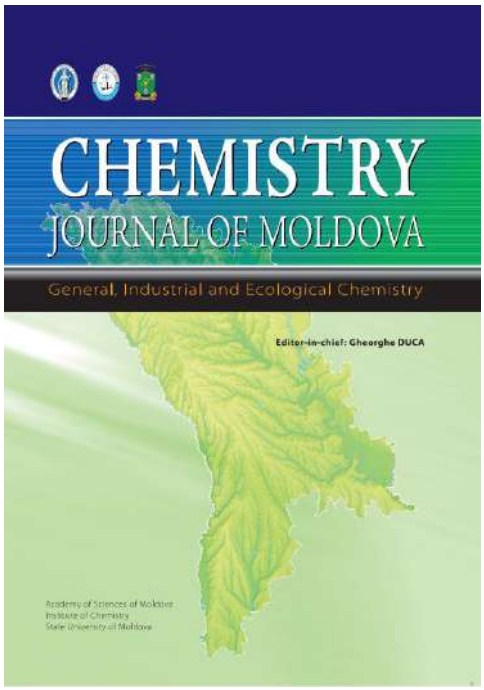


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DFT STUDY OF ABSORPTION AND EMISSION SPECTRA OF FORMYL-SUBSTITUTED AZULENYL DITHIENYLCYCLOPENTENE

Raluca-Ioana Jalba [a], Isabela-Costinela Man [a], Iolanta Balan [b], Mikhail Gorbachev [b], Marius Andruh [a], Gheorghe Duca [b], Simona Nica [a*]

[a]*"C. D. Nenitzescu" Institute of Organic and Supramolecular Chemistry, 202B, Splaiul Independentei str., Bucharest, RO-060023, Romania*
[b]*Institute of Chemistry, Moldova State University, 3, Academiei str., Chisinau, MD-2028, Republic of Moldova*
**e-mail: simona.nica@icoscdn.ro*

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[b]Institute of Chemistry, Moldova State University, 3, Academiei str., Chisinau, MD-2028, Republic of Moldova
*e-mail: simona.nica@icoscdn.ro

Abstract. Rational control of the optical properties of azulene-based photoswitches requires a detailed understanding of how molecular functionalization influences the electronic structure. DFT and TD-DFT calculations have been used to investigate formyl-substituted azulenyl dithienylcyclopentenes in comparison to experimental spectra and to pristine azulene. The calculated absorption spectrum reproduces the main experimental features and the calculated $S_2 \rightarrow S_0$ emission energy deviates from the experimental emission maximum. The molecular electrostatic potential and the dipole moment indicate a polarized ground-state charge distribution, consistent with the electron-withdrawing formyl groups. Frontier molecular orbital and natural transition orbital analyses suggest that the electronic excitations remain predominantly $\pi \rightarrow \pi^*$ with locally excited character and a possible small intramolecular charge-transfer contribution. These results provide a molecular-level description of the electronic structure of the compound and a basis for tailoring the photophysical response of azulene-based molecular photoswitches.

Keywords: azulenyl-functionalized dithienylcyclopentenes, DFT, TD-DFT, MEP, FMO, NTO, absorption, emission, fluorescence.

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Introduction

Photochromic molecules capable of reversibly switching between distinct molecular states upon light irradiation have attracted considerable attention owing to their potential applications in optical data storage, molecular electronics, sensing, responsive materials, and super-resolution fluorescence microscopy [1]. These systems undergo structural transformations induced by specific wavelengths of light, leading to marked changes in their optical and electronic properties, including absorption spectra, fluorescence emission, and redox behaviour [2]. Fluorescence photoswitching generally originates from photochemical transformations that alter the excited-state dynamics of the chromophore [3]. Among the most extensively investigated photochromic systems are diarylethenes and azobenzenes, which undergo reversible photoinduced isomerization or ring-opening/ring-closing processes [1]. In diarylethene-based photoswitches, ultraviolet irradiation typically induces cyclization to the closed-ring isomer, whereas visible light restores the open-ring form [4]. Depending on the extent of electronic conjugation and the excited-state relaxation pathways, these structural transformations may either activate or suppress fluorescence through modulation of radiative and non-radiative decay processes [3,4].

Among diarylethene derivatives, azulenyl-functionalized dithienylcyclopentenes are particularly attractive photochromic systems because they combine the excellent switching performance of the dithienylcyclopentene (DTE) core with the distinctive electronic and photophysical properties of azulene [5]. Owing to its non-alternant aromatic structure, intrinsic dipole moment, unusual fluorescence behaviour, and rich redox chemistry, azulene provides opportunities of tunning the optical response of DTE photoswitches beyond what is achievable with conventional aromatic substituents [6]. Besides extending the π-conjugated framework, the azulene substituents can be rationally functionalized to introduce additional molecular

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functionality. In particular, the introduction of aldehyde groups on the azulene moieties provides versatile synthetic sites for dynamic covalent chemistry, enabling the construction of increasingly complex supramolecular architectures through reversible condensation reactions [7,8]. Therefore, such carbonyl-functionalized azulenyl DTEs constitute promising molecular precursors for the preparation of photoswitchable organic cages, in which reversible light-induced structural transformations may be coupled with host-guest recognition. In the longer term, these multifunctional systems could serve as responsive molecular platforms for the selective detection or controlled encapsulation of environmentally relevant species, where guest binding may be translated into measurable optical responses through changes in fluorescence or absorption properties [9,10].

