Photophysical study of the Dibenzylideneacetones and 3-Benzylidenethiochroman-4-ones

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Abstract. In this work, a study of the optical properties of Dibenzylideneacetones (a−c) and 3-Benzylidenethiochroman-4-ones (d−e) is presented. Optical measurements and theoretical approaches are used to establish the contribution of electron donor-acceptor groups in the apparition of fluorescence emission.

Keywords: Dibenzylideneacetones, 3-Dibenzylidenethiochroman-4-ones and fluorescence

1. Introduction

The Benzylideneacetones as part of a broad group of compounds, some of them of natural origin and found in several plant species [1], are of great interest in pharmaceutical and polymers areas [2, 3]. Also, these compounds have optical properties of interest in photonics [4,5]. Recently, it has been demonstrated that 1,3-diketone ligands in complex compounds with lanthanide ions, containing groups of donors and acceptors of electrons, are responsible for the absorption and emission of light in the near infrared (NIR) [6]. Dibenzylideneacetones (DBA) derivatives have been studied for the last two decades in group donors and acceptors of electrons located in the molecule, particularly, due to their large molecular hyperpolarizability, depending on where they are located in the molecule [7]. For this reason, these systems can lead to a wide range of applications in photonics (second harmonic generation (SHG), mixing of frequency, electro-optical modulation and parametric effects among others).

The basic structure of organic materials with nonlinear optical properties (NLO) is based on a set of π bonds and the electronic effect which induce to charge delocalization. A molecular system with high conjugation and appropriate group donors and acceptors of electrons can obtain a great optical response [8]. In this work, group donors and acceptors of electrons attached to both extremes of a molecule such as DBA or 3-Benzylidenethiochroman-4-ones (BTC) are used in forming highly conjugated push-pull systems. The behavior of these groups acts like an on-off switch which activates or not radiative relaxation processes.

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2. Experimental details

DBA (b-c) and BTC (d-e) compounds were obtained by Claisen-Schmidt condensation [9] between the \( p \)-Methoxybenzylideneacetone and Thiochroma-4-one, with the corresponding aldehyde. The DBA (a) was produced commercially by Aldrich Co. The solutions were prepared in CHCl\(_3\) and the concentrations used in the experimental spectra of UV-Visible and Fluorescence emission were between \( 10^{-5} \) M and \( 10^{-4} \) M respectively.

3. Computational details

Quantum chemical calculations were performed by using version 98 of the Gaussian software [10], ArgusLab 4.0.1 [11] and SWIZARD [12]. The molecular geometries were optimized at the level of theory HF using 6-31G(d) basis set. The excitations were calculated at the semi-empirical level of theory via ZINDO/SCI with 10 excited states.

4. Results and discussion

Figures 2–6 show the typical band shifts between both theoretical and experimental spectra. These bands correspond to \( n \rightarrow \pi^* \) and \( \pi \rightarrow \pi^* \) transitions. The width of the bands in the theoretical spectrum was obtained by using the SWIZARD software, pseudo-Voigt shape and width at half-height of
Fig. 4. Absorption spectra for DBA (a).

Fig. 5. Absorption spectra for N(CH₃)₂-BTC (d).

Fig. 6. Absorption spectra for NO₂-BTC (e).

Fig. 7. Fluorescence emission spectra for (b) and (d) compounds.

3000 cm⁻¹. The spectra of fluorescence emission for (b) and (d) compounds are shown in Fig. 7 while the other molecules did not show fluorescence. In Fig. 8 HOMO and LUMO orbitals are represented for structures (a), (b) and (c). These figures show a symmetrical distribution of the LUMO orbital and exhibit a great localization in the carbonyl group and its adjacent regions in compounds (a) and (b). On the other hand, the LUMO orbital is located asymmetrically on one side of the molecule in (c) probably, due to the inductive effect of nitro group. This difference in localization of the LUMO orbital may be related to the changes in the relaxation processes and the emission of fluorescence. The LUMO orbital (d) and (e) shows a similar trend (Fig. 9). The molecule (d) has a great localization of charge on the region of the carbonyl group and its surroundings which exhibit a great radiative emission of photons in comparison with (e). The LUMO orbital (e) is located on one side of the molecule where the group acceptor of electrons is located. To conclude, it is determined that the inductive effect of the nitro group in compounds (c) and (e) acts like an off switch for the fluorescence emission. The Dimethylamine and Methoxy groups in structures (b) and (d), as groups of donors of electrons switching on the fluorescence emission, are probably responsible for activating the radiative relaxation processes (Fig. 7).
Table 1 shows the relationship between the experimental and theoretical parameters accounting only for the structures of fluorescence emission (b) and (d). The quantum yield of fluorescence ($\Phi_{F(X)}$) decreases with the increment of the HOMO-LUMO band gap, decreasing consequently the energy of emission (increase of wavelength $\lambda_F$). In addition to this, the quantum yield of fluorescence increases in as much as the transition dipole moment ($\mu_T$). This suggests an improvement of transition from the ground state to the first excited state, favoring this way the subsequent emission of fluorescence.

Another important aspect of the mechanism of fluorescence is the non-radiative decay from the excited
Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{exc}(nm)</th>
<th>λ_{F}(nm)</th>
<th>Φ_{F/X}</th>
<th>Δ\text{HOMO−LUMO}(kcal/mol)</th>
<th>μ^T(\text{D} \text{eb} \text{ye})</th>
</tr>
</thead>
<tbody>
<tr>
<td>b) CH₃O-DBA-N(CH₃)₂</td>
<td>400</td>
<td>553</td>
<td>0.65</td>
<td>160.08</td>
<td>10.37</td>
</tr>
<tr>
<td>d) N(CH₃)₂BTC</td>
<td>400</td>
<td>560</td>
<td>0.03</td>
<td>166.54</td>
<td>7.41</td>
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Table 2

<table>
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<tr>
<th>Structure</th>
<th>Group</th>
<th>Wave Number(cm⁻¹)</th>
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<tbody>
<tr>
<td>b C=O</td>
<td>1642</td>
<td></td>
</tr>
<tr>
<td>C=C</td>
<td>1600</td>
<td></td>
</tr>
<tr>
<td>C=C(Ar)</td>
<td>1511</td>
<td></td>
</tr>
<tr>
<td>d C=O</td>
<td>1647</td>
<td></td>
</tr>
<tr>
<td>C=C</td>
<td>1608</td>
<td></td>
</tr>
<tr>
<td>C=C(Ar)</td>
<td>1521</td>
<td></td>
</tr>
</tbody>
</table>

5. Conclusions

The presence of the electron donor groups in the structures (b) and (d) leads to a high emission of fluorescence while the presence of an electrons acceptor group as in the structures (c) and (e), disables the channels of radiative relaxation such as the fluorescence emission. The location of the orbitals involved in the electronic transition of a molecular fragment where there is an intense vibrational mode can improve the decay from excited state to ground state through the emission of light. However, it is necessary to extend these studies to corroborate the hypotheses established.

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References


