 4.627 268 0.122 0.557 4.432 280 0.122 0.557 4.415 281 0.137 0.53 5.355 232 0.024 0.436 5.355 232 0.024 0.436 5.165 240 0.137 0.53	VEE (eV) VEE (nm) f Amp. 1.650 752 0.441 0.956 3.795 327 0.853 0.779 3.862 321 0.853 0.779 3.862 321 0.055 0.663 4.627 268 0.122 0.557 4.432 280 0.247 0.464 4.415 281 0.137 0.53 5.355 232 0.0247 0.436 5.355 232 0.0247 0.436 5.165 232 0.128 0.53 5.165 240 0.128 0.563 5.100 243 0.132 0.563
	VEE (eV) VEE (nm) f		1.650 752 0.441	1.650 752 0.441 3.795 327 0.853	1.650 752 0.441 3.795 327 0.853 3.862 321 0.055	1.650 752 0.441 3.795 327 0.853 3.862 321 0.055 4.627 268 0.122	1.650 752 0.441 3.795 327 0.853 3.862 321 0.055 4.627 268 0.122 4.432 280 0.247	1.650 752 0.441 3.795 327 0.853 3.862 321 0.055 4.627 268 0.122 4.432 280 0.247 4.415 281 0.137	1.650 752 0.441 3.795 327 0.853 3.862 321 0.055 3.862 321 0.055 4.627 268 0.122 4.432 280 0.247 4.415 281 0.137 5.355 232 0.024	1.650 752 0.441 3.795 327 0.853 3.862 321 0.055 4.627 268 0.122 4.432 280 0.247 4.415 281 0.137 5.355 232 0.024 5.165 240 0.128	1.650 752 0.441 3.795 327 0.853 3.862 321 0.055 3.862 321 0.055 4.627 268 0.122 4.432 280 0.247 4.415 281 0.137 5.355 232 0.024 5.165 240 0.128 5.100 243 0.132
VEE (eV) VEE (nm		1.650 752		3.795 327	3.795 327 3.862 321	3.795 327 3.862 321 4.627 268	3.795 327 3.862 321 4.627 268 4.432 280	3.795 327 3.862 321 4.627 268 4.432 280 4.415 281	3.795 327 3.862 321 4.627 268 4.432 280 4.415 281 5.355 232	3.795 327 3.862 321 4.627 268 4.432 268 4.415 281 5.355 232 5.165 240	3.795 327 3.862 321 4.627 268 4.432 268 4.415 281 5.355 232 5.165 240 5.100 243
Amp. VEE 0.975 1.6	0.975 1.6		0.867 3.7		0.890 3.8	0.890 3.8 0.690 4.6	0.890 3.8 0.690 4.6 0.691 4.4	0.890 3.8 0.690 4.6 0.691 4.4 0.754 4.4	0.890 3.8 0.690 4.6 0.691 4.4 0.754 4.4 0.863 5.3	0.890 3.8 0.690 4.6 0.691 4.4 0.754 4.4 0.863 5.3	0.890 3.8 0.690 4.6 0.691 4.4 0.754 4.4 0.753 5.3 0.863 5.3 0.727 5.1 0.694 5.1
1) f /	0.489 (0.095 (0 662 0	0.000	0.434	0.434 0.119 0.119	0.434 0.0119 0.028	0.434 0.119 0.028 0.032 0.032	0.434 0.434 0.119 0.028 0.028 0.032 0.075 0.075	0.075 0.006 0.006 0.006 0.005
VEE (nm)	611	0	330	292	1	289	289 282	289 282 252	289 282 252 245	289 282 252 245 237	289 282 252 245 237 237
VEE (eV)		2.018	3.757	5VC V	1.140	4.293	4.293 4.394	4.293 4.394 4.922	4.293 4.293 4.394 4.922 5.054	4.293 4.394 4.922 5.054 5.238	 4.293 4.394 4.392 5.054 5.238 5.468
	Amp.	0.977	0.778	0 643	2000	0.646	0.646 0.562	0.646 0.562 0.721	0.646 0.562 0.721 0.662	0.646 0.562 0.721 0.662 0.662	0.662 0.562 0.721 0.733 0.733 0.839
	÷	0.466	0.003	0 166	>>	0.246	0.246 0.359	0.246 0.359 0.249	0.246 0.359 0.249 0.249	0.246 0.246 0.359 0.249 0.092 0.092	0.246 0.359 0.249 0.249 0.092 0.161
	VEE (nm)	713	423	358	>>>>	336	336 329	336 329 323	336 329 323 312	336 329 323 312 294	336 329 323 323 294 284
	VEE (eV)	1.740	2.930	3 161	- 01.0	3.688	3.688 3.768	3.688 3.768 3.838	3.688 3.688 3.768 3.838 3.974	3.688 3.768 3.768 3.838 3.974 4.220	3.688 3.768 3.838 3.974 4.220
	Amp.	0.967	0.717	0.670	0.00	0.636	0.636 0.636 0.922	0.636 0.922 0.564	0.636 0.922 0.564 0.768	0.000 0.636 0.922 0.564 0.768 0.702	0.636 0.636 0.922 0.564 0.768 0.768 0.702
	+	0.467	0.001	0 045	2.2.2	0.063	0.063	0.063 0.014 0.337	0.063 0.014 0.337 0.420	0.063 0.014 0.337 0.420 0.133	0.063 0.063 0.337 0.337 0.420 0.133 0.007
	VEE (nm)	743	502	415)	411	411 380	411 380 372	411 380 372 368	411 380 372 368 335	411 380 372 368 335 335
	VEE (eV)	1.668	2.471	2.988		3.017	3.017 3.265	3.017 3.265 3.329	3.017 3.265 3.329 3.365	3.017 3.265 3.329 3.365 3.704	3.017 3.265 3.329 3.365 3.704 3.744
	N_EXC.	-	N	ო		4	4 LO	4 ú 0	4 û 0 h	4 vo vo vo xo	4 ら の と の の

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