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DFT Study of the Reactivity of Some Methylenepyran Derivatives Used in Dye-Sensitized Solar Cells

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Abstract

Solar energy is one of the best alternatives for combating climate change. Its development has led to the creation of dye-sensitized solar cells (DSSCs). To improve the solar energy conversion efficiency of DSSCs, several organic compounds, including methylenepyran derivatives, have been synthesized. This work contributes to the understanding of some methylenepyran derivatives as dyes. To do this, the physicochemical and photovoltaic properties are evaluated through the dipole moment, the HOMO-LUMO energy gap, UV-Visible absorptions, and the Light Harvesting Efficiency (LHE). The calculations are carried out with DFT and TD-DFT methods in gas and aqueous phases. In both phases, the results show that compound C_P, containing the phenyl group, is favorable for good intramolecular charge transfer, while compound C_I, with the iodine substituent, is favorable for good light harvesting. C_P and C_I compounds are the best dyes among the six that were the subjects of this study.

Keywords

Methylenepyran, Dyes, HOMO-LUMO Energy Gap, UV-Visible, DFT

1. Introduction

Fossil energies are the primary energy source in the world. However, these energy sources have an impact on the environment and the health of populations. In the fight against global warming, solar energy appears as one of the best alternatives. Indeed, solar energy is the most accessible and cleanest renewable energy source

[1] [2]. The development of solar energy has enabled the creation of several types of solar cells, including dye-sensitized solar cells (DSSC) [3] [4]. DSSCs have attracted considerable attention [5]-[7]. However, one of the main research challenges is to improve the conversion efficiency of photovoltaic energy while keeping production costs low. Calogero *et al.* reported a conversion yield of 0.66% using a red dye made from Sicilian orange juice as a sensitizer [5]. Wongcharee *et al.* obtained a conversion yield of 0.70% with Roselle as a sensitizer [6]. A conversion yield of 2.09% was obtained with the Rose Bengal dye [7]. Many other studies have demonstrated the effectiveness of organic compounds in photoconversion [8]-[10]. The choice of dye, therefore, appears crucial to improving yield. Indeed, a good dye must be able to transfer electrons from its excited state to the conduction band of the semiconductor, which is titanium dioxide (TiO_2), and regenerate the charges after the photo-oxidation process. These Intramolecular Charge Transfer (ICT) processes are well understood in theoretical chemistry.

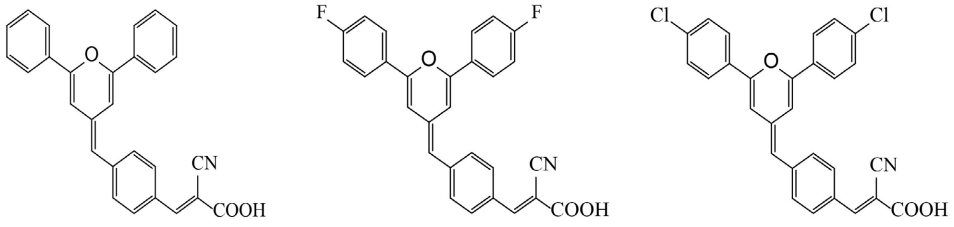
Thus, the aim of our work is to theoretically study the electronic properties of some methylenepyran derivatives of type donor-π-acceptor (D-π-A) used as electrodonor fragments in type push-pull complexes [11] [12]. Six methylenepyran derivatives were chosen for this purpose. Four of them were studied experimentally and theoretically [13]. Theoretically, the energies of the frontier molecular orbitals (HOMO, LUMO) and the UV-visible absorptions of these compounds have been calculated at the B3LYP/6-31G(d) level. In this work, these electronic properties are evaluated at the B3LYP/LANL2DZ level. In addition to these properties, the polarity and the Light Harvesting Efficiency (LHE) are determined. Thus, the Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) methods, with the B3LYP functional associated with the basis LANL2DZ, are used in this work [14]-[17]. The effect of the solvent on the properties was also taken into account with Tomasi's conductor-like polarizable continuum model (CPCM) in order to bring more precision to the literature data [18].