Our previous experimental studies have demonstrated that azulenyl dithienylcyclopentenes exhibit intense fluorescence centred at approximately 524 nm upon excitation at 360 nm. Furthermore, the nature of the substituents attached to the azulene moieties was found to significantly influence the emission intensity while exerting only a minor effect on the position of the fluorescence maximum [5]. Although these observations clearly contribute to the conjecture of strong influence of substitution on the photophysical behaviour of this family of photoswitches, the electronic origin of these effects and the structure–property relationships governing their fluorescence modulation remain insufficiently understood.

To gain deeper insight into the phenomena, it was performed a comprehensive DFT investigation of the optical and electronic properties of formyl-substituted azulenyl dithienylcyclopentenes. Density functional theory (DFT) has been widely applied to investigate the electronic structures and molecular properties of organic compounds, providing a theoretical framework for interpreting their structural and electronic characteristics [11,12]. The molecular structures of the azulenyl dithienylcyclopentenes investigated in this work, together with their reversible photochromic interconversion, are depicted in Figure 1. The study focuses on elucidating the origin of the fluorescence, the nature of the excited states underlying the photochromic response, and the influence of the carbonyl substituents on the electronic structure and photophysical properties. The combination of theoretical calculations and experimental characterization can provide complementary insights into molecular properties and structure–property relationships [13,14]. In this context, DFT and time-dependent DFT (TD-DFT) are employed in the present study to investigate the electronic structure and optical transitions of the formyl-substituted azulenyl dithienylcyclopentene. By correlating the electronic structure with the experimentally observed photophysical behaviour, this work provides new insight into the structure-property relationships governing this family of photoresponsive molecules and highlights their potential as versatile building blocks for the development of photoswitchable organic cages.

Computational details

All calculations were performed using the Gaussian 16 software package [15] and molecular structures together with the calculated electronic properties were analyzed using GaussView 6.0 [16]. Ground-state geometries of the designed formyl-substituted azulenyl dithienylcyclopentene were fully optimized without symmetry constraints at the B3LYP/6-31G (d, p) [17] level of theory. Frequency calculations confirmed that all optimized structures correspond to true minima on the potential energy surface, as evidenced by the absence of imaginary frequencies. Unless otherwise stated, all ground-state optimizations were carried out in the gas phase. The molecular electrostatic potential (MEP) surface plots of compounds were generated using the 0.001 a.u. isosurface and the same level of theory.

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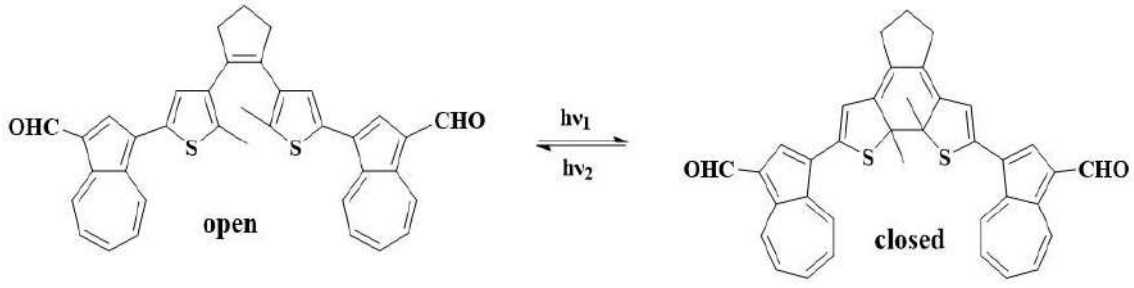


Figure 1. Chemical structure and the photoswitching process of the herein studied compound.

Vertical excitation energies and electronic absorption properties were investigated using time-dependent density functional theory (TD-DFT) [18]. Single-point excited-state calculations were performed on the optimized ground-state geometries employing the ωB97X-D functional with the 6-31G (d, p) basis set and the IEFPCM implicit solvation model [19] for dichloromethane (DCM), considering the lowest 20 singlet excited states. The calculated excitation energies were benchmarked against the corresponding B3LYP/6-31G (d, p) and CAM-B3LYP/6-31G (d, p) results [20]. Because these calculations describe vertical excitations from the optimized ground-state geometries, they directly estimate the excitation energies underlying the absorption process. The ωB97X-D functional [21] was employed owing to its accurate treatment of charge-transfer excitations and its demonstrated ability to reproduce absorption spectra in both the gas phase and solution.

