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“PETRU PONI” Institute of Macromolecular Chemistry, Iași

Theoretical and experimental studies of some dynamic molecular systems based on hetero-organic compounds containing nitrogen

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-PhD Thesis summary-

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To Mr./Mrs.____________________________________

We would like to inform you that on 16th of December 2019, at 12:00 pm, in the library of the "Petru Poni" Institute Of Macromolecular Chemistry of Iasi, will be held the public presentation of the doctoral thesis entitled "THEORETICAL AND EXPERIMENTAL STUDIES OF SOME DYNAMIC MOLECULAR SYSTEMS BASED ON HETERO-ORGANIC COMPOUNDS CONTAINING NITROGEN", elaborated by Dragoş-Lucian Isac, in order to obtain the scientific title of Doctor.

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PhD Anton Airinei, Senior Researcher (CS I), Director of "Petru Poni" Institute of Macromolecular Chemistry Iaşi.

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3. **Associate Prof. Ionel Humelnicu,** "Alexandru Ioan Cuza" University from Iaşi.

According to the Regulation regarding the organization and conducting the doctorate for obtaining the scientific scientific titles within the Romanian Academy, we are sending you the abstract of the doctoral thesis with the request to communicate in writing your appreciations and remarks

We invite you to participate to the public presentation of the doctoral thesis.

DIRECTOR,

PhD Anton Airinei

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Content

SURVEY OF THE LITERATURE DATA

PERSONAL CONTRIBUTIONS

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Abbreviations

AB	Azobenzen
MI	Maleimidă
PCM	Polarizable continuum model
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
FC	Franck-Condon
DFT	Density functional theory
TD-DFT	Time-dependent density functional theory
STO	Slater type orbitals
GTO	Gaussian type orbitals
HF	Hartree-Fock
CSF	Configurational state functions
CI	Configuration interaction
CIS	Configurational interaction singles
CIS(D)	CI-second order perturbation correction
MRCI	Multi-reference configurational interaction
CCSD	Coupled cluster single and double excitations
SAC-CI	Symmetry adapted cluster/configuration interaction
CASSCF	Complete active space self-consistent field
MP	Møller-Plesset
MR	Multi-reference
PT	Perturbational theory
CASPT2	Complete active space second order perturbation theory
NEVPT2	n-electron valence state perturbation theory
LDA	Local density approximation
GGA	Generalized gradient approximation
SVWN	Slater-Vosko-Wilk- Nusair
B3LYP	Becke, three-parameter, Lee-Yang-Parr
PBE0	Perdew–Burke-Ernzerhoff, corrected by Adamo and Barone

CAM-B3LYP	Coulomb-attenuating method B3LYP
wB97XD	Head-Gordon and coworkers functional with empirical dispersion
M062X	Minnesota functionals (Truhlar and Zhao)
TPSS	Staroverov, Scuseria, and Perdew
BLYP	Becke, Lee-Yang-Parr
LR-PCM	Linear-response PCM
IEFPCM	Integral equation formalism variant PCM
CT	Charge transfer
ICT	Intramolecular charge transfer
SC-NEVPT2	Strongly contracted NEVTP2
SA	State averaged
UNOs	Unrestricted natural orbitals
QROs	Quasi-restricted orbitals
GS	Ground state
PICT	Planar intramolecular charge transfer
TICT	Twisted intramolecular charge transfer
MEP	Molecular electrostatic potential
SAS	Solvent-accessible surface area
MD	Molecular dynamics
YASARA	Yet another scientific artificial reality application
PME	Particle-mesh Ewald
ESP	Electrostatic surface potential
PES	Potential energy surface

I. Introduction

Chemical molecular systems that have one or more nitrogen atoms in their structure represent a broad field of research, both for fundamental and applicative purposes, thanks to the special intrinsic properties that these systems can offer. The number of nitrogen atoms introduced in certain positions such as in exocyclic bonds leads to a specific molecular property, namely the existence of different conformations when these molecular systems are subjected to an external stimulus. The molecular property of a system, being dynamic, in that it can adopt multiple conformations, as well as the intramolecular nitrogen content, make that these chemical compounds to be the subject of a large number of studies, especially in the fields of photochemistry [1-3], photophysics [1] and biology [4].

The dynamics of the molecular structure is determined by the fact that these compounds can exhibit modification by changing the molecular isomer when an external stimulus (such as UV-VIS [3], thermal [5-7] photoelectric [8] or photomechanical [9-11]) were applied.

The introduction of one or more nitrogen atoms in a chemical system has as a consequence the modification of the electronic structure of these compounds, but also a reorganization of the electronic density throughout the molecular symmetry. Therefore, the introduction of nitrogen atoms in a double bond or in an aromatic cycle determines the appearance of high energy electronic $\pi \rightarrow \pi^*$ transitions, as well as low energy $n \rightarrow \pi^*$ transitions forbidden by symmetry point of view.

The *azo* compound structure under study has the aromatic character with two benzene rings linked by a double bond of type -N=N-. In the case of the presence of the double bond of type -N =N- (with σ and one π type bonds) the atoms participating in this bridge are hybridized sp^2 and can lead to the formation of trigonal plane geometry. Furthermore, the presence of the double bond -N=N- in the *azo* structural unit contributes to the formation of a geometrical isomeric conformational effect. Therefore, the azo compound and its derivatives exhibit geometric isomerism in the form trans- (E, *entgegen*) and cis- (Z, *zusammen*). These isomers can be isolated, according to computational studies and *X-ray* diffraction analysis [18-22].

The conversion from the more thermodynamically stable trans isomer to the cis metastable conformation is achieved by a photoisomerization process, by irradiating the molecules with ultraviolet (UV) radiation around 300 - 360 nm [2-4]. This reaction is reversible because the cis isomer defined by its metastable character can return to its initial form through two channels (i) one radiative stimulated when the molecule is irradiated in the visible range of the electromagnetic spectrum at about 430 - 460 nm or (ii) spontaneously by a thermal process occurring in dark [15]. The trans → cis photoisomerization in unsubstituted azobenzene occurs much faster than the thermal isomerization, which separates the two processes in time, giving the possibility of their independent analysis.

The mechanism of the isomerization process in azobenzene compounds is not yet fully established and it is an open field for research. It is well known that the isomerization of azobenzene chromophores can occur through four mechanisms: rotation, inversion, concerted inversion, and rotation assisted inversion. Theoretical and experimental models provide important contributions to the establishment of the specific isomerization mechanism for these compounds, but these mechanisms are still mattered of debate [3,32-34]. The isomerization mechanism in all the cases encountered, depends on the polarity of the molecule described by the nature of the functional groups in the vicinity of the azo core.

The experimental results, in conjunction with the theoretical ones, showed that the trans isomer, as well as the cis isomer, always have the minimum energy in the fundamental state S_0. The transition from the more stable state to the metastable one is accomplished by the two excited states $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$, being assisted by four isomerization mechanisms: rotation; inversion, concerted inversion and rotation assisted by inversion. According to the theoretical and experimental studies for the $S_0 \rightarrow S_2$ isomerization, the predominant mechanism is by rotation, and for the $S_0 \rightarrow S_1$ isomerization, the predominant mechanism is by inversion. The other mechanisms (concerted inversion and rotation assisted inversion) may appear as contributions to the molecular interconversion process in addition to those mentioned above. Therefore, the isomerization process of azobenzene described by these mechanisms is a multidimensional one.

