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Theoretical investigation of the substituent effects on the electronic and optical properties of 6-substituted coumarin derivatives

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HIGHLIGHTS

- Theoretical analysis of 6-substituted coumarins was performed by Gaussian 09.
- Frontier MOs, absorption and emission spectra were analyzed.
- Some 6-substituted coumarins are predicted as luminescence materials.
- 6-substituted coumarins are calculated to be with large Stokes shifts.
- 6-substituted coumarins are potential candidates for multicolor labeling and FACS.

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ABSTRACT

The electronic structures, absorption and emission spectra of selected 6-substituted coumarins were investigated and compared with unsubstituted coumarin by using density functional theory (DFT) and time-dependent DFT (TD-DFT) methods with Gaussian 09 software package.

Results revealed that the presented absorption and emission spectra were affected by the substituent groups apparently. The maximum absorption wavelength of a coumarin molecule can be shifted to a longer one by introducing a large conjugated substituent, an electron donating group or a group which can form a rigid structure with the parent moiety at 6-position. The lowest energy emission of a 6-substituted coumarin can be greatly red-shifted by modifying the substituent to one which can be strongly conjugated with the phenyl ring. A group which has a strongly electron-withdrawing effect may cause a large excitation intensity and a short wavelength in emission. Most selected molecules are predicted to give the lowest-energy emissions in the purple or blue light region, which are supposed to be selected and modified as purple or blue luminescent materials. 6-nitrocoumarin is predicted as an invisible fluorescent material. 6,7-benzocoumarin, which forms a rigid conjugated ring with the parent moiety, is expected to be modified as a green luminescent material. Many of these 6-substituted coumarins are expected to be potential candidates as large Stokes shift dyes for multicolor labeling and fluorescence-activated cell sorting (FACS), especially those molecules, which bear —$CONH_2$, —CN, and —CH_3 respectively.

Introduction

Coumarins, known for their pleasant odor, are widely used in perfumery, foods and beverage manufacture [1–3]. Also coumarin derivatives can be used as intermediates in the manufacture of agrochemicals and pharmaceuticals with strong anti-bacterium, anti-cancer, anti-HIV activities, etc. [4–8].

Moreover, Coumarins are known to be strongly fluorescent with absorption and emission phenomena, and can be used as photoluminescent materials [9–12]. Some substituted derivatives yield intense fluorescence and can be widely used in different branches of chemistry, biology, medicine and physics [13–15]. Additionally, the high thermal- and photo-stabilities make the coumarins promising candidates for optoelectronic applications such as fluorescence probes, memories or switches [16–19].

To determine which coumarin derivative may be the optimal candidate for use as an optoelectronic material, it is necessary to understand the influence of the molecular structures on the electronic and optical properties [20–22].

However, the relationship between structures and optical properties is still a major problem. There are many works reported about the optical properties of the 3-, 7- and 4-substituted coumarins [23–25], but few can be found about the 6-substituted

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coumarins. To this end, we are interested in studying the electronic and optical properties of a series of 6-substituted coumarin molecules with general sketches depicted in Scheme 1. To give a better comparison, the properties of unsubstituented coumarin (**12**) are also described. And the substituent effects on the electronic and optical properties of 6-substituted coumarins are studied consequently.

Computational details

All calculations were performed by using Gaussian 09 program package [26].

The density functional theory (DFT) methods, combining the hybrid exchange–correlation functional Becke-3-Lee–Yang–Parr (B3LYP) with the standard 6-311G+ (d, p) basis set, yield good and consistent results in lots of organic molecular analyses [27–32]. As a result, the singlet ground state (S_0) geometries in their C_1 symmetry were optimized by using DFT at the B3LYP/6-311+G (d, p) level. For each molecule, the geometry optimization is followed by a vibrational spectrum analysis in order to check that all vibrational frequencies are real to ensure a minimum energy structure.

It is found that time-dependent density functional theory (TD-DFT) at the B3LYP/6-311+G (d, p) level correctly reproduced the absorption wavelength and intensity of many organic molecules [33–36]. And as you can see in our previous work, in the case of 6-fluoro coumarin, the calculated absorption and emission spectrum at this level were found to be in good agreement with the experimental values [37].