2. Materials and Methods

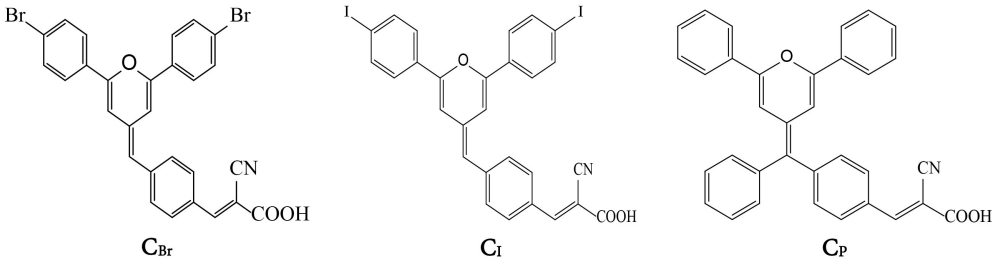
2.1. Materials

This study focuses on six methylenepyran derivatives that differ in the presence of fluorine, chlorine, bromine, iodine, and phenyl atoms in their structures. They are named C, C_F, C_{Cl}, C_{Br}, C_I, and C_P, and are shown in **Figure 1**.

These calculations are carried out with the GAUSSIAN-09 program [19].



C C_F C_{Cl}



C_{Br} C_I C_P

Figure 1. Methylenepyran derivatives.

2.2. Methods

The dipole moment, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest vacant (LUMO), as well as UV-visible absorptions, are physicochemical parameters that characterize intramolecular charge transfer [20]-[22]. To determine these parameters, the compounds were first optimized in their ground state (charge = 0) using Density Functional Theory (DFT) and the B3LYP hybrid functional, associated with the LANL2DZ basis [15] [16]. The RMS gradient norm is practically zero for all compounds, indicating good convergence of the calculations and good stability of the optimized geometries. Then, UV-visible absorptions were calculated using the TD-DFT method from the initially optimized molecules at the B3LYP/LANL2DZ level [17]. Six excited states were investigated. Finally, all calculations were also performed in the aqueous phase using Tomasi's conductor-like polarizable continuum model (CPCM) [18].

The energy gap between the frontier molecular orbitals, HOMO and LUMO, is calculated from Equation (1).

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \tag{1}$$

According to Koopmans' theorem, the smaller the ΔE, the more reactive the molecule [23].

The ionization potential is calculated from Equation (2).

$$\text{IP} = -E_{\text{HOMO}} \tag{2}$$

IP indicates the ability of an atom or molecule to donate electrons.

The conversion efficiency of the incident monochromatic photon into an electron in DSSCs depends in part on the Light Harvesting Efficiency (LHE) of the dye [24] [25]. LHE is calculated from Equation (3).

$$\text{LHE} = 1 - 10^{-f} \tag{3}$$

f: oscillator strength associated with its maximum absorption wavelength $\lambda_{\max}$.

3. Results and Discussion

3.1. Dipole Moments

The calculated dipole moment values are presented in Table 1.

Table 1 shows that the values of the dipole moment in the gas phase are between 5.72 and 7.90 D. The unsubstituted chromophore C is the most polar, with a dipole moment of 7.90 D. It is followed by the compound C_p with a dipole moment

of 6.74 D. Adding a phenyl ring to compound C therefore results in a decrease in its dipole moment. This decrease is greater when halogens, which are electro-attracting inductive groups, are added, particularly chlorine. The dipole moments of all compounds increase in aqueous solution. Compound C remains the most polar. In general, all compounds possess a large dipole moment, which increases in solution. These high dipole moment values correspond to efficient intramolecular charge transfer in these dyes.

Table 1. Dipole moments.