Excited-state (S_2) geometry optimizations and vibrational frequency calculations were subsequently carried out within the TD-DFT framework using the B3LYP/6-31+G (d, p) level of theory, employing ultrafine integrals and symmetry constraints where appropriate. The S_2 excited state was chosen for geometry optimization because the characteristic emission of azulene and its derivatives arises from the second excited singlet state ($S_2 \rightarrow S_0$) rather than from S_1 [22], making S_2 the key state for describing their photophysical behaviour. Single-point energies on the optimized S_2 geometries were further evaluated at the B3LYP/6-31+G (d, p), CAM-B3LYP/6-31+G (d, p), and ωB97X-D/6-31+G (d, p) levels of theory. Solvent effects were included using the IEFPCM model with dichloromethane (DCM) as the solvent. The B3LYP/6-31+G (d, p) methodology was selected for excited-state geometry optimization based on its favourable balance between computational efficiency and accuracy, as previously demonstrated for related azulene-based systems.

To facilitate the interpretation of the electronic transitions, an analysis of Natural Transition Orbital (NTO) was performed for the relevant excited states, allowing visualization of the hole and particle distributions associated with the optical excitations [23].

Frontier molecular orbitals, including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), together with the corresponding HOMO–LUMO energy gaps (E_{gap}), were analysed for both the ground and excited-state optimized structures.

Results and discussion

The ring-open isomer structure of the studied compound was investigated from a theoretical point of view using DFT, according to the reaction scheme shown in Figure 1. The optimized gas-phase molecular structure was obtained using Density Functional Theory (DFT) at the B3LYP/6-31G (d, p) level.

Molecular electrostatic properties and polarity

The optimized structures, together with the atom-numbering scheme, are shown in Figure 2. The molecule exhibits a symmetric, non-planar conformation, with the substituted azulenyl rings linked through sulphur atoms to the central π-conjugated core. Table S1 from the Supporting Information summarizes the selected optimized geometric parameters of the compound.

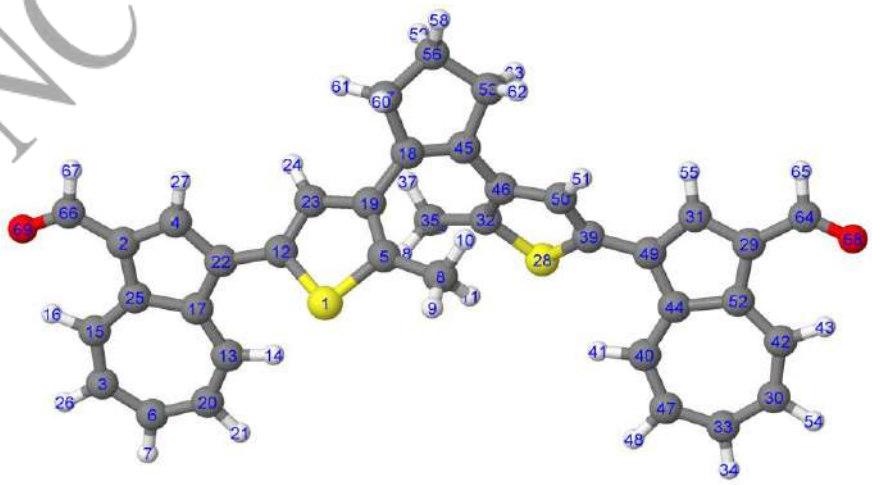


Figure 2. The optimized molecular geometry at DFT B3LYP/6–31 G (d, p) in gas phase of the studied compound.

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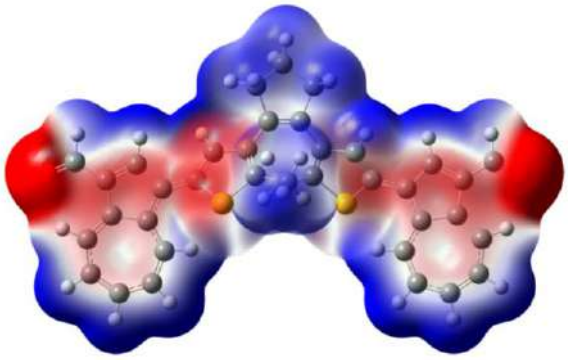


Figure 3. The molecular electrostatic potential surfaces (MEP) at DFT B3LYP/6–31 G (d, p) basis set in gas phase of the studied compound at the 0.001 a.u. contour level. Red and blue denote regions of negative and positive potential, spanning between -0.025 (red) and 0.025 (blue) a.u.

The molecular electrostatic potential (MEP) surface calculated for the optimized structure is depicted in Figure 3. As expected, the electrostatic potential distribution closely reflects the electronic structure of the molecule. The π-conjugated aromatic framework is predominantly electron-rich, exhibiting negative electrostatic potential, whereas the central dithienylcyclopentene core displays localized regions of positive potential, highlighting the intrinsic polarization of the molecular backbone. A characteristic feature of the MEP surface is the distinct charge separation within the azulene moieties. The five-membered rings exhibit a more negative electrostatic potential than the seven-membered rings, in agreement with the well-established charge-separated resonance description of azulene [6]. This observation confirms that the electronic characteristics of the azulene units are largely preserved after their incorporation into the photochromic framework.