Following those references, the lowest singlet excited state (S_1) geometries in their C_1 symmetry were optimized by using TD-DFT theory at the B3LYP/6-311+G (d, p) level , and the electronic absorption and emission spectra of 6-substituted coumarins were thereby carried out on the basis of the optimized ground and excited structures, respectively. The data for the longest wavelengths of the absorption and emission transitions were then listed and compared in a spreadsheet. In addition, the assignments of the transitions observed in the calculations were depicted. Finally, the maximum wavelengths of absorption and emission transitions were plotted and compared for each molecule using the origin software program.

Results and discussion

Molecular geometries in ground states

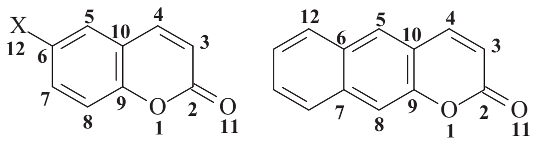
From the calculated results on the optimized geometry parameters of the studied compounds in singlet ground state (S_0), we noticed that most geometrical parameters of these 6-substitued coumarins are close to each others, the main differences arise from the parameters related to those bonds of $C_{\mathbf{6}}{-}X_{\mathbf{12}}$, $C_{\mathbf{2}}{-}O_{\mathbf{1}}$ and $C_{\mathbf{2}}{-}O_{\mathbf{11}}$, on which we will focus our attention. And these differences may be mainly resulted from the electron donating abilities of the substituent groups. Among these substituent groups selected, we can judge from the reaction constants of the substituent groups on phenyl ring that $-NHCH_3$ has the highest overall electron donating ability and $-NO_2$ has the lowest one [38,39]. When the substituent group is $-NHCH_3$, the single bond length of $C_{\mathbf{2}}{-}O_{\mathbf{1}}$ is 1.390 Å, which is much shorter than the one when the substituent group is $-NO_2$ (1.406 Å). And the double bond length of $C_{\mathbf{2}}{-}O_{\mathbf{11}}$ is 1.205 Å when the substituent group is $-NHCH_3$, which is the longest one; while the bond length of $C_{\mathbf{2}}{-}O_{\mathbf{11}}$ become 1.198 Å when the substituent is $-NO_2$, which is the shortest one. This means an electron donating 6-substituted group can result a stronger resonance effect on the coumarin molecule than an electron withdrawing substituent can do. Results also show that the values of bond angles and dihedral angles in the 6-substituted coumarin molecules are not strongly affected by the substituent groups.

Frontier molecular orbital analysis

Molecular orbitals, in particular the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), are important quantities in elucidating both the spectral properties and luminous efficiency. For this reason, molecular orbitals involved in the lowest energy transition of the coumarins plotted by GaussView as well as the energy gap between the HOMO and LOMO (HLG) have been depicted in Table 1. To further study the electronic structure of the studied compounds, we provide the calculated energy level diagram of the frontier MOs for molecules **1**–**16** in Fig. 1.

From the orbital figures in Table 1, we can see that for most of those molecules, the electron distributions of the frontier HOMOs are more extended along the phenyl ring than along the pyran ring, comparing with those of the LUMOs. However, when the substituent is $-NO_2$, it is on the opposite situation. We noticed that in molecule **9**, the electron distribution of the HOMO is delocalized over the entire molecule, whereas the electron density of its LUMO clearly shifts away from the pyran ring onto the phenyl ring. From above we can conclude that when the substituted group on the 6-position is an electron donating group or a relatively weak electron withdrawing one, the electron density of the HOMO would be apparently affected by the group. While when the group is strongly electron withdrawing, the electron density of the LUMO would be greatly affected.

Furthermore, the results of the contour plot depicted in Fig. 1 show that molecules **1**–**5**, **7**, **10** exhibit apparent increase in the energy of HOMOs comparing with molecule **12**; molecules **13**–**16** exhibit small decrease in the energy of HOMOs comparing with **12**. While the changes for those LUMOs comparing with **12** are not so distinctive. On the other hand, one can notice that **9** and **11** show similar decrease in both HOMO and LUMO. Those results are corresponding to the conclusion deduced from Table 1. Therefore, we can give a rough prediction that when the substituted group is an ordinary electron-withdrawing one, the HLG would



1, 2, 4-16 **3**

X= **1**. $NHCH_3$, **2**.NH_2, **4**.OCH_3, **5**.OH, **6**.$NHCOCH_3$, **7**. Ph, **8**. Br, **9**. NO_2, **10**. CH_3, **11**.CN, **12**. H,

13. $CONHCH_3$, **14**. $CONH_2$, **15**. $COOCH_3$, **16**. $COCH_3$

Scheme 1. Sketches of the considered 6-substituted coumarins.