Compounds	μ_{gas} (D)	$\mu_{aqueous}$ (D)
C	7.9	11.44
C_F	5.72	8.87
C_{Cl}	5.60	8.61
C_{Br}	5.79	8.83
C_I	6.03	9.16
C_P	6.74	9.26

3.2. Frontier Molecular Orbital Energies

Table 2 contains the energy values of the frontier molecular orbitals, the associated energy gaps, and the ionization potential of the compounds. A dye would be a good photosensitizer in dye solar cells (DSSCs) if its LUMO energy is above the edge of the conduction band of TiO_2, and if its HOMO energy is less than the redox potential of the electrolyte (I_3^-/I^-).

Table 2. Frontier orbital energies and energy gaps.

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	IP (V)
Gas-phase				
C	−5.426	−2.873	2.553	5.426
C_F	−5.647	−3.041	2.606	5.647
C_{Cl}	−5.667	−3.065	2.602	5.667
C_{Br}	−5.639	−3.047	2.592	5.639
C_I	−5.607	−3.028	2.579	5.607
C_P	−5.244	−2.875	2.369	5.244
Aqueous phase				
C	−5.404	−3.033	2.371	5.404
C_F	−5.458	−3.061	2.397	5.458
C_{Cl}	−5.475	−3.078	2.397	5.475
C_{Br}	−5.467	−3.076	2.391	5.467
C_I	−5.457	−3.071	2.386	5.457
C_P	−5.244	−3.028	2.216	5.244

Figure 2 shows that all LUMO energies are above the conduction band energy level (−4.0 eV). This reflects a good ability to inject electrons from dyes in the excited state. Moreover, all the HOMO energies of the dyes are less than the redox potential of the electrolyte (−4.8 eV) [26]. All dyes would therefore have a good charge regeneration capacity. The energy gap ΔE is lower in compound C_p (2.369 eV) compared to compound C (2.553 eV), while halogenated compounds exhibit higher energy differences compared to compound C. The phenyl ring therefore leads to a decrease in the energy gap of 0.184 eV, while the halogen groups cause an increase. The decrease in the energy gap reflects a bringing together of the frontier orbitals, which would lead to better intramolecular charge transfer [27] [28]. The C_p compound would therefore be more favorable for charge transfer than the unsubstituted C compound and halogenated compounds. The same trend is observed in the aqueous phase. Therefore, the order of reactivity of the dyes would be:

$$C_P > C > C_I > C_{Br} > C_{Cl} > C_F.$$

This order is confirmed by the values of the ionization potential. Indeed, the ionization potential of compound C_p (5.244 V) is lower than that of C (5.426 V), which is itself lower than those of halogenated compounds. This translates to easier charge transfer in the C_p compound compared to the other compounds.

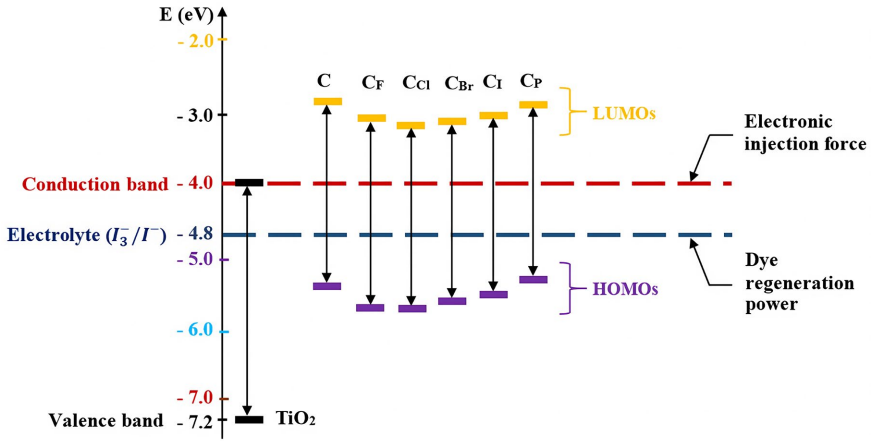


Figure 2. Gas-phase energy diagram.