The formyl substituents generate regions of pronounced negative electrostatic potential localized around the carbonyl oxygen atoms, reflecting the high electron density associated with their lone pairs. In contrast, the central π-conjugated framework exhibits comparatively positive electrostatic potential (blue regions in Figure 3), which is consistent with the electron-withdrawing character of the aldehyde groups, that polarize the conjugated backbone and the MEP surface, therefore, indicates a clearly polarized ground-state charge distribution. These characteristics suggest that the functionalized molecule may more susceptible to intramolecular charge redistribution upon photoexcitation, although neither molecular polarizability nor the extent of charge-transfer is directly quantified by the MEP analysis.

To characterize the ground-state molecular polarity, the dipole moment was calculated at the B3LYP/6-31G (d, p) level in the gas phase. Pristine azulene possesses an intrinsic dipole moment of 1.08 D, arising from its non-alternant aromatic structure and the asymmetric distribution of electron density between the electron-rich five-membered ring and the electron-deficient seven-membered ring [6]. For the formyl-substituted azulenyl dithienylcyclopentene, the calculated dipole moment is 3.55 D. This larger value is consistent with the combined contribution of the two polarized azulene units, the extended conjugated framework and the electron-withdrawing formyl groups, although the present calculations do not separate these contributions, and the value depends on the conformation of the open isomer. A larger dipole moment can be expected to favour stronger electrostatic interactions with polar environments, but it is not a direct measure of molecular polarizability or charge-transfer character, and neither quantity was computed here. These properties are therefore discussed in relation to the qualitative electronic-structure and excited-state analyses presented below, in the FMO and NTO analyses.

Theory of frontier molecular orbitals

Frontier molecular orbital (FMO) energies provide useful information on electronic, optical, and electrical properties, reactivity, and kinetic stability [24]. Figure 4 presents the calculated frontier molecular orbitals corresponding to the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) of azulene and formyl azulenyl dithienylcyclopentene at B3LYP/6-31G (d, p) level of theory for absorption and Figure 5 for emission at B3LYP/6-31+G (d, p). The FMO reveals how extension of the π-conjugated framework and substitution with electron-withdrawing groups modulate the electronic structure and the optical properties. Compared with pristine azulene, the formyl-azulenyl DTE exhibits a slight reduction in the HOMO–LUMO energy gap, indicating enhanced π-electron delocalization and lower excitation energies. The frontier orbitals are predominantly π-delocalized over the conjugated dithienylcyclopentene–azulene framework. The HOMO is distributed across the photochromic core, whereas the LUMO exhibits increased localization on the azulene acceptor moiety, suggesting that the lowest-energy excitation may involve both $\pi \rightarrow \pi^*$ excitation and intramolecular charge redistribution, the photoexcitation

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promoting electron density from the electron-rich thiophene framework toward the azulene fragments.

The HOMO-LUMO orbitals were analysed at the optimized ground-state geometry, these FMOs corresponding to the ground-state Kohn-Sham electronic solution, while the vertical electronic excitation energies and the associated absorption transitions were evaluated using TD-DFT in UV-Vis spectral analysis chapter.

Pristine azulene possesses a HOMO-LUMO gap of 3.37 eV. Both the HOMO and LUMO are delocalized over the fused bicyclic π-system, with the HOMO predominantly localized on the electron-rich five-membered ring, whereas the LUMO exhibits a larger contribution from the electron-deficient seven-membered ring. This orbital distribution reflects the intrinsic donor–acceptor character of azulene arising from its non-alternant aromatic structure. According Tsuchiya, T. *et al.* [25], the distinctive optical properties of azulene arise from its unconventional electronic structure. Although the molecule displays a low-energy $S_0 \rightarrow S_1$ absorption near 580 nm, the transition is characterized by an unusually low oscillator strength, resulting in a weak absorption band. This behaviour stems from the symmetry-forbidden HOMO–LUMO transition, which reflects the unique distribution of the frontier molecular orbitals across the non-alternant aromatic framework. Therefore, rational modulation of these frontier orbital energies through molecular engineering offers a powerful approach for tailoring the photophysical and electronic properties of azulene-derived chromophores.

