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ARTICLE *in* COMPUTATIONAL AND THEORETICAL CHEMISTRY · SEPTEMBER 2014

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



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ARTICLE INFO

Article history:

Received 8 March 2014

Received in revised form 1 June 2014

Accepted 10 June 2014

Available online 18 June 2014

Keywords:

First hyperpolarizability

Hemicyanine

Absorption spectra

Molecular frontier orbitals

Quantum chemistry calculation

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.

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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,

$$\mu_i = \mu_i^0 + \alpha_{ij}E_j + \frac{1}{2!}\beta_{ijk}E_jE_k + \frac{1}{3!}\gamma_{ijkl}E_jE_kE_l + \dots \quad (1)$$

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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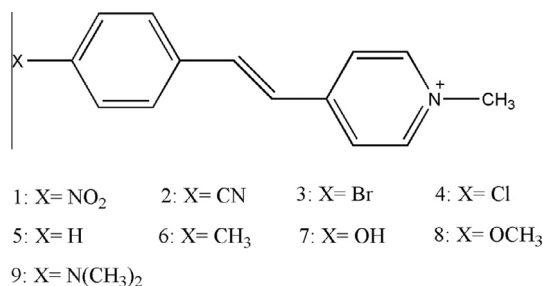


Fig. 1. Chemical structures of hemicyanine dye derivatives 1–9.

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,

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

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 ,

$$\beta = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (3)$$

Before the theoretical calculation of first hyperpolarizability 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

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.

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.

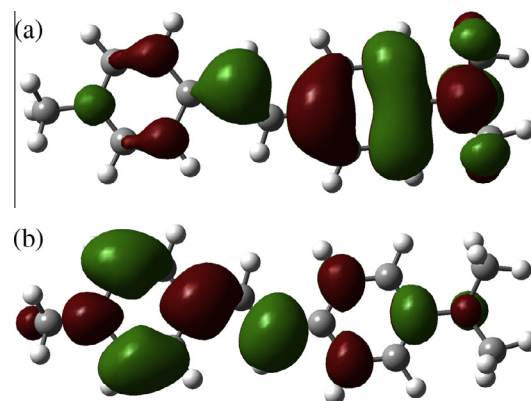


Fig. 2. Molecular frontier orbitals of derivative 9 calculated by B3LYP/6-31+G(d,p) method. (a) HOMO, and (b) LUMO.

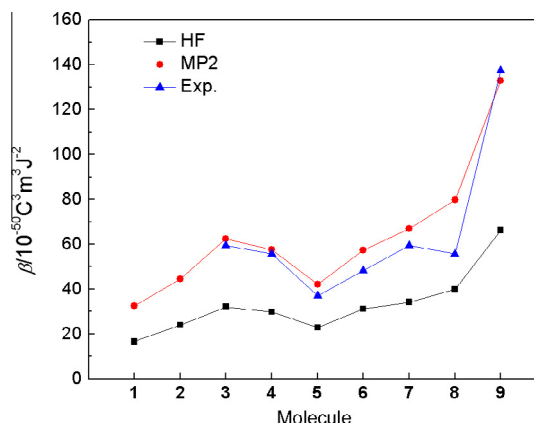


Fig. 3. The HF/6-31+G(d,p) and MP2/6-31+G(d,p) calculated β values for derivatives 1–9, together with available experimental results.

Table 2

The calculated E_{HL} (in 10^{-19} J), β and the largest component β_{xxx} (in 10^{-50} C³ m³ J⁻²) for derivatives **1–9**.

No.	E_{HL}^{a}	$\beta_{\text{xxx}}^{\text{b}}$	β^{b}	$\beta_{\text{exp}}^{\text{c}}$
1	5.27	32.71	32.50	—
2	4.96	44.57	44.40	—
3	4.60	62.79	62.31	59.38
4	4.76	57.92	57.51	55.67
5	5.06	42.69	42.18	37.11
6	4.83	57.75	57.25	48.25
7	4.61	67.67	66.96	59.38
8	4.48	80.66	79.84	55.67
9	3.95	134.93	132.97	137.31

^a Calculated by B3LYP/6-31+G(d,p) level of theory.

^b Calculated by MP2/6-31+G(d,p) level of theory.

^c Experimental results obtained from [26].