Table 3 shows that the HOMO orbitals are located on the pyran ring and the π bridges, while the LUMO orbitals are located on the π bridges and the cyanoacrylic acid function. The intramolecular charge transfer will therefore take place from the pyran ring to the cyanoacrylic acid function.

3.3. UV-Visible Absorptions

Table 4 groups the electronic transitions, the coefficients of the orbitals, the maximum wavelengths, the absorption energies, and the corresponding oscillator forces. Figure 3 shows the absorption spectra of the six derivatives. The results show that all the compounds studied have two absorption bands. For each of the

compounds, the transition with the longest wavelength has the greatest oscillator strength. All absorption maxima are located in the 495 - 567 nm region. The dyes studied therefore absorb in the visible range, which extends from 400 to 800 nm. The maxima correspond to a transition from the HOMO to the LUMO orbital (H → L). The gas-phase values show that compound C_P has the longest absorption length (λ = 567 nm), while that of compound C is 502 nm. The addition of the phenyl ring induces a bathochromic shift of 65 nm. The addition of iodine results in a weak bathochromic effect of 1 nm. However, the other halogenated compounds exhibit a hypsochromic effect relative to compound C. These results indicate that intramolecular charge transfer will be better in C and C_P compounds. In aqueous phase, wavelengths increase by an average of 60 nm. Compounds C_P and C_I are accompanied by a bathochromic effect of 65 and 2 nm, respectively, compared to compound C. The electronic transition energy of compound C_P is the lowest, followed by that of compound C_I. The general trend is:

$$C_P > C_I > C > C_{Br} > C_{Cl} > C_F.$$

Table 3. HOMO and LUMO orbitals of compounds in the gas phase.

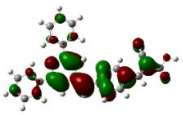
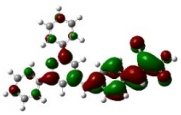
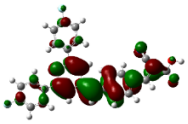
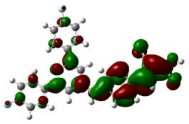
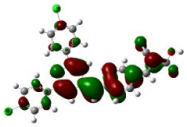
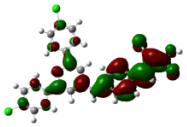
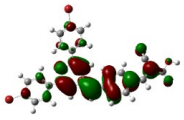
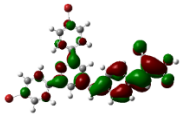
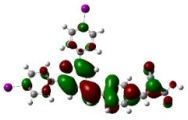
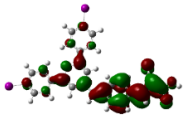
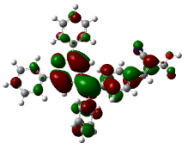
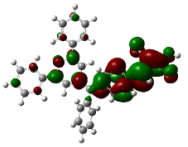
Compounds	HOMO	LUMO
C		
C_F		
C_{Cl}		
C_{Br}		
C_I		
C_P		

Table 4. Transitions, wavelengths, absorption energies, oscillator strengths, and light harvesting efficiency.

Compounds	Transitions	λ (nm)	$\Delta\lambda$ (nm)	ΔE (eV)	f	LHE
Gas-phase						
C	H → L	502	0	2.469	1.252	0.944
C_F	H →L	495	−7	2.506	1.237	0.942
C_{Cl}	H → L	497	−5	2.496	1.280	0.947
C_{Br}	H → L	499	−3	2.483	1.300	0.950
C_I	H →L	503	1	2.467	1.328	0.953
C_P	H → L	567	65	2.188	0.704	0.802
Aqueous-phase						
C	H → L	560	0	2.215	1.513	0.969
C_F	H →L	555	−5	2.234	1.496	0.968
C_{Cl}	H → L	557	−3	2.227	1.530	0.970
C_{Br}	H → L	559	−1	2.218	1.546	0.971
C_I	H →L	562	2	2.207	1.559	0.972
C_P	H → L	625	65	1.984	0.874	0.866