Upon incorporation of the extended conjugated dithienylcyclopentene scaffold, the HOMO–LUMO gap decreases to 2.84 eV. Inspection of the frontier orbitals shows that both the HOMO and LUMO become extensively delocalized over the entire π-conjugated backbone, including the azulene core. Such orbital delocalization facilitates electronic delocalization throughout the molecule. The HOMO-LUMO gap decreases from 3.37 eV in azulene to 2.84 eV in the azulenyl-DTE, which is consistent with the bathochromic shift in the TD-DFT absorption spectra (Figure 6). This reduction originates from the increased conjugation introduced by the aromatic bridge, which stabilizes the frontier molecular orbitals and lowers the excitation energy. The HOMO is extensively delocalized over the entire conjugated backbone, encompassing the basal plane of cyclopentene, the azulene moiety and the central aromatic linker, indicating efficient electronic delocalization throughout the molecule. In contrast, the LUMO displays a different spatial distribution. Rather than being uniformly delocalized over the molecular framework, it is primarily localized on the two terminal azulene moieties The substantial overlap between the HOMO and LUMO nevertheless indicates that the lowest-energy excitation remains predominantly a π→π* transition. The aldehyde substituents indirectly stabilize the electronic structure through electron-withdrawing character while leaving the overall topology of the LUMO largely unchanged.

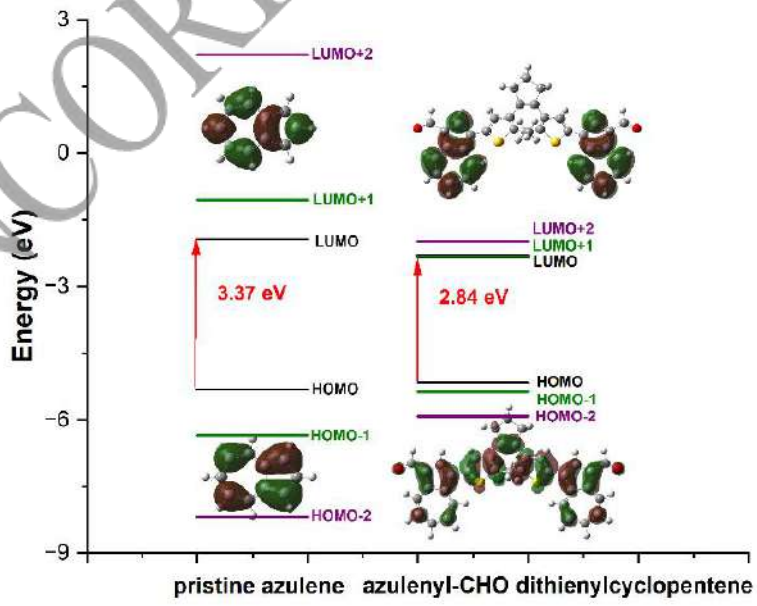


Figure 4. Frontier molecular orbitals (HOMO, LUMO) at B3LYP/6-31G (d, p) level of theory of the ground-state geometry, in DCM, for pristine azulene and formyl-substituted azulenyl dithienylcyclopentene.

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An additional feature emerging from the orbital energy diagram is the presence of closely spaced frontier orbitals in formyl-substituted azulenyl dithienylcyclopentene, in contrast to azulene. The extended π-conjugated architecture generates several occupied (HOMO, HOMO-1 and HOMO-2) and unoccupied (LUMO, LUMO+1 and LUMO+2) molecular orbitals that lie within a narrow energy interval. Although these orbitals are not strictly degenerate, they are quasi-degenerate, reflecting the increased molecular size, molecular symmetry and extensive π-electron delocalization.

The frontier molecular orbitals were analysed at the optimized second excited singlet-state geometry at B3LYP/6-31G+ (d, p) level of theory, in DCM, and are depicted in Figure 5, corresponding to the ground-state Kohn-Sham electronic solution evaluated at the relaxed excited state geometry. Comparing the corresponding orbital distributions and energy levels provides insight into the changes in the electronic structure associated with excited-state geometry relaxations. Unlike most aromatic hydrocarbons, azulene is well known to violate Kasha's rule, exhibiting fluorescence predominantly from the second excited singlet state (S_2) rather than from the lowest excited singlet state (S_1) [18]. Since the azulene framework is preserved in the formyl-substituted azulenyl dithienylcyclopentene, it is reasonable to expect that their emissive properties are likewise governed by transitions involving the S_2 state. Relative to the ground-state geometry, the excited-state structure exhibits a further reduction of the HOMO–LUMO energy separation, reflecting the structural and electronic relaxation that accompanies excitation.

For pristine azulene, the calculated HOMO–LUMO gap decreases from 3.37 eV at the ground-state to 3.09 eV at the geometry optimized for the excited singlet state. These Kohn-Sham orbitals, evaluated at the relaxed geometry, are used only as a qualitative measure of geometric and electronic relaxation. The HOMO is delocalized over the azulene π-system, whereas the LUMO preserves its characteristic localization on the complementary region of the non-alternant aromatic framework, preserving the intrinsic electronic polarization of azulene.

In the formyl-substituted azulenyl dithienylcyclopentene, the calculated frontier orbital gap decreases to 2.03 eV, a reduction of 1.06 eV relative to azulene at the relaxed geometry, which indicates a stronger stabilization of the frontier orbitals in the extended system. The HOMO remains largely delocalized over one azulene moiety, while the LUMO becomes predominantly localized on the adjacent arm of the dithienylcyclopentene bridge incorporating the same azulene unit. This redistribution of the virtual frontier orbital points to a more localized excited-state electronic structure than that observed for the ground state optimized structure. It is important to note that HOMO-LUMO orbital gaps do not correspond directly to electronic transition energies, as they do not account the electron-hole interactions, hence the emission energies are obtained from the TD-DFT calculations and discussed in the following section.

