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Quantum chemistry study on nonlinear optical properties of hemicyanine dye derivatives with different electron donor groups

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ABSTRACT

We have designed 9 hemicyanine dye derivatives with different electron donor groups. The geometric structures are optimized by using density functional theory approach at B3LYP/6-31G(d,p) level of theory. The static first hyperpolarizability, absorption spectra and molecular frontier orbital properties of hemicyanine dyes are studied by using second-order Møller–Plesset perturbation theory (MP2) and time-dependent density functional theory (TDDFT) methods, respectively. It is found that the first excited state transition corresponds to charge transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and is responsible for molecular second-order nonlinear optical (NLO) properties. Our results reveal that the static first hyperpolarizability of hemicyanine derivatives has a linear relationship with the HOMO–LUMO energy gap. In addition, we also find the linear effect of charge transfer magnitude Δq on the first hyperpolarizability β. Our study may be helpful to further understand the structure–property relationship of the organic NLO materials.

1. Introduction

In recent years, organic molecules with delocalized π electrons have attracted increasing attention owing to their potential applications in new-generation optical and molecular electronic devices [1]. The delocalized π electrons and the charge transfer between the electron donor and electron acceptor are responsible for the first hyperpolarizability (β). Theoretical prediction of the hyperpolarizability is quite useful both in understanding the relationship between the molecular structure and nonlinear optical (NLO) properties and in providing a guideline to experimentalists for the design and synthesis of organic NLO materials [2–4].

Many works [5–7] have addressed the relationship between the first hyperpolarizability and other parameters including excitation energies, donor–acceptor strengths, external electric field, etc. These relationships are generally complex. On the other hand, the molecular frontier orbitals have much effect on the hyperpolarizability. However, researchers have not made clear the molecular frontier orbitals how to influence the hyperpolarizability in detail. In this work, hemicyanine dye derivatives with different electron donors in gas phase are chosen as prototype systems (see Fig. 1). Hemicyanine dyes which contain electron donors and electron acceptors connected by a large conjugated π bond, are often used to form Langmuir–Blodgett film [8] due to their large β and stable forming film capacity on water surface. Here, the static first hyperpolarizability, absorption spectra and molecular frontier orbital properties of hemicyanine dyes were studied by using second-order Møller–Plesset perturbation theory (MP2) [9] and time-dependent density functional theory (TDDFT) [10] methods, respectively. This study may be helpful to understand the structure–property relationship of the organic NLO materials.

2. Computational methods

In nonlinear optics, the polarization of a molecule by an external radiation field is often approximated as the creation of an induced dipole moment by an external electric field. In the present of external electric field, the molecule dipole can be written as,

$$\mu_i = \mu_i^0 + \alpha_{ij}E_j + \frac{1}{2!}\beta_{ijk}E_jE_k + \frac{1}{3!}\gamma_{ijkl}E_jE_kE_l + \cdots \tag{1}$$

where the subscripts i, j, and k represent component x, y and z of Cartesian coordinate, respectively. μ^0 is the dipole moment in the absence of the applied electric field. α, β, γ are the linear, first and second hyperpolarizability tensors, respectively. Here we use the Einstein's summation convention.

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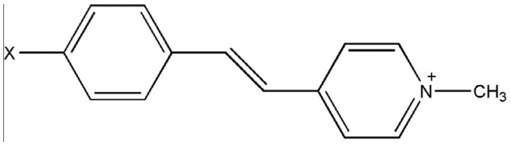

1: X= NO_2 2: X= CN 3: X= Br 4: X= Cl
5: X= H 6: X= CH_3 7: X= OH 8: X= OCH_3
9: X= $N(CH_3)_2$

Fig. 1. Chemical structures of hemicyanine dye derivatives **1**–**9**.

The general quantum chemical methods on calculating molecular first hyperpolarizability include the Sum-Over-State method [11,12] and the Finite-Field method [13]. Here the Finite-Field method is used to calculate the static first hyperpolarizability. In the Finite-Field method the tensor components of β are obtained by the numerical differentiation of the energy or dipole moment with respect to the perturbing electric field. The step size for numerical differentiation is 0.001 atomic unit which has been widely used in many studies [14–17]. The components of β can be calculated by using the following equation,

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji}) \tag{2}$$

where i, j designate different components of x, y or z. The magnitude of the first hyperpolarizability at zero frequency can be calculated by using the x, y and z components of β,

$$\beta = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \tag{3}$$

Before the theoretical calculation of first hyperpolarizablity of selected system, the geometric structures of hemicyanine dye derivatives were optimized by density-functional theory method at B3LYP/6-31G(d,p) level. It is shown that there are no imaginary frequencies in all derivatives. It should be noted that frequency-dispersion effect, solvent effect, electronic correlation effect, and basis set effect are important for the calculation of first hyperpolarizability, which have been discussed in our previous works [18–20]. For clarity, here we only take MP2/6-31+G(d,p) method as an example to shed light on the relationship between molecular frontier orbitals and NLO properties of the studied compounds. All calculations are performed by using Gaussian 09 program [21].