II. Theoretical chemistry methods used in the study of azobenzene systems

Computational molecular modeling methods have a wide applicability in the field of chemical, physical, biological systems, as they are able to predict the properties of the materials utilized in reaction and manufacture processes, but are very useful for example for the study of drug transporters, as well as in interactions of these biological materials and molecules [115].

Molecular simulation can start from simple molecular systems, with a small number of atoms, and can reach very complex systems with thousands of atoms, such as systems of interest in the life sciences. The techniques used in the theoretical or computational approaches correspond to the size and complexity of the described systems, the approach varying between quantum ab initio methods, functional based on electronic density, very precise, but expensive as resources, and atomistic methods, such as molecular dynamics or Monte Carlo simulations, less precise, but capable of quickly describing large systems (such as biological systems).

The main goal of this doctoral thesis was the study of the modification of the electronic structure under the influence of external stimuli of some dynamic molecular systems based on hetero-organic compounds containing nitrogen. The first part of this section includes a systematic analysis of substituted azobenzene structures using the DFT, TD-DFT, and *ab initio* methods. Firstly, the research considers an analysis of the electronic structures in the ground state, followed by an excited state investigation and an analysis of the solvent effect (using implicit and explicit models). The second part of this section has the aim to exploring the mechanism of preferential processes of molecular interconversion in azomaleimide derivatives.

Personal contributions

III. Electronic structure of azobenzene compounds substituted with maleimide

In this Ph.D. thesis, eight AB−MI derivatives in the *trans* form (E) and their cis isomers (Z) shown in Figure 10 were investigated, and they will be considered for discussion as follows: (E1): (E)-1-(4-(phenyldiazenyl) phenyl)-1H-pyrrole-2,5-dione; (Z1): (Z)-1-(4-(phenyldiazenyl)phenyl)-1H-pyrrole-2,5-dione; (E2): (E)-1,1′-(4-(p-tolyldiazenyl)-1,3-phenylene)-bis-(1H-pyrrole-2,5-dione); (Z2): (Z)-1,1′-(4-(p-tolyldiazenyl)-1,3-phenylene)-bis-(1H-pyrrole-2,5-dione); (E3): (E)-1,1′-(4-(o-tolyldiazenyl)-1,3-phenylene)-bis-(1H-pyrrole-2,5-dione); (Z3): (Z)-1,1′-(4-(o-tolyldiazenyl)-1,3-phenylene)-bis-(1H-pyrrole-2,5-dione); (E4): (E)-4-(2,5-dioxo-2H-pyrrol-1(5H)-yl)-N-(4-(phenyldiazenyl)phenyl)benzamide; and (Z4): (Z)-4-(2,5-dioxo-2H-pyrrol-1(5H)-yl)-(4-(phenyldiazenyl)phenyl)-benzamide. The preparation and characterization of these AB-MI compounds have been described previously [75,146,147].

The optimization calculations of the molecular geometries together with the excited states were performed using the Gaussian G09 simulation program [148]. All the compounds under study were initially minimized in their single-state fundamental states (S_0). Two different DFT functionals were selected: hybrid density functional PBE0 [138] and the long-range-corrected CAM-B3LYP [140] with the 6-31+G(d) basis set to characterize the AB−MI systems. TD-DFT calculations [130] using the CAM-B3LYP functional have been indicated reliable results for the description of the optimized geometries with a good estimation of the first electronic transitions in AB and substituted Abs [59,149,150]. However, it has been reported that the combination of the parameter-free PBE0 functional and the CAM-B3LYP method with the 6-31+G(d) basis set can also provide adequate results with a reasonable computational cost [13,151]. Ultrafine integration grid and tight convergence thresholds were used in geometry optimization. Calculations of vibrational frequencies gave no negative eigenvalues of the Hessian matrix.

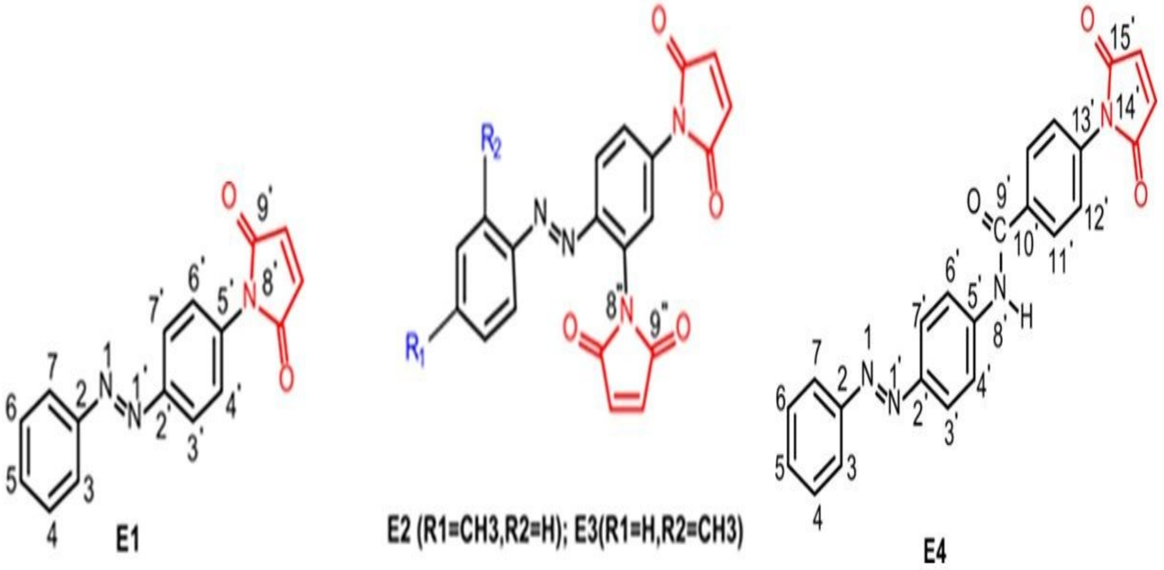

Figure 10. Target compounds and numbering scheme adopted for selected atoms.

In order to describe the transition states, as well as the excited states with charge transfer (CT) character, and the intramolecular effect of the charge transfer (ICT) in detail, the density functionals PBE0, CAM-B3LYP that first followed by the ab initio CIS, CIS (D) method analysis [119]. All of these calculations were performed to find possible underestimation/overestimation of the CT state energy when these common functionals are used in studying spurious long-range CT* excited states [13,156,157]. A spurious low-lying CT is difficult to represent because of the high sensitivity of this characteristic transition, especially in cases of weak donor−acceptor interactions (e. g. in our case AB-MI system). Even, the CIS and CIS(D) methods can overestimate the CT* state energies resulting in an incorrect order [158]. The state-averaged of multiconfigurational self-consistent field method (SA-CASSCF) [124,125] in particular, when supplemented by the n-electron valence state multireference perturbation theory SA-CASSCF-NEVPT2 (and strongly contracted SC-NEVPT2) [128,129,159], provides a more appropriate scheme to obtain reliable results.