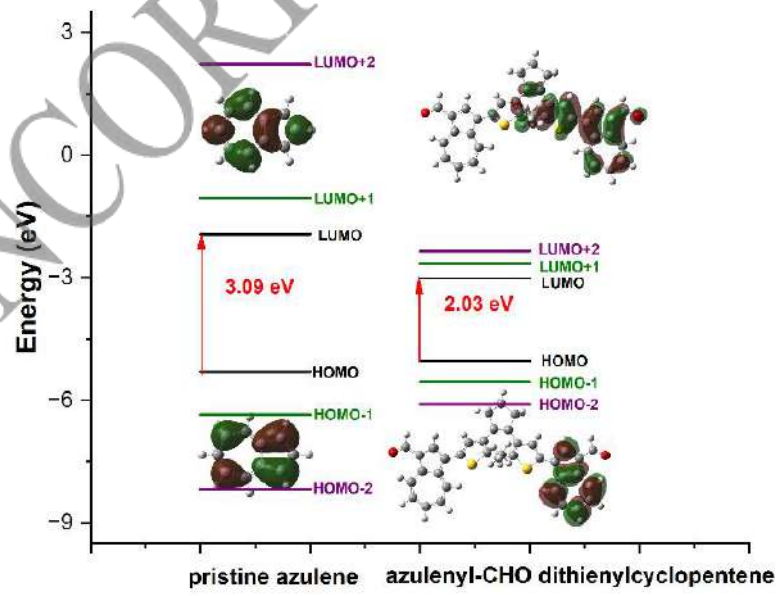


Figure 5. Frontier molecular orbitals (HOMO, LUMO) at B3LYP/6-31G+ (d, p) level of theory of the optimized second excited singlet state geometry, in DCM, for pristine azulene and formyl-substituted azulenyl dithienylcyclopentene.

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UV-Vis spectral analysis

To theoretically describe the absorption spectrum of the formyl-substituted azulenyl dithienylcyclopentene, DFT calculations were performed at the ωB97X-D/6-31G (d, p) level of theory. The calculated spectrum shows good agreement with the experimental one recorded in DCM at room temperature (Figure 6). For comparison, the absorption spectrum of pristine azulene was also calculated at the same level of theory. A comparison of the experimental spectrum with those calculated at the B3LYP/6-31G (d, p), CAM-B3LYP/6-31G (d, p), and ωB97X-D/6-31G (d, p) levels of theory is provided in Figure S1 (Supporting Information).

The positions of the characteristic maximum absorption wavelengths in the calculated spectra reproduce the main experimental features with a modest systematic deviation. In particular, the two most intense absorption bands are hypsochromically-shifted relative to the experimental peak position maximum. Overall, the computed transition energies show good agreement with experiment, especially at the ωB97X-D/6-31G (d, p) level of theory. The residual discrepancies likely arise from limitations in the treatment of solvation effects. Specifically, the use of an implicit solvent model may not fully capture specific solute-solvent interactions and local polarization effects, which can contribute to the observed shifts in the absorption spectra. The natural transition orbitals (NTOs) associated with the most intense calculated excited states are shown in Figure 6 to provide further insight into the nature of the corresponding electronic excitations. The most intense calculated absorption band occurs at 286.26 nm, with a high oscillator strength (f = 0.8501), and corresponds to a strongly allowed electronic transition. The associated particle NTO is extensively delocalized over the entire π-conjugated framework, including the azulene core, central aromatic bridge, and terminal formyl-substituted azulenyl rings. Upon excitation, the hole NTO remains distributed over the conjugated framework, although with a greater concentration of electron density within the central π-system and adjacent aromatic fragments. Notably, no significant electron density is localized on the carbonyl oxygen atoms, indicating that the formyl groups do not directly constitute the accepting orbital electron-withdrawing character on the π-framework. The substantial spatial overlap between the hole and particle NTOs indicates a predominantly π→π* character, accompanied by moderate intramolecular charge redistribution. A second absorption band is calculated at approximately 364 nm, with an oscillator strength of f= 0.3383. In contrast to the higher-energy transition, the corresponding NTOs display a more pronounced spatial redistribution of electron density. The particle orbital is predominantly localized on one side of the azulene moiety, whereas the hole orbital is concentrated toward one of the dithienyl-containing part of the molecule. The increased spatial separation between the hole and particle orbitals indicates a greater degree of charge redistribution upon excitation.