3. Results and discussion

3.1. The absorption spectra and the frontier molecular orbitals

Table 1 lists the electronic absorption spectra of derivatives **1**–**9** calculated by TD-B3LYP approach at 6-31+G(d,p) basis set level. Many previous studies [22–25] have shown the reliability of B3LYP/6-31+G(d,p) method for TD calculation of electronic absorption spectra. From Table 1, we can see that the calculated maximum absorption wavelength λ_{max} of derivative **9** is 476 nm, which is close to the experiment result [26,27]. In addition, we can also find the first excited state transition corresponds to charges transfer from HOMO to LUMO, and the corresponding oscillator strength f is maximal for each molecule studied. Passing from derivative **1** to derivative **9**, the electron-donating ability of the electron donor groups enhances, leading to the maximum absorption wavelength redshift from 390.8 nm to 476.0 nm. In order to illustrate the process of the charge transfer from HOMO to LUMO, we calculate the distributions of electron clouds of HOMO and LUMO of derivatives **1**–**9**, respectively. Fig. 2 shows the frontier molecular orbitals of derivative **9**. From Fig. 2, it can be seen that HOMO mainly localizes in the donor group whereas LUMO in the acceptor group. The results of other derivatives **1**–**8** also have the similar trends. Obviously, the charge transfer from HOMO to LUMO is determined by electron donor and electron acceptor group, which is responsible for the second-order NLO response.

Table 1
The absorption spectra of derivatives **1**–**9** calculated by TD B3LYP/6-31+G(d,p) method.

No.	The first excited state[a]			Other excited states	Exp.
	λ (nm)	f	Orbital components	f	λ_{max} (nm)
1	390.8	0.9684	H → L (92%)	<0.2	
2	410.6	1.0460	H → L (100%)	<0.2	
3	440.5	0.9693	H → L (100%)	<0.3	
4	423.5	1.0169	H → L (100%)	<0.2	
5	400.1	0.7050	H → L (79%)	<0.3	
6	414.0	1.0457	H → L (100%)	<0.2	
7	424.9	1.0660	H → L (100%)	<0.2	
8	436.0	1.1325	H → L (100%)	<0.2	
9	476.0	1.2673	H → L (100%)	<0.2	470[26], 473[27]

[a] λ-excitation wavelength, f-oscillator strength, H → L denotes the excitation from HOMO to LUMO, the percentage values in parentheses denote corresponding frontier orbital component contributions.

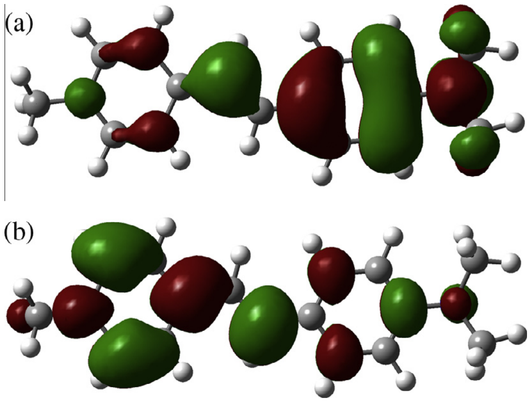

Fig. 2. Molecular frontier orbitals of derivative **9** calculated by B3LYP/6-31+G(d,p) method. (a) HOMO, and (b) LUMO.

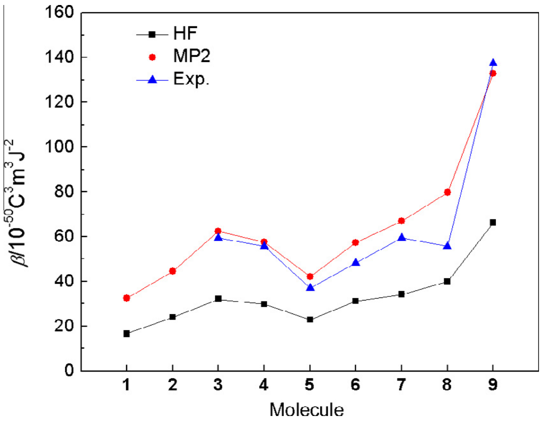

Fig. 3. The HF/6-31+G(d,p) and MP2/6-31+G(d,p) calculated β values for derivatives **1**–**9**, together with available experimental results.