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ABSTRACT

A theoretical calculation of the ground and first excited states of two 7-phenylamino-substituted coumarin compounds are performed. In order to study the effect of phenyl substituted in amino group and fluorine atoms substituted in methyl group, 7-amino-4-methyl coumarin (C120) and 7-amino-4-(trifluoromethyl) coumarin (C151) were also studied. The geometries of the ground state and the first ground state were optimized using density function theory and configuration interaction singles levels of theory. Molecular orbitals (MO) of the ground and first excited states of the four coumarin compounds were obtained to explain the change of the structures. ZINDO and TD-DFT methods with different basis sets were applied to predict the UV absorption spectra. The solvent effect had also been taken into account using self-consistent isodensity polarized continuum model. The predicted spectra are in agreement with the experimental data.

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1. Introduction

Derivatives of 1,2-benzopyrone, commonly known as the coumarin dyes, are the well-known laser dyes for the blue-green region. Among these dyes, coumarins which have different amino groups at 7-position (commonly known as 7-aminocoumarins) are of special significance [1-12]. Because of their widespread occurrence in nature, their medicinal properties, and their use as optical brighteners, coumarins have long occupied the interests of synthetic chemists. In many of these uses it is often advantageous to be able to control the optical properties such as ultraviolet absorption maxima or fluorescence excitation and emission maxima of the dves by suitable alterations in their structures. For example, 7-diethylamino-4-methyl coumarin (C1) is a good photosensitizer because of its absorption in long wavelength area [13]. As electron donors, coumarins, especially 7-amino coumarins can improve sensitizing efficiency of initiating systems by absorbing visible lights. In recent years, they have received increasing attentions because of their applications as laser dyes [14,2,15].

Study of the structure and electronic spectra of 7-amino coumarin compounds by quantum chemical method is very important because these can not only interpret the absorption and emission spectra, but also estimate the direction of the electronic density redistribution of the compounds before and after transition, which are the determining factors of their reactivity and optical activity. Therefore, the electronic structures of some 7-amino coumarin compounds such as 7-amino-4-methyl coumarin (C120), 7-amino-4-(trifluoromethyl) coumarin (C151) and coumarin 153 have been studied by UV spectroscopy, fluorescence and quantum chemical methods [16–20]. However, there are few reports concerning 7-arylamino-substituted coumarins.

In this paper, the properties of the ground and excited states of 7-phenylamino-4-methyl coumarin (PAC) and 7-phenylamino-4-(trifluoromethyl) coumarins (PAFC) are studied by quantum chemical calculation to determine the geometrical structures, molecular orbitals and electronic spectra.

2. Experimental process

In order to get the photosensitizer with absorption maximum about 360 nm, amino group was introduced into the coumarin molecule. The amino-coumarins were synthesized according to Scheme 1.

Amino-phenol (0.1 mol), 0.1 mol acetacetic ether (or triflourin acetacetic ether) and 10.0 g ZnCl₂ were dissolved in 100 ml ethanol. The mixture was refluxed for 12 h, and then cooled at room temperature. The solid was deposited and recrystallized in ethanol. In order to study the properties of amino coumarins, different amino groups were introduced into coumarin structures.

The UV spectra of PAC, PAFC and C151 were measured in acetonitrile solution using 1 cm quartz cell on a Perkin-Elmer Lambda 20 UV-vis spectrophotometer. The concentration of compounds is 4×10^{-5} mol/L. The UV spectra characteristics of C120 were obtained from literature [21].

3. Computational methods

Quantum chemical calculations were carried out using the Gaussian 03 program [22] package. Geometrical optimizations of





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Scheme 1. Synthesis of amino-coumarin.