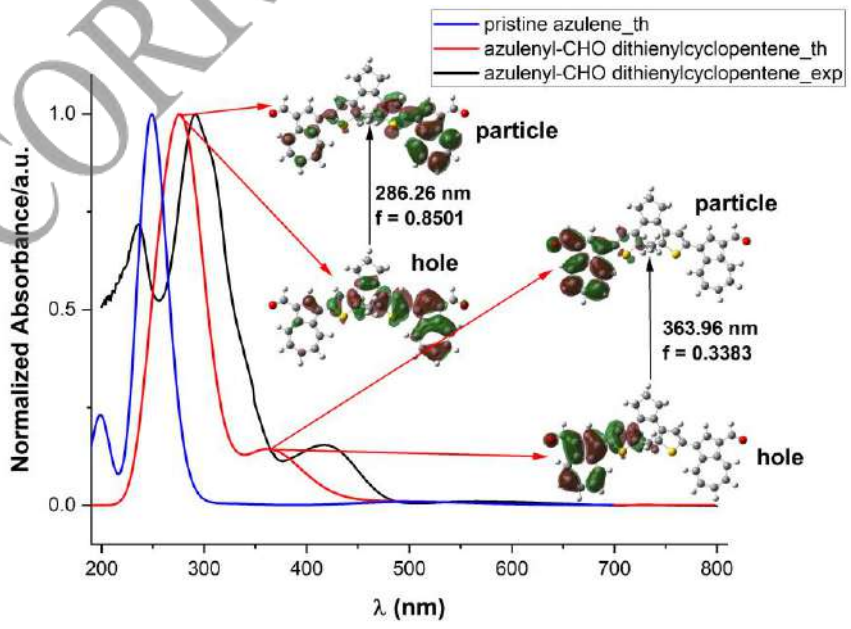


Figure 6. Simulated UV-VIS spectra at ωB97X-D/6-31G (d, p) level of theory in DCM for pristine azulene and formyl-substituted azulenyl dithienylcyclopentene *vs* experimental spectra. The insets show the NTOs.

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However, because both orbitals remain electronically connected through the continuous π-conjugated framework, this transition is more appropriately described as having an intramolecular charge-transfer (ICT) character. The electron-withdrawing formyl substituents contribute to the increased molecular polarization and facilitate this charge redistribution, while not acting as the principal acceptor sites.

Relative to pristine azulene, the extended π-conjugated architecture of the investigated derivative leads to a pronounced bathochromic shift and broadens the absorption profile toward the visible region. This effect is further influenced by the electron-withdrawing formyl substituents.

Emission spectral analysis

Emission was modeled from the relaxed second excited single state. S_2 was chosen as the target of the excited-state optimization because azulene is the classical example of $S_2 \rightarrow S_0$ fluorescence [18] and the azulene unit is retained in the studied compound. This is an assumption carried over from azulene and was not tested independently for the azulenyl-DTE. The character of the second root was not followed explicitly along the optimization.

Vertical emission energies were obtained from TD-DFT single point calculations at the S_2 optimized geometry in DCM (IEFPCM) with the B3LYP/6-31+G (d, p) level of theory. Figure 7 shows the calculated spectrum, normalized to its own maximum of the azulenyl-DTE and of pristine azulene, together with the experimental fluorescence spectrum of the azulenyl-DTE, whose maximum is at 524 nm. The calculated bands are much broader than the experimental one, the calculated width coming from the arbitrary Gaussian broadening, since vibronic structure is not included, and it should not be interpreted.

At the S_2-optimized geometry, the $S_2 \rightarrow S_0$ transition of the azulenyl-DTE is calculated at 506.37 nm and it appears as a shoulder. This is the transition compared with the experimental maximum at 524 nm, from which it differs by 0.08 eV, a small deviation for a vertical TD-DFT emission energy. Even that, the most intense transition, at 375.79, dominates the calculated curve in Figure 7, it is not the emissive state, the oscillator strength measuring how allowed the transition is, not which state emits.

For pristine azulene, the most intense bands at about 270 and 210 nm arise from higher excited states and are not related to fluorescence. The $S_2 \rightarrow S_0$ transition appears as the weak feature near 350 nm. The $S_2 \rightarrow S_0$ energy of the azulenyl-DTE is therefore lower than that of azulene at the same level of theory. This is consistent with a stabilization of the relaxed S_2 state by the extended π-conjugated framework.

The NTOs of the two transitions are inserted in Figure 7. In both cases the hole and the particle are located on the same half of the molecule, on one azulenyl-thienyl arm and the adjacent part of the cyclopentene bridge, whereas the second azulene unit carries no visible density. After relaxation, the excitation is therefore localized on one arm, which agrees with the localized LUMO in the FMO analysis (Figure 5).