High-level SA-CASSCF-NEVPT2 computations were performed with the Orca program package [160] with the CAS chosen based on single-point DFT calculations (CAM-B3LYP/6-31+G(d)) using both unrestricted natural orbitals and quasi-restricted orbitals (UNOs and QROs keywords in Orca).

The study begins with a theoretical analysis of the energetically favorable conformational effects in the fundamental state, which were analyzed by an adiabatic approach along the surface of the energy potential, which implies a calculation of a single iteration by modifying the spatial interactions between maleimide and azo group (Figure 10). The scan involved the change of orientation of the MI group by small steps of 10° of the angle C4′−C5′−N8′−C9′, across the range 0−180°, with respect to the AB structure (for each trans and cis isomer, respectively). During the PES scan, the methyl group from compounds **E2**/**Z2** and **E3**/**Z3** were kept frozen because the rotation of this functional group did only insignificantly affect the potential energy.

The specific orientation of the MI moiety (around 140° for C4′−C5′−N8′−C9′ dihedral angle, see numbering scheme in Figure 10) with respect to the AB plane depends most likely on two competing interactions: intramolecular hydrogen bond and steric effect. Indeed, a weak intramolecular C−H···O interaction could be formed between the electron-rich oxygen (MI) and the hydrogen atoms from the adjacent aromatic sp^2 C6′ and C4′ when the AB and MI rings are in-plane. The deviation of AB and MI rings from coplanarity is caused by the steric repulsion because of the electron lone-pairs of the N atoms of the -N=N− moiety and of oxygen atoms of MI (in the ortho position in compounds **E2**/**Z2** and **E3**/**Z3**) which repel each other, counteracting the intramolecular hydrogen bond (favored when the C2′−C3′−N8″−C9″ dihedral angle is planar). The balancing of these effects leads to a global minimum having a dihedral angle C2′−C3′−N8″−C9″ around 120° with all levels of theory used in our calculations. Indeed, the MI group in the para position, and thus distant from the azo group, has a smaller deviation from coplanarity (torsion of ca. 140°, Figures 12 and 15).

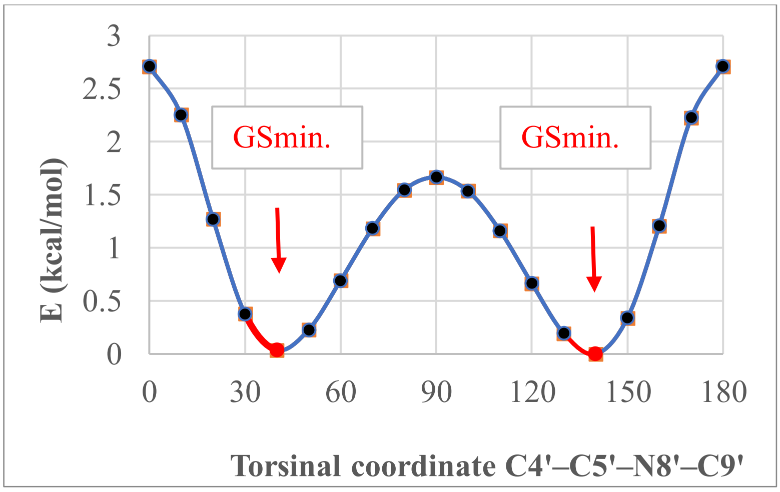

Figure 12. Potential energy surface scan for the dihedral angle C4'–C5'–N8'–C9' in **E1** isomer (PBE0/6-31+G(d).

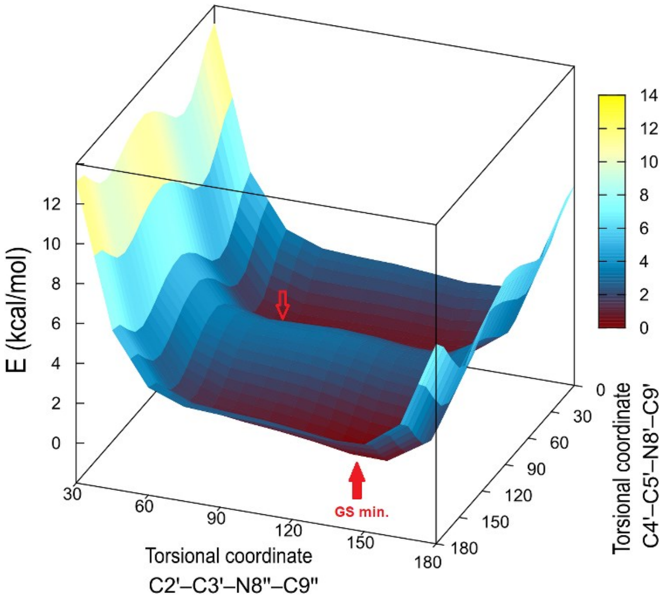

Figure 15 Potential energy surface scan for the dihedral angles C4'–C5'–N8'–C9' and C2'–C3'–N8''–C9'' in **Z2** isomer (PBE0/6-31+G(d).

A description of the electron transitions, present in the UV−vis spectra, can be based on the representation of the MOs using the Kohn−Sham frontier orbital theory [162]. A hybrid exchange−correlation functional using the Coulomb-attenuating method (CAMB3LYP) with the 6-31+G(d) basis set was chosen for the MO representation in the ground and the first singlet excited states in Figures 15 and 19, together with the relevant data concerning the transitions. The CAM-B3LYP functional has been recommended to compute and to predict the vertical transition (even for CT character) into the electronic spectra of organic compounds [156]. Transition energies were calculated at the TD-CAM-B3LYP/6-31+G(d) level of theory in the gas phase.

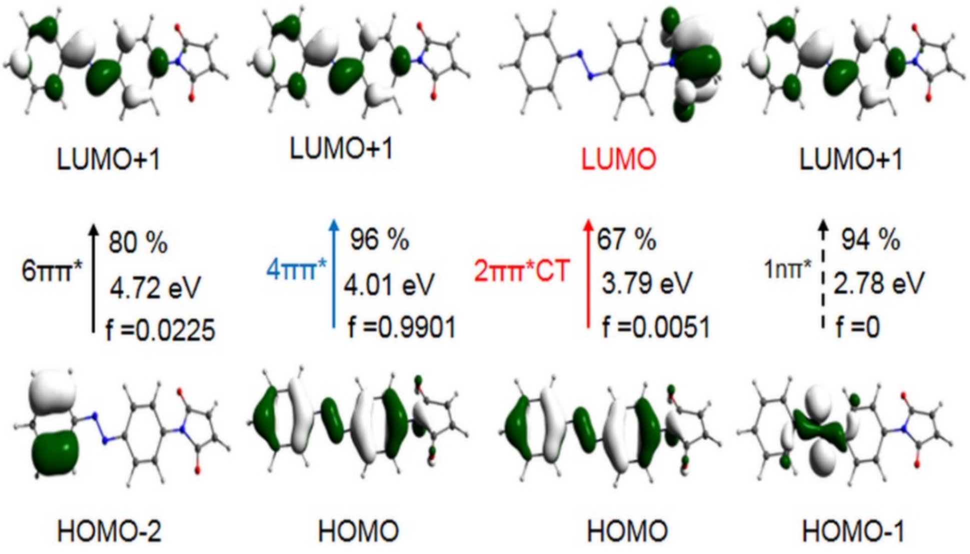

Figure 16. Representation of Kohn−Sham frontier MOs using CAMB3LYP/6-31+G(d) level of theory for electronic transitions of **E1** derivative.