Fig. 1. The ground state structures of compounds PAC, PAFC, C120 and C151 optimized with B3LYP/6-31G(d) method.

the ground states were done using B3LYP method with 6-31G(d) basis set. The geometries of the first singlet excited state in gas phase were optimized using the configuration interaction singles (CIS) [23] method with 6-31G(d) basis set. On the basis of optimized structures for the ground state, TD-DFT method with 6-31G(d) and 6-31+G(d) basis sets were used to predict the absorption wavelengths. In the TD-DFT calculations the B3LYP functions were used. The solvent effect on spectrum was considered using the SCIPCM model [24]. The solvent used in our calculations was acetonitrile (ACN). In this work the molar extinction coefficient were calculated by the TD-DFT method, which are very helpful in assigning the calculated electronic transitions to experimental absorption spectra.

4. Results and discussion

4.1. Geometries and charges of the ground states

Bond lengths of PAC, PAFC, C120 and C151 are shown in Fig. 1 and the serial numbers of atoms are also indicated. Only one conformation for PAC and PAFC is studied. In PAC and PAFC the torsion angles of C1—C2—N3—C4 are 12.4° and 11.0°, respectively. As shown in Fig. 1, bond lengths of N3—C2 are all about 1.38 Å, which are shorter than the length of a normal N—C single bond (1.47 Å) and longer than the length of a normal N—C double bond (1.30 Å). It indicates that bonds N3—C2 of coumarin compounds have partly the characteristic of double bond. Phenyl substituted in amino group stretches the N3—C2 bond lengths slightly with 0.001–0.002 Å. Fluorine atoms substituted in methyl group stretch the C5—C6 bond lengths with more extent 0.006–0.007 Å because of its stronger electron-attracting effect.

Mulliken charges of coumarins are also obtained, and the charges of atoms N, O and O(C=O) are listed in Table 1. As shown

Fable 1	
Mulliken charges (e) of coumarins obtained by B3LYP/6-31G(d) method	

Violecules	Ν	0	0(C=0)
PAC	-0.799	-0.522	-0.476
PAFC	-0.797	-0.518	-0.464
2120	-0.797	-0.524	-0.478
2151	-0.800	-0.519	-0.464



PAC, LUMO+2, π^*



PAC, HOMO, π



PAFC, LUMO+2, π^*



PAFC, HOMO, π



C120, LUMO+2, π*



С120, НОМО, π



C151, LUMO+2, π *



С151,НОМО, π



PAC, LUMO+1, π^*



PAC, HOMO-1, π



PAFC, LUMO+1, π *



PAFC, HOMO-1, π



C120, LUMO+1, π*



С120, НОМО-1, π



C151, LUMO+1, π *



С151,НОМО-1, π



PAC, LUMO, π*



PAC, HOMO-2, π



PAFC, LUMO, π^*



PAFC, HOMO-2, π



C120, LUMO, π*



C120, HOMO-2, n



C151, LUMO, π *



C151,HOMO-2, n

Fig. 2. The plots of the frontier molecular orbital of compounds PAC, PAFC, C120 and C151obtained by B3LYP/6-31G(d) method.

in Table 1, phenyl substituted in amino group has little effect on nitrogen atoms and oxygen atoms. Fluorine atoms substituted in methyl decrease the negative charges in oxygen atoms. Especially, the negative charges in carbonyl oxygen atoms are decreased evidently. It is also attributed to the electron-attracting effect of fluorine atoms.

4.2. Electronic structures of the ground states

Molecular orbital (MO) calculations were performed on the base of the geometrical structures optimized by B3LYP/6-31G(d) method. Shapes and types of molecular orbitals (MOs) of PAC, PAFC, C120 and C151 were presented in Fig. 2. The lowest unoccupied molecular orbital (LUMO), the second unoccupied molecular orbital (LUMO+1) and the third unoccupied molecular orbital (LUMO+2) of four compounds are π^* -type MO. The highest occupied molecular orbital (HOMO) and the second occupied molecular orbital (HOMO-1) of four compounds and the third occupied molecular orbital (HOMO-2) of PAC and PAFC are π -type MO. The third occupied molecular orbital (HOMO-2) of C151 and C120 are *n*-type MO.