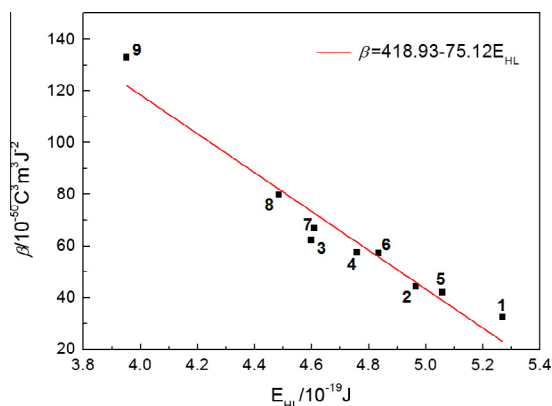


Fig. 4. Linear relationship between MP2/6-31+G(d,p) calculated β and HOMO–LUMO energy gap E_{HL} . The numbers near the data point in figure label the corresponding derivatives.

3.2. The relationship between the first hyperpolarizability and HOMO–LUMO energy gap

In order to validate the accuracy of the Finite-Field method, we calculated the β value of derivatives **1–9** by using the analytic HF method and numerical MP2 calculation at 6-31+G(d,p) basis set, respectively. The results are shown in Fig. 3. We found that HF and MP2 calculated β values show the similar change trends when passing from derivative **1** to derivative **9**. However, for a hemicyanine dye derivative the HF calculated β is much smaller than the MP2 result due to ignoring the effect of electronic correlation in HF calculation. Considering the electronic correlation effect, MP2 calculated β values are in a good agreement with the experimental results. For example, the calculated β value of derivative **9** is 133×10^{-50} C³ m³ J⁻², which is close to the experimental value of 137×10^{-50} C³ m³ J⁻² [27]. In addition, we also found that electron donor group has an important effect on the first hyperpolarizability.

Table 3

The charge q (in 10^{-19} C) of substituents X and the dipole moments μ (in 10^{-30} C m) of the ground and first excited states for derivatives **1–9**, calculated by CIS/6-31G(d,p) method.

No.	1	2	3	4	5	6	7	8	9
X	NO ₂	CN	Br	Cl	H	CH ₃	OH	OCH ₃	N(CH ₃) ₂
q_{g}	−0.8704	−0.3760	0.3616	0.2480	0.3824	0.1344	−0.5280	−0.0096	−0.4256
q_{e}	−0.8768	−0.3280	0.4496	0.3216	0.4112	0.0096	−0.4768	−0.4608	−0.2128
$\Delta q = q_{\text{e}} - q_{\text{g}}$	−0.0064	0.0480	0.088	0.0736	0.0288	0.0512	0.0512	0.0768	0.2128
μ_{g}	77.85	63.82	68.15	57.24	32.84	36.52	39.26	41.80	42.51
μ_{e}	63.78	44.09	46.14	36.28	13.57	15.85	19.39	21.11	11.75
$\Delta\mu = \mu_{\text{e}} - \mu_{\text{g}} $	14.07	19.73	22.01	20.96	19.27	20.67	19.87	20.69	30.76

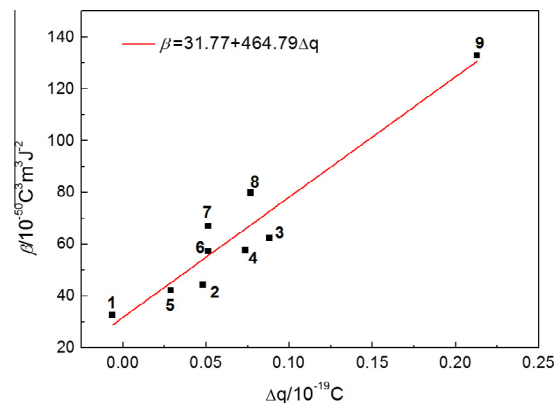


Fig. 5. The dependence of β (calculated by MP2/6-31+G(d,p) method) on Δq (calculated by CIS/6-31G(d,p) method). The numbers near the data point in figure label the corresponding derivatives.

When the electron donor group moves from NO_2 to $\text{N}(\text{CH}_3)_2$, the β value increases by about 4 times.