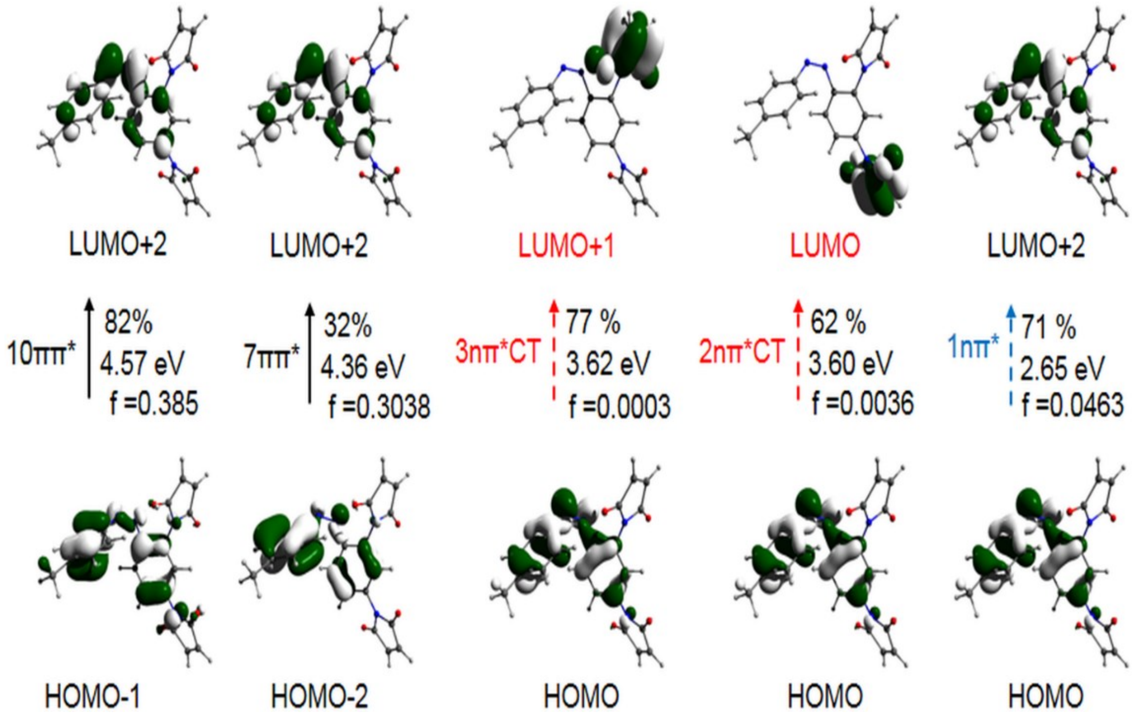

Figure 19. Representation of Kohn-Sham frontier molecular orbitals using CAM-B3LYP/6-31+G(d) level of theory for electronic transitions of **Z2** derivative.

The major contribution to the specific molecular orbitals from AB regions is labeled in blue, and the electron density depletion region from AB to MI units (CT) is labeled in red in Figures 15 and 19. The MOs labeled with black color represent other transitions that are closer to the $\pi\pi^*$, $n\pi^*$ character, or to the CT states, but with a minor contribution. The excited states are represented by corresponding numbers. Electron density surfaces in the ground and excited states represented in green (dark) and white (intense) were drawn at 0.004 au iso-density level. Ten vertical excitations were considered to describe the involved transition states including the lowest energy transitions.

The CT transition is present in both the *trans* and *cis* structures of the azo derivatives. It is also important to point out that the CT excited-state energy depends both on the number and position of the MI fragments [especially in compounds **E2**/**Z2** and **E3**/**Z3** where two MI fragments are in ortho and para positions, respectively (Figure 19)]. Even when the MI unit is not directly bound to the AB structure (compound **E4** and **Z4**), the CT transition is observed.

In most cases, the electronic density CT occurs between HOMO → LUMO frontier molecular orbitals. However, other transfer pathways such as HOMO → LUMO + 1, HOMO − 3 → LUMO + 1, HOMO − 4 → LUMO + 1 (when the number of MI functional groups is two), and HOMO − 3 → LUMO + 1 (when the MI group is not directly linked to the main AB structure in compound **E4** and **Z4**) can also be considered. The values of the vertical transition energies (ΔEv) and the corresponding CI coefficients (C %) of the CT states were found in most cases close to those of the main azobenzene transitions (Figures 15 and 19).

IV. Theoretical (TD-DFT) and experimental study of the solvent effect on the absorption spectra of azobenzene derivatives

In this section, the influence of the solvent on the electronic absorption spectra of the **E4** derivative was investigated using solvents of different polarities. The electronic structure of **E4** has been detailed by the DFT method at B3LYP/6–311++G(d,p) level of theory. Also, the diagram of the electrostatic potential for the **E4** derivative, the surface accessible to the solvents was established to investigate the possible interactions between the spectral sample (**E4**) and the solvent. The changes in the electronic absorption band positions as a function of the solvent polarity were discussed using different solvent parameters such as Catalan and Laurence scales. The theoretical absorption spectra of compound **E4** were calculated with time-dependent density functional theory at TD-B3LYP/6-311+G(d,p) and TD-CAM-B3LYP/6-311++G(d,p). The absorption spectral data calculated for **E4** were in agreement with the experimental results [50].

The molecular electrostatic potential (MEP) generated in the space around a molecule by the charge distribution can provide information about electrophilic and nucleophilic attack along with the hydrogen bonding interactions of solvent [51,186,187]. The mapped surface depicting the electrostatic potential of the **E4** molecule was computed by the B3LYP method and it is displayed in Figure 50. Different levels of the electrostatic potential at the surface can be distinguished by different colors in the MEP plot. The negative regions (red) of MEP represent the sites of electrophilic attack. By contrast, the positive regions (blue) correspond to the sites of the nucleophilic attack. The regions with the potential near to zero are given as green. As can be seen from the MEP surface of **E4**, the most negative region is mainly localized near the oxygen atom from the amide group. Partial negative zones are extended on the oxygen atoms from maleimide moiety as well as around the azo –N=N- bridge. On the other hand, the most positive potential level is pinpointed near the nitrogen atom from the amide group, this being the most probable site for the nucleophilic attack. The regions with partial positive potential are located around of hydrogen atoms from the maleimide ring. These sites give the possibility to estimate the regions where **E4** can have intermolecular interactions in the solute-solvent systems.

The accessible surface for solvent (SAS) represents the surface of the molecule that can interact with a solvent. This algorithm calculates an average of equidistant points from each atom that takes into account the van der Waals radius of the molecule and uses the number of these points to determine the surface accessible to the solvent. The solvent accessible surface (SAS) calculated for the E4 molecule was equal to 650 Å^2. The accessible surface encloses a volume of 1044 Å^3. Figure 51 displays the solvent accessible surface of the molecule depicted as the wire-frame (Figure 51a) and solid surface (Figure 51 b). SAS shows the interaction regions of **E**4 with the solvents.