Different orbital energies and HOMO–LUMO energy gaps of the four coumarin compounds are presented in Table 2. As shown in Table 2, phenyl substituted in amino group raise energies of HOMO and HOMO–n (n = 1, 2), and lower energies of LUMO and LUMO+n (n = 1, 2). So the difference of energy between HOMO and LUMO is reduced, and the transition from HOMO to LUMO becomes easier for PAC and PAFC. Fluorine atoms substituted in methyl also makes the transition from HOMO to LUMO easier because the energy gap of PAFC is lower than that of PAC and the energy gap of C151 is lower than that of C120.

Phenyl substituted in amino group make PAC and PAFC have more π and π^* type MOs. LUMO+2 of PAC and HOMO-2 of PAFC are mostly localized on benzene ring. Furthermore, phenyl substituted in amino group activates the whole conjugated system and raises energies of π -orbitals.

4.3. Ionization potential

Ionization potential indicates the ability of losing electron. Table 3 lists the calculated ionization potentials (I_P) of the four coumarins PAC, PAFC, C120 and C151 using B3LYP/6-31G(d) level. In Table 3 there are two parameters including vertical ionization potential (I_{PV}) and adiabatic ionization potential (I_{Pa}). Vertical ionization potential (I_{PV}) denotes the energy difference between cation and molecule on the base of the optimized structure of neutral molecule. Adiabatic ionization potential (I_{Pa}) means the energy difference between molecule and cation on the base of the optimized structures of neutral molecule and cation, respectively. From the data we can see that the vertical ionization potential and adiabatic ionization potential from PAC to C151 is increased in turn, i.e. the ability of losing electron is reduced gradually (PAC < PAFC < C120 < C151). This means PAC and PAFC can act as good electron-donating materials.

 Table 2

 Energies (eV) of frontier molecular orbitals obtained by B3LYP/6-31G(d) method

Orbitals	PAC	PAFC	C120	C151
LUMO+2	-0.218	-0.463	0.479	0.008
LUMO+1	-0.278	-0.515	-0.120	-0.412
LUMO	-1.483	-2.054	-1.372	-1.995
НОМО	-5.414	-5.680	-5.664	-5.997
HOMO-1	-6.454	-6.790	-6.589	-6.907
HOMO-2	-6.924	-7.163	-7.095	-7.544
Energy gap	3.931	3.626	4.292	4.002

4.4. UV absorption spectra

Experimentally, UV absorption spectra of PAC, PAFC and C151 were measured in acetonitrile and the UV absorption spectra of C120 were obtained from literature [21]. In order to find out the method which can predict absorption spectra of coumarins more accurately, the experimental data were compared with the calculated data by ZINDO, TD-B3LYP/6-31G(d) and TD-B3LYP/6-31+G(d) methods. The comparisons of results in gas phase were listed in Table 4 and the peaks with the largest wavelength (λ_{max}) were selected to be compared. There are 10–30 nm differences between the calculated λ_{max} by ZINDO method and the experimentally measured λ_{max} . The predict results using TD-DFT method is more accurate than ZINDO method for PAC and PAFC, but less accurate than ZINDO method for C151 and C120. Furthermore, using dispersion basis set such as 6-31+G(d) can improve the accuracy of the calculations for absorption spectra.

The calculations above-mentioned are all in gas phase, not in solvent. The experimental data are obtained in ACN. So the calculations by TD-DFT in solvent were done using SCIPCM model. The results are also listed in Table 5. As shown in Table 5, the solvent effect induces the red shifts of absorption wavelengths of coumarins and makes the calculated values nearer to the experimental data. For ACN solvent, the maximal absorption wavelengths of PAFC are red-shifted compared with those of PAC which is because that the substitution of hydrogen atoms of the 4-methyl group by fluorine atoms in PAFC has a better electron delocalization than that in PAC. And the maximal absorption wavelengths of PAFC are red-shifted compared with those of C120 and C151 which is because of the substitution of one hydrogen atom in the amino group by one phenyl group in PAC and PAFC.

The average deviations (nm) for four coumarin compounds by five methods are listed in Table 6. It is indicated that TD-B3LYP/ 6-31+G(d) with SCIPCM model is the most accurate method for coumarins in this work.