Table 2 shows calculated HOMO–LUMO energy gap (E_{HL}), β and the largest component β_{xxx} values of derivatives **1–9**, together with the available experimental β values. The dependence of calculated β on E_{HL} are also plotted in Fig. 4. From Fig. 4, it is found that there exists the linear relationship between the calculated β and E_{HL} , respectively. Good linear fitting results (with the regression coefficient $R = 0.97$) show that the static first hyperpolarizabilities increase with the decrease of the HOMO–LUMO energy gap. It should be noted that this linear relationship exists not only in present hemicyanine dye derivatives but also in some other series of π conjugated compounds [28–30].

In order to understand the first hyperpolarizabilities of hemicyanine dye derivatives **1–9**, the charge distribution and charge change from the ground state to the first excited state were calculated by CIS/6-31G(d,p) method. In Table 3, we displayed the net charges q_{g} and q_{e} of donor group X in the ground and first excited states, the ground state dipole moment μ_{g} , the first excited state dipole moment μ_{e} , and the dipole moment difference $\Delta\mu$, respectively. As we known, the magnitude of Δq (i.e., the difference between q_{e} and q_{g}) of substituents X reflects the electron-donating ability of donor groups. Accordingly, from Table 3 we found that the sequence of electron-donating abilities of donor groups is $\text{N}(\text{CH}_3)_2 > \text{Br} > \text{OCH}_3 \approx \text{Cl} > \text{OH} \approx \text{CH}_3 > \text{CN} > \text{H} > \text{NO}_2$. Then we depicted the dependence of MP2 β value on Δq in Fig. 5, and found that there is a linear relationship between β and Δq . In addition, we also found that calculated β value increases linearly with $\Delta\mu$ (see Fig. 6).

A strongly simplified model to describe β is the two-level model (TLM) of Oudar and Chemla [31]. They made the assumption that only one excited state (the intramolecular charge transfer state, generally the lowest energy transition observed in the absorption spectrum) yields the dominant contribution to the static β [32],

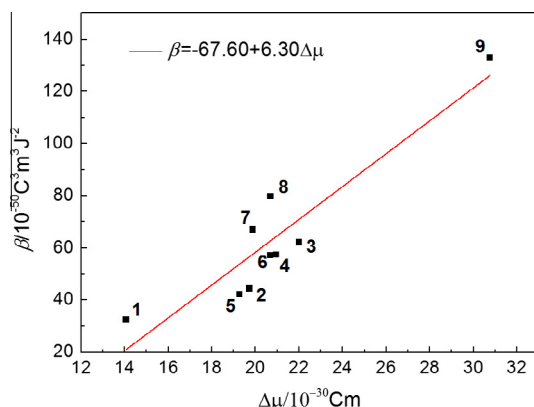


Fig. 6. The dependence of β (calculated by MP2/6-31+G(d,p) method) on $\Delta\mu$ (calculated by CIS/6-31G(d,p) method). The numbers near the data point in figure label the corresponding derivatives.

Table 4

Low-lying excited states calculated by TD B3LYP/6-31+G(d,p) and TLM analysis of β for derivative **9**.

Transitions $S_0 \rightarrow S_i$	$\hbar^2 e^2 f / m_e$ ($10^{-76} \text{ C}^2 \text{ m}^2 \text{ J}$)	$\Delta\mu_{0 \rightarrow i}$ (10^{-30} C m)	$\Delta E_{0 \rightarrow i}$ (10^{-19} J)	β^{TLM} ($10^{-50} \text{ C}^3 \text{ m}^3 \text{ J}^{-2}$)
$S_0 \rightarrow S_1$	3.9704	40.36	4.17	33.21
$S_0 \rightarrow S_2$	0.0323	106.27	5.18	0.37
$S_0 \rightarrow S_3$	0.0166	44.65	5.88	0.05
$S_0 \rightarrow S_4$	0.5831	19.76	6.20	0.73
$S_0 \rightarrow S_5$	0.1053	38.27	6.94	0.18
$S_0 \rightarrow S_6$	0.1078	35.05	7.39	0.14
$S_0 \rightarrow S_7$	0.0069	135.14	7.62	0.03
$S_0 \rightarrow S_8$	0.0088	2.64	7.83	0.00
$S_0 \rightarrow S_9$