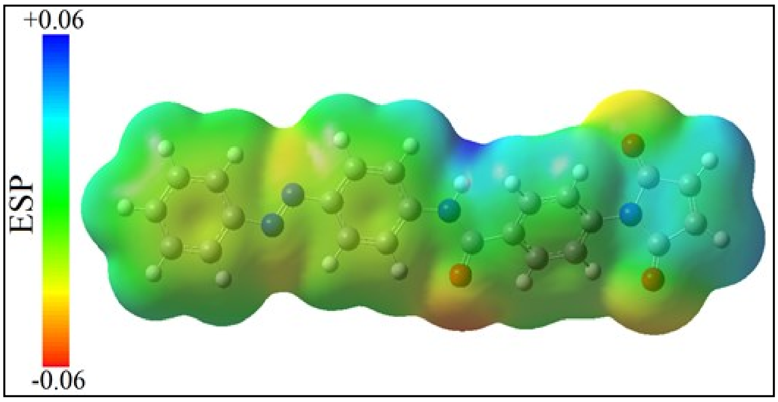

Figure 50. Molecular electrostatic potential diagram of **E4**.

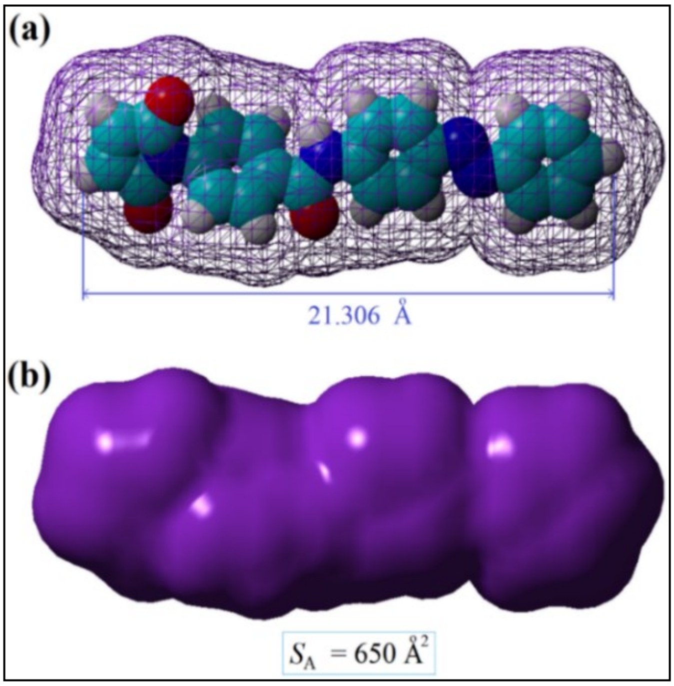

Figure 51. Solvent accessible surface of **E4** calculated for the optimized geometry at B3LYP/6-311++G(d,p) level of theory: (a) wire-frame rendering of the accessible surface; (b) solid rendering of the accessible surface.

To bring more insights regarding solute-solvent interactions, we performed additionally the molecular dynamics (MD) simulations of **E4** molecule solvation in two polar solvents (acetone and ethylene glycol). In this approach, both solvents were considered as explicit molecules surrounding the solute. Short-term MD simulations of 10 ps were performed at the level of YASARA molecular mechanics force field. The MD simulation results of solute-solvent interactions are presented in Figure 52. The computational results revealed the formation of hydrogen bonds (H-bonds) between solute and polar solvents. The H-bonds are spotlighted as yellow dot lines in Figure 52. For clarity, the H-bonds that emerged from solute-solvent interactions were encircled. According to Figure 52 (a), the **E4** molecule formed one hydrogen bond with a molecule of the acetone solvent. In this case, the group N-H from the amide moiety of **E4** acted as hydrogen bond donor, whereas the oxygen atom from acetone as hydrogen bond acceptor.

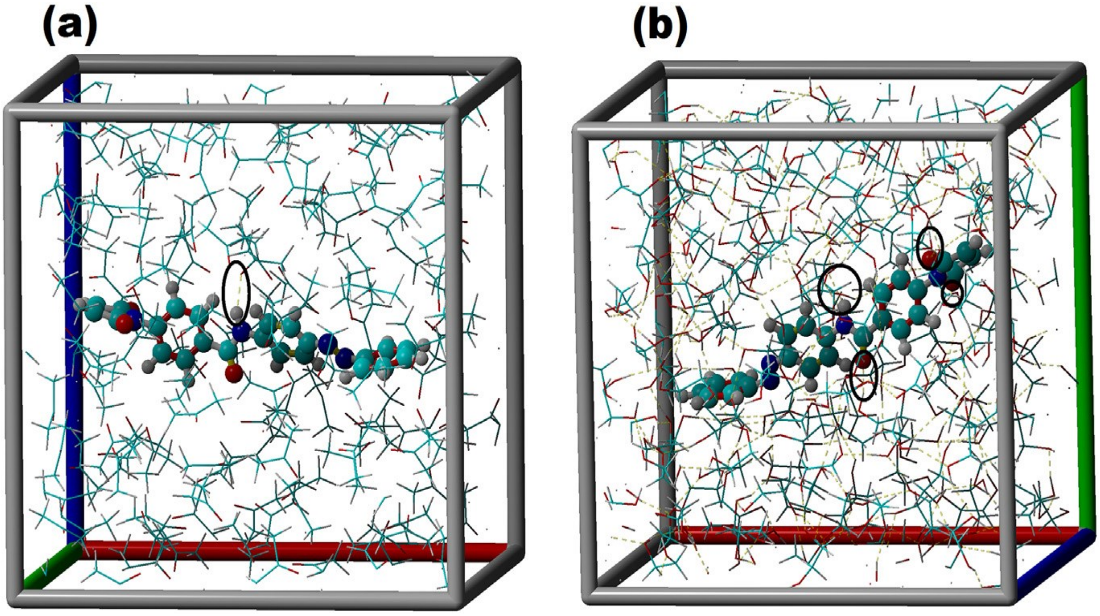

Figure 52. Computational snapshots showing solvation interactions of **E4** molecule with explicit solvents: (a) acetone and (b) ethylene glycol; equilibrated molecular systems after energy minimization and short molecular dynamics simulations (10 ps); computations were done at the level of YASARA force field. The calculated distance of this H-bond was of 1.94 Å and the associated energy of the hydrogen bond was equal to 5.47 kcal/mol.

V. Isomerization processes in azomaleimide derivatives

In this subsection, a systematic study on the dynamics of trans-cis, thermal cis-trans backward and light induced cis-trans isomerization of **E4** azomaleimide derivative was performed. The computational method based on the B3LYP/6-31+G(d,p) theory level was used to analyze the mechanism of thermal isomerization. The isomerization reactions were followed by electronic absorption spectra. The experimental results obtained allowed the calculation of kinetic parameters (activation energy (Ea), isomerization rate constant (k)) and thermodynamic parameters (activation enthalpy ($\Delta H^{\ddagger}$), Gibbs free energy ($\Delta G^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$)). Also, these activation parameters were theoretically estimated using a DFT model. In order to determine the type of reaction mechanism occurring in the thermal isomerization process, several modifications of the geometric parameters related to the dihedral angle C-N=N-C, valence C-N=N angle, valence N=N-C angle, dihedrals C-C-N=N and N=N-C-C respectively were used. Based on the modifications of the main parameters above mentioned, it was tried to establish the mechanism of thermal isomerization of compound **E4** (rotation, inversion, inversion assisted by rotation and concerted inversion), using in theoretical calculation the level of theory B3LYP/6-31+G(d,p) (Figures 64, 65 and 70).