UV absorption strengths f can be expressed by extinction coefficients ε_{cal} . The extinction coefficients were calculated by the formula [25]:

$$\varepsilon_{\rm cal} = f \times 5.398 \times 10^4 \tag{1}$$

Table 3

Ionization potential (I_p) of compounds PAC, PAFC, C120 and C151 obtained by B3LYP/ 6-31G(d) method

Molecules	$I_{\rm PV}$ (eV)	I _{Pa} (eV)
PAC	6.90	6.84
PAFC	7.17	7.09
C120	7.44	7.22
C151	7.79	7.57

Table 4

Comparison between the experimental and calculated max absorption wavelength (λ_{ab}) and molar extinction coefficients (L/(mol cm)) of PAC, PAFC, C151 and C120 in gas phase^a

Molecules	ZINDO	TD-B3LYP/6-31G(d)	TD-B3LYP/6-31+G(d)	Exp.
PAC	344.48 3.21 × 10 ⁴	344.89 $2.51 imes 10^4$	352.72 2.60×10^4	$360 \\ 2.24 \times 10^4$
PAFC	356.89 $3.33 imes 10^4$	372.19 $2.21 imes 10^4$	384.03 2.22×10^4	$\begin{array}{c} 385\\ 2.08\times10^4 \end{array}$
C120	331.71 2.61 × 10 ⁴	307.97 $1.75 imes 10^4$	313.93 1.88 × 10 ⁴	$\begin{array}{c} 342^{b} \\ 2.53 \times 10^{4} \end{array}$
C151	$\begin{array}{c} 342.45\\ 2.78\times10^4\end{array}$	$\begin{array}{c} 329.20 \\ 1.67 \times 10^4 \end{array}$	$\begin{array}{c} 337.87 \\ 1.74 \times 10^4 \end{array}$	$\begin{array}{c} 367 \\ 1.49 \times 10^4 \end{array}$

^a The italic values are the molar extinction coefficients (ε_{cal}).

^b Ref. [21].

Table 5

Comparison between the experimental and calculated max absorption wavelength (λ_{ab}) and molar extinction coefficients (L/(mol cm)) of PAC, PAFC, C151 and C120 in acetonitrile^a

Molecules	TD-B3LYP/6-31G(d)	TD-B3LYP/6-31+G(d)	Exp.
PAC	356.96	365.03	360
	$2.37 imes 10^4$	$2.47 imes 10^4$	2.24×10^{4}
PAFC	393.73	407.92	385
	$2.05 imes 10^4$	$2.06 imes 10^4$	2.08×10^4
C120	317.94	324.17	340 ^b
	1.69×10^4	$1.82 imes 10^4$	$1.49 imes 10^4$
C151	346.51	357.37	367
	$1.56 imes 10^4$	1.62×10^4	$2.53 imes 10^4$

^a The italic values are the molar extinction coefficients (ε_{cal}).

^b Ref. [21].

Table 6

The average deviations (nm) between the experimental and calculated max absorption wavelength (λ_{ab}) and molar extinction coefficients (L/(mol cm)) for four coumarin compounds by five methods^a

ZINDO in gas phase	TD-B3LYP/ 6-31G(d) in gas phase	TD-B3LYP/ 6-31+G(d) in gas phase	TD-B3LYP/ 6-31G(d) in acetonitrile	TD-B3LYP/ 6-31+G(d) in acetonitrile
19.62 0.90 × 10 ⁴	$\begin{array}{c} 24.94 \\ 0.34 \times 10^4 \end{array}$	$16.36 \\ 0.35 \times 10^4$	$\begin{array}{c} 14.08 \\ 0.27 \times 10^4 \end{array}$	$\begin{array}{c} 13.85 \\ 0.27 \times 10^{4} \end{array}$

^a The italic values are the molar extinction coefficients (ε_{cal}).