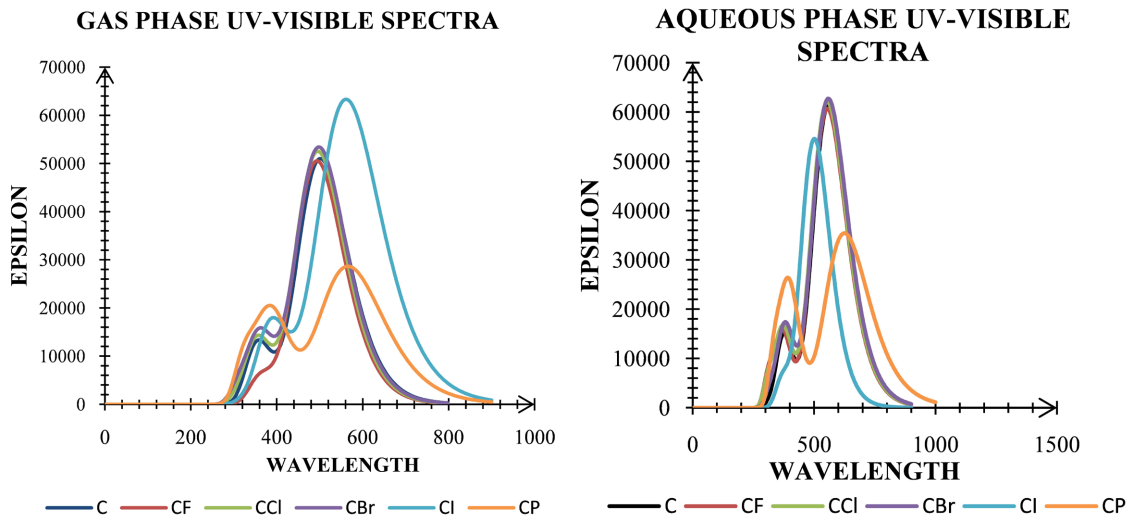


Figure 3. UV-visible absorption spectra of compounds in the gas and aqueous phases.

The photovoltaic properties of dyes can be estimated from their Light Harvesting Efficiency (LHE). LHE of a dye is its ability to absorb solar radiation. The higher the LHE, the more efficient the dye. The LHE values range from 0.802 to 0.953 in the gas phase and from 0.866 to 0.972 in the aqueous phase. These values lead to the following order:

$$C_I > C_{Br} > C_{Cl} > C_F > C > C_p.$$

These results indicate that halogenated compounds have a greater capacity to absorb solar radiation compared to the unsubstituted compound C and the

compound containing the phenyl group C_p. However, light harvesting efficiency increases with the size of the halogen. Thus, compound C_I would absorb solar radiation better compared to the other compounds. This result is consistent with experimental data [13].

4. Conclusions

This work is a theoretical study of the reactivity of some derivatives of methylenepyran used in photovoltaics, using the DFT and TD-DFT methods, associated with the LANL2DZ basis, in the gas and aqueous phases.

The evaluation of the polarity of the different compounds shows that all the compounds are highly polar. The unsubstituted compound C and the compound C_p with the phenyl substituent are the most polar. They are followed by the compound C_I, which is the most polar of the halogenated compounds. Energy gaps (LUMO-HOMO) and UV-Visible absorption spectra reveal good intramolecular charge transfer in C_P and C_I compounds compared to other methylenepyran derivatives. This qualitative comparison of the reactivity of the dyes shows that compound Cp is the most reactive. Light Harvesting Efficiency (LHE) is better for compound C_I.

Compounds C_P and C_I are the best colorants among the six that are the subject of this study.

Author Contributions

Yacouba Bakayoko: Conceptualization, Writing;
Amon Benjamine Assoma: Validation, Writing;
Georges Stéphane Dembélé: Writing;
Mawa Kone: Validation.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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