The theoretical results of the representations of the potential energies obtained by modifying the main geometric parameters (C-N=N-C, C-N=N, N=N-C) responsible for the azomaleimide isomerization showed that the favored mechanism is rotation assisted inversion for which the energy value of this state is around 40,72 kcal/mol.

Theoretical calculations obtained from the analysis of the thermal isomerization mechanism have highlighted the emergence of new transition states (TScis and TStrans), states that appear under thermodynamic conditions [197] and can favor the mechanism by rotation assisted inversion following modification of the dihedral angles C-C-N=N and N=N-C-C, respectively.

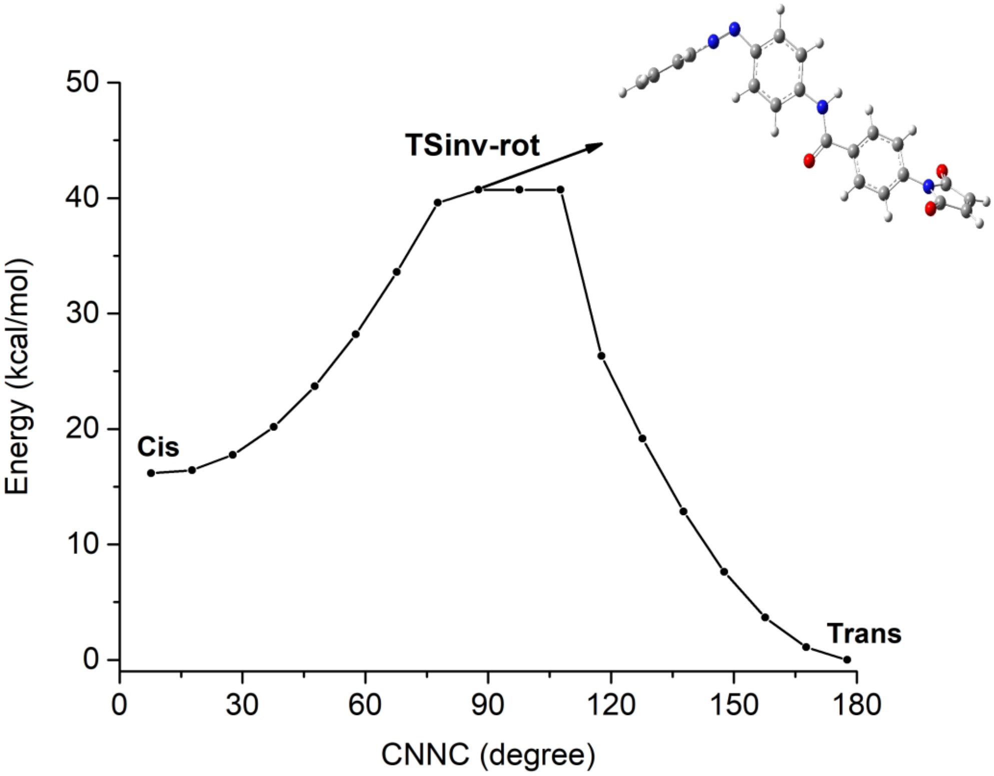

Figure 64 PES scans for E4 along C-N=N-C coordinate starting from cis to trans state using B3LYP/6-31+G(d,p) method.

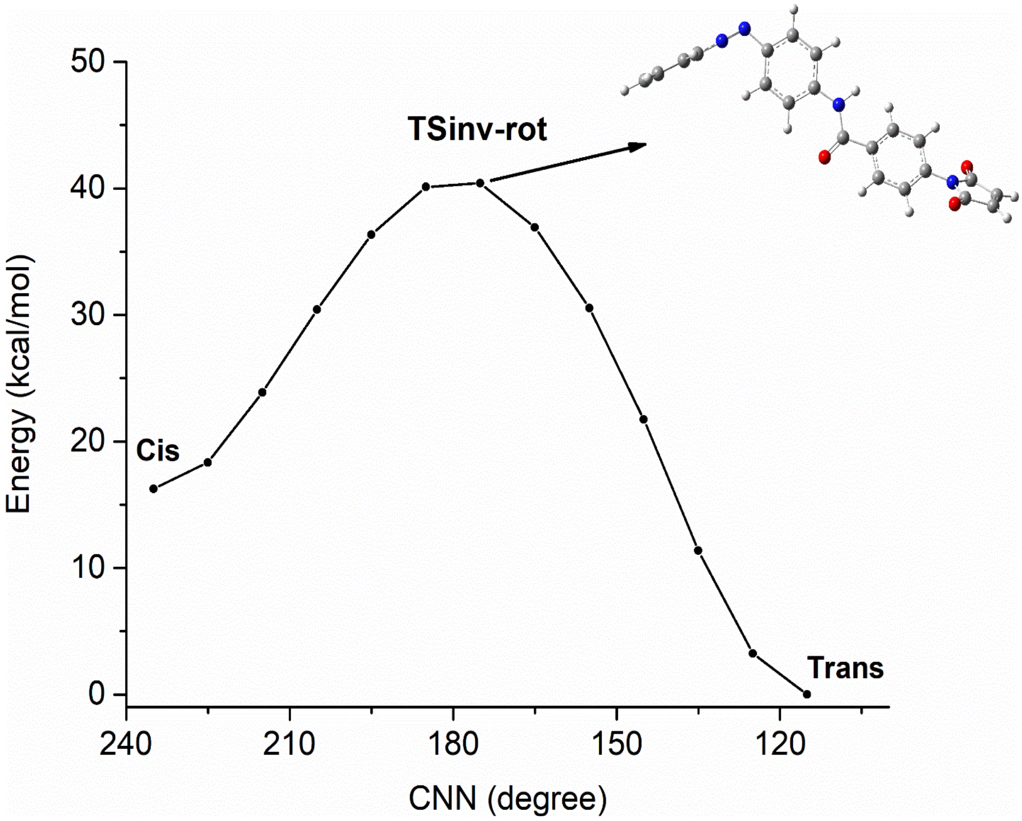

Figura 65. PES scans along the C-N=N valance angle for **E4** starting from cis to trans state using B3LYP/6-31+G(d,p) method.