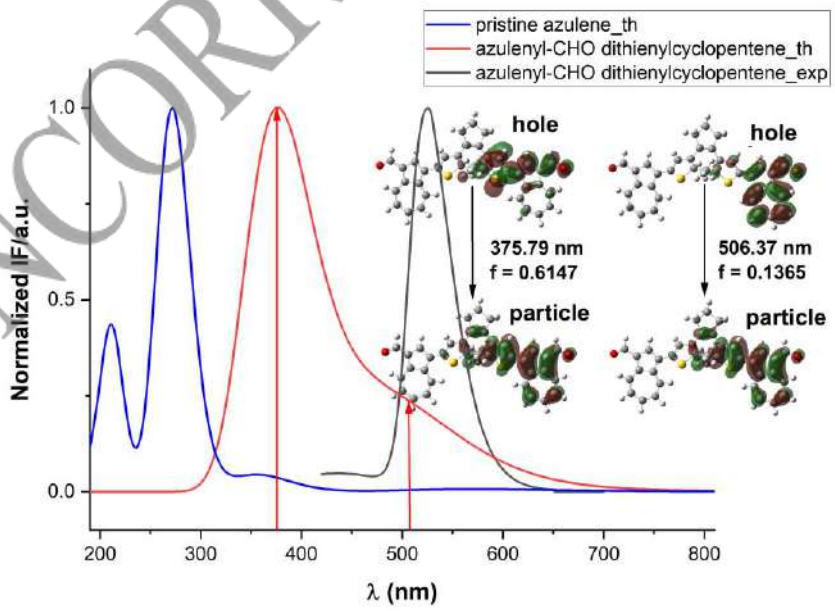


Figure 7. Simulated fluorescence spectra at B3LYP/6-31+G (d, p) level of theory in DCM for pristine azulene and formyl-substituted azulenyl dithienylcyclopentene vs experimental spectra. The insets show the NTOs.

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For the 375.79 nm transition, the hole spreads over the DTE core and the five-membered ring of the azulene unit, and the particle over the same branch, with considerable overlap, which indicates a predominantly π→π* locally excited-state. For 506.37 nm transition, the hole is more concentrated on the terminal formyl-substituted azulene unit and the particle is spread over the azulene, the thiophene and the basal plane of cyclopentene. The spatial separation is modest, and the excitation involves only a small redistribution of density along the arm. These descriptors rest on visual inspection of the NTOs and no charge-transfer descriptor, such as the hole-electron distance, was computed. We therefore describe the excitations as predominantly locally excited, with a possible small intramolecular charge-transfer contribution. The carbonyl oxygen atoms carry little density in the NTOs shown so the formyl groups do not appear to be the main acceptor region.

Previous studies have shown that the optical response of aldehyde-substituted azulene derivatives is governed mainly by the electron-withdrawing nature of the formyl group, which modulates the π-electronic structure rather than introducing additional low-lying excited states [26]. Our results are consistent with this picture. Since the non-formylated analogue was not calculated, the contribution of the CHO groups cannot be disentangled from that of the extended π-system.

The calculated emission energies are vertical transition energies at a fixed geometry in an implicit solvent. Vibronic effects (Franck-Condon overlap, which sets the band width and the offset between the vertical energy and the 0-0 transition, and Herzberg-Teller coupling), non-radiative decay and non-adiabatic dynamics between S_2 and S_1 were not included. Since S_2 was imposed as the optimized state, the calculations are consistent with S_2-based emission as known for azulene.

Conclusions

Overall, the DFT calculations provide a consistent description of the electronic and photophysical properties of the formyl-substituted azulenyl dithienylcyclopentene and the calculated absorption spectrum reproduces the main experimental features. Extending the π-conjugated backbone reduces the frontier orbital energy gap compared to unsubstituted azulene (from 3.37 to 2.84 eV). The formyl substituent, through their electron-withdrawing character, are expected to modulate the frontier electronic structure and the polarization of the excited states. Since non-formylated analogue was not calculated, the contribution cannot be separated from that of the extended π-system. Natural transition orbital analysis indicates that the optical excitations are predominantly π→π* in character, with a locally excited nature and a possible small intramolecular charge-transfer contribution. This assessment is based on visual inspection of the orbitals, and no charge-transfer descriptor was computed. The emission was modelled from the relaxed S_2 state, following the $S_2 \rightarrow S_0$ emission of azulene. Because S_2 was imposed as the optimized state, the calculations are consistent with S_2-based emission, but they do not by themselves show that the anti-Kasha behaviour of the azulene is retained in this compound. Overall, the computational calculations results provide a molecular-level description of the electronic structure and optical properties of the studied compound and they highlight the potential of the azulenyl dithienylcyclopentene as a versatile building block for the development of stimulus-responsive molecular systems. In particular, the combination of photoinduced structural switching, extended π-conjugation, and optical response offers prospects for the design of photoswitchable organic cages with tunable guest-recognition properties. Such systems may eventually find applications in environmental chemistry, particularly for the selective recognition and capture of pollutants or metal ions, light-controlled molecular separation, and optical sensing, areas where the reversible modulation of the cage cavity and its electronic properties would provide an additional level of control.

The incorporation of this photoswitchable system into the development of organic cages is currently being explored in our laboratory.

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Supplementary information

Supplementary data are available free of charge at http://cjm.ichem.md as PDF file.

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