Table 7

The calculated and experimental excited energies, transition, composition and assignment of the S1 state for PAC, PAFC, C120 and C151 in acetonitrile at the TD-B3LYP/6-31+G(d) level

Molecules	Excited energy (eV)	Exp.	Transition	Composition	Assignment
PAC	3.40	3.21	$HOMO \rightarrow LUMO$	66 → 67 (88.4%)	$\pi \to \pi^{*}$
PAFC	3.04	3.05	$HOMO \rightarrow LUMO$	78 → 79 (87.1%)	$\pi \rightarrow \pi^{*}$
C120	3.82	3.65	$HOMO \rightarrow LUMO$	46 → 47 (83.9%)	$\pi \rightarrow \pi^{*}$
C151	3.47	3.42	$HOMO \rightarrow LUMO$	58 → 59 (82.4%)	$\pi ightarrow \pi^{*}$

where *f* is the oscillator strength. In Tables 4–6, we list and compare between the calculated and experimental extinction coefficients. From average deviation, we can see TD-B3LYP/6-31+G(d) with SCI-PCM model is also the most accurate method for coumarins to predict the molar extinction coefficients. The average deviation is 0.27×10^4 L/(mol cm).

The max absorption wavelengths correspond to the S1 state. Table 7 lists the calculated and experimental excited energies, transition, composition and assignment of the S1 state. From the results, we can see that the calculated excited energies agree well with the experimental data. For the four compounds, the S1 states are mainly HOMO \rightarrow LUMO transition, and the percentages are 88.4%, 87.1%, 83.9% and 82.4%, respectively. The assignments are all $\pi \rightarrow \pi^*$.

4.5. Geometries and electron distribution of the first excited states S1

The geometries of the first excited state were optimized at the CIS/6-31G(d) level of theory. The optimized geometrical parameters for PAC, PAFC, C120 and C151 are listed in Fig. 3 and the serial numbers of atoms are also indicated. In PAC and PAFC the torsion angles of C1—C2—N3—C4 is 22.2° and 18.1°, respectively, which are all larger than those of the ground states. As shown in Fig. 3, the bond lengths of both of bonds N3—C2 and C5—C6 are shorter than those of the ground states. The lowest singlet transitions for the four coumarins are the transition from the HOMO to LUMO, so the change of bond length can be understood by analyzing the



Fig. 3. The excited state structures of compounds PAC, PAFC, C120 and C151 optimized with CIS/6-31G(d).

HOMO and LUMO orbitals. There is smaller density on the N3—C2 bond for the HOMO, but the electron density for the LUMO increases. So the bond length of N3—C2 decreases. The shorter bonds C5—C6 can also be interpreted in terms of the patterns of HOMO and LUMO.

5. Conclusions

In this work, the structures and electronic spectra of the ground and excited states of coumarins PAC, PAFC, C120 and C151 have been investigated by quantum chemistry methods. Geometrical structures, molecular orbitals, ionization potential, absorption spectra of these coumarin compounds have been discussed.

Because of the effects of phenyl substituted in amino group and fluorine atoms substituted in methyl group, the bonds N3—C2 and C5—C6 are elongated. Besides the structure changes from the ground to the first excited state can be explained using the shapes of HOMO and LUMO orbitals. The substitutions of phenyl group and fluorine atoms reduce the energy gaps between HOMO and LUMO orbitals and make the transition from HOMO to LUMO easier. The calculated results of ionization potentials shows PAC and PAFC can act as good electron-transfer materials.

The UV absorption spectra are calculated using the ZINDO and TD-DFT methods with two different basis sets. The solvent effect has also been taken into account using SCIPCM model. The calculated results using TD-B3LYP/6-31+G(d) methods agree well with the experimental data. The solvent effect makes the absorption spectra red-shifted. For ACN solvent, the maximal absorption wavelengths of PAFC are red-shifted compared with those of PAC which is because that the substitution of hydrogen atoms of the 4-methyl group by fluorine atoms in PAFC has a better electron delocalization than that in PAC. And the maximal absorption wavelengths of PAC and PAFC are red-shifted compared with those of C120 and C151 which is because of the substitution of one hydrogen atom in the amino group by one phenyl group in PAC and PAFC. The calculated excited energies and molar extinction coefficients of max absorption spectra (S1 state) agree with the experimental values.

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