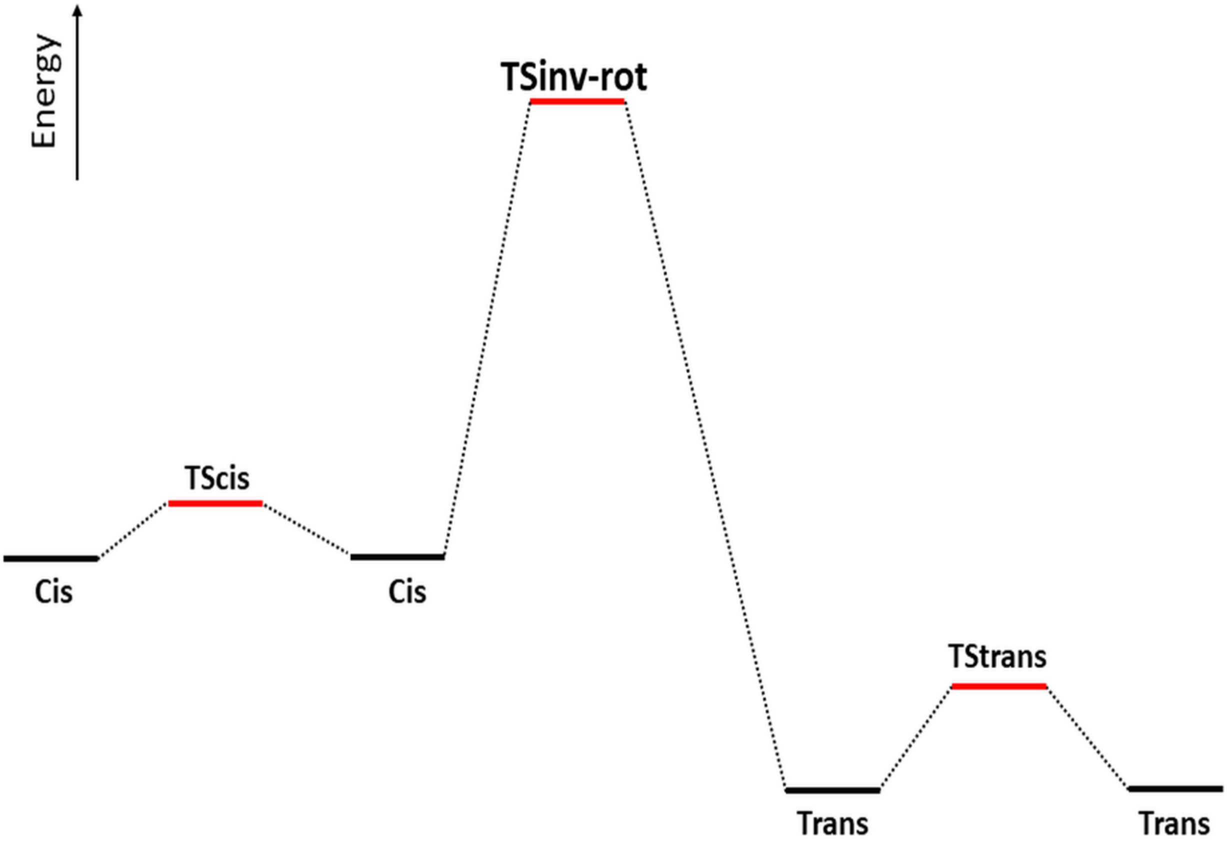

Figure 70. Transition states along to thermal isomerization reaction.

General conclusions

The present Ph.D. thesis, entitled: "Theoretical and experimental studies of some dynamic molecular systems based on hetero-organic compounds containing nitrogen", includes a systematic analysis in which theoretical and experimental methods were applied in order to investigate the electronic structure of some azobenzene derivatives substituted with maleimide. Eight azobenzene derivatives substituted with maleimide and bismaleimide in trans and cis isomeric forms were considered for investigation.

The results obtained from theoretical analyses and experimental determinations through personal contributions led to the following general conclusions:

- Following the optimization process using DFT methods based on PBE0 and CAM-B3LYP levels of theories, together with the People basis sets such as 6-31+G(d), 6-311+G(d,p) and 6-311++G(2df,2pd) it was shown that the main azobenzene structure substituted with functional groups of maleimide type (**E1**): (E)-1-(4-(phenyldiazenyl) phenyl)-1H-pyrrole-2,5-dione; (**Z1**): (Z)-1-(4-(phenyldiazenyl) phenyl)-1H-pyrrole-2,5-dione; (**E2**): (E)-1,1′-(4-(p-tolyldiazenyl)-1,3-phenylene)-bis-(1H-pyrrole-2,5-dione); (**Z2**): (Z)-1,1′-(4-(p-tolyldiazenyl)-1,3-phenylene)-bis-(1H-pyrrole-2,5-dione); (**E3**): (E)-1,1′-(4-(o-tolyldiazenyl)-1,3-phenylene)-bis-(1H-pyrrole-2,5-dione); (**Z3**): (Z)-1,1′-(4-(o-tolyldiazenyl)-1,3-phenylene)-bis-(1H-pyrrole-2,5-dione); (E4): (E)-4-(2,5-dioxo-2H-pyrrol-1(5H)-yl)-N-(4-(phenyldiazenyl)phenyl)benzamide; and (**Z4**): (Z)-4-(2,5-dioxo-2H-pyrrol-1(5H)-yl)-(4-(phenyldiazenyl)phenyl)-benzamide was planar and the results were consistent with other ab initio methods such as MP2/6-311 ++G(2d,2p), as well as with the experimental *X-ray* diffraction determinations reported in the literature.
- The orientation of the maleimide group with respect to the azo molecular plane was around 140 ° in all the compounds studied (**E1**-**Z4**). This orientation depends on two competing interactions such as the formation of a weak intramolecular hydrogen bond between the lone pairs oxygen electrons (from the maleimide functional group) with the hydrogen atoms in the vicinity of the aromatic nuclei in the azobenzene structure, as well as the occurrence of a steric volume repulsion of maleimide group, and both phenyl moieties in the azo group.
- The main azo electronic transitions ($\pi \rightarrow \pi^*$ [$S_0 \rightarrow S_2$] and $n \rightarrow \pi^*$ [$S_0 \rightarrow S_1$]) can be changed or replaced by the transitions from Sn to CT or from Sπ to CT, especially in case of low energy transitions ($n \rightarrow \pi^*$). The existence of such excited states

nπ*CT and ππ*CT was proved here for the first time for this group of molecular systems.

- The binding of the MI groups to the AB structure induces low-energy transitions that can change the order of the main transitions or replace them.
- The analysis of the CT states was performed with methods based on both TD-DFT (PBE0 and CAM-B3LYP) functionals and post Hartree−Fock methods (CIS, CIS(D) and CASSCF-NEVPT2, respectively). Both categories of methods indicate the presence of CT states but do not predict the same order for the transitions.
- The CT effect appears from the azo fragment (which acts as an electron donor) to the maleimidic group (which acts as an electron acceptor group).
- The CT mechanism occurs through either a planar or twisted pathway in an intramolecular process.
- The existence of CT states depends on both the number and positions of MI moieties.
- The presence of the MI moiety in the azo structure induces an increase in the number of low-lying (nπ*,nπ*CT, and ππ*CT) excited states both in the trans and cis isomers.
- The evolution of the excited states shows that the mechanism of ICT occurs for the trans isomer by a transfer from ππ* to ππ*CT, on the other hand in the case of the cis isomer from nπ* to nπ*CT states occurs.
- The presence of the nearly degenerate energy levels in AB−MI derivatives and a polarization introduced by the MI groups on the AB structure in the excited states favors the appearance of the mixed and novel type of CT transitions.
- The DFT results based on the functional B3LYP and CAM-B3LYP employed with the 6-311++G(d,p) basis set were in agreement with other data reported in the literature.
- Following the theoretical analysis (using the MEP and SAS representations) the active regions of the interaction of compound **E4** with the solvent were highlighted.
- The ability of hydrogen bond formation (using an explicit model of solute-solvent interaction) was investigated also through theoretical models based on classical mechanics (using the Yasara-type force field) and DFT-type quantum chemical calculations (using the B3LYP and CAM-B3LYP methods with the basic set 6-311++G (d,p)), and the results obtained were in agreement with the Catalan and Laurence models, as well as with the estimates represented by MEP and SAS.

- The lengths of hydrogen bonds formed between the compound studied (azomaleimide derivative **E4**) with solvents (ethylene glycol, acetone, acetonitrile) varied between 1.710 and 2.195 Å depending on the nature of the solvent.
- The presence of specific azo transitions (π → π* and n → π*) was confirmed based on the representation of the boundary molecular orbitals.
- Following the investigation of the dynamics of trans → cis isomerization induced by UV light, the existence of the two isomers (trans-azobenzene maleimide and cis-azobenzene-maleimide) was revealed. Also, it has been found that the isomerization process for the **E4** derivative is reversible, and the cis → trans isomerization can take place in two ways: radiative (using light from the visible domain) and thermal.
- The thermodynamic and kinetic parameters of the thermal isomerization process were calculated using the Arrhenius and Eyring equations.
- The results obtained from the thermodynamic parameter calculations showed that $\Delta H^{\ddagger}$=16.86 kcal/mol, $\Delta G^{\ddagger}$=23.84kcal/mol and $\Delta S^{\ddagger}$=-23.43cal/Kmol and are in agreement with other data from the literature.
- Theoretical values of the activation parameters: thermodynamic and kinetic were obtained by the DFT method using the B3LYP/6-31+G(d,p) and M062X/6-31+G(d,p) theory levels and the results of computations were consistent with the experimental data.
- The theoretical results obtained for the activation entropy ($\Delta S^{\ddagger}$) following the theoretical calculations with B3LYP/6-31+G(d,p) and M062X/6-31+G(d,p) were underestimated compared to the data experimental.
- By means of DFT/B3LYP/6-31+G(d,p) method, we observed that the inversion assisted by the rotation pathway was the predominant mechanism for the thermal isomerization into the ground state. During the cis → trans thermal isomerization via inversion assisted by rotation transition state by DFT method, two new processes were identified. These new processes involved the modification of C-C-N=N dihedral and C-C-N valence angles which, lead to the internal modification of C-N=N-C and C-N=N/N=N-C primary coordinates in the inversion assisted by rotation pathway.
- According to computational results, during the thermal isomerization, the main bond length N=N decreased from cis (1.250 Å) to transition state geometry (1.226 Å), and then increased for the trans isomer (1.260 Å). On the other hand, the values of adjacent bonds decreased in the case of C-N and increased in the case of N-C for

TSinv-rot geometry, as compared to trans and cis isomers of AAzM. As regards the unsubstituted azobenzene, the N=N (1.226 Å) and C-N (1.334 Å) distances of TSinvrot were shorter; but in the case of N-C (1.445 Å) bond the length was greater.

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Dissemination of results

The scientific results presented in this PhD thesis have made been the subject of two scientific articles published in ISI journals and one submitted for publication (under review), four participations in national scientific conferences (three oral communications and one poster) and four participation in international conferences (three oral communications and one poster).

I) Works published in ISI-rated journals reported to the PhD thesis:

1. **D. L. Isac**, A. Airinei, D. Maftei, I. Humelnicu, F. Mocci, A. Laaksonen, M. Pinteala, On the charge-transfer excitations in azobenzene maleimide compounds: a theoretical study, Journal of Physical Chemistry A, 123, 5525−5536, **2019** (IF= 2,641).

2. A. Airinei, **D. L. Isac**, M. Homocianu, C. Cojocaru, C. Hulubei, Solvatochromic analysis and DFT computational study of an azomaleimide derivative, Journal of Molecular Liquids, 240, 476–485, **2017** (IF= 4,561).

3. **D. L. Isac**, A. Airinei, M. Homocianu, N. Fifere, C. Cojocaru, C. Hulubei, Photochromic properties of some azo maleimide derivatives and DFT quantum chemical study of thermal cis-trans isomerization pathways, send to publication at Journal of Photochemistry and Photobiology A: Chemistry, under review (IF= 3,261).

II) Works published in ISI-rated journals related to the subject of the PhD thesis:

1. A. Airinei, R. Tigoianu, R. Danac, C. M. Al Matarneh, **D. L. Isac**, Steady state and time resolved fluorescence studies of new indolizine derivatives with phenanthroline skeleton, *Journal of Luminescence*, 199, 6-12, **2018** (IF= 2,732).

2. D. Maftei, **D. L. Isac**, M. Dumitraș, Ș. Bucur, A. C. Dîrțu, Trends in bond dissociation energies of brominated flame retardants from density functional theory, *Structural Chemistry*, 29, 921-927, **2018** (IF= 1,624).

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III) Works published in BDI-rated journals related to the subject of the PhD thesis:

1. M. Dumitras, D. Maftei, **D. L. Isac**, A. Airinei, A. C. Dîrtu, *Acta Chemica Iasi*, 24(2), 76-87, **2016**.

IV) Participation at national and international events

a) Oral communications:

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2. **D. L. Isac**, A. Airinei, D. Maftei, R. Cîrdei, I. Humelnicu, C. Cojocaru, A. Neamtu, M. Pinteală, A new pathway of azobenzene interconversion assisted by DFT and *ab initio* methods, Molecular Modeling in Chemistry and Biochemistry, MOLMOD 2018, 27-30 October **2018**, Cluj-Napoca, România.

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6. **D. L. Isac**, D. Maftei, A. Airinei, I. Humelnicu, M. Pinteală Theoretical perspectives regarding the substituted azobenzene maleimide structure as a result of the DFT and TD-DFT approach, Molecular Modeling in Chemistry and Biochemistry, MOLMOD 2016, 13-15 November **2016**, Cluj-Napoca, România.

b) Poster communications:

1. **D. L. Isac**, D. Maftei, A. Airinei, I. Humelnicu, M. Pinteala, New insights in isomerization mechanism pathways in the ground state of unsubstituted azobenzene: assessment of computational procedures/methodologies, Eighth Cristofor I. Simionescu Symposium Frontiers in Macromolecular and Supramolecular Science, 1-3 June **2016,** "Petru Poni" Institute of Macromolecular Chemistry Iași, România.

2. **D. L. Isac**, D. Maftei, A. Airinei, I. Humelnicu, M. Pinteală, Theoretical study of the isomerization mechanisms in the ground state of some push-pull substituted azobenzenes, Zilele Universităţii "Alexandru Ioan Cuza" din Iaşi, Conferinţa Facultăţii de Chimie, 29-31 Octombrie **2015**, România.

V) Internship abroad

1. "Molecular Modeling: Real Applications and New Approaches", 29th July- 2nd Aug. **2019**, Technology Park of Sardinia, Italia.

2. Joint innovative training and teaching/learning program in enhancing development and transfer knowledge of application of ionizing radiation in materials processing, Sept. 7-17, **2015**, Warsaw, Poland, and Sept. 28-Oct. 2, 2015, Palermo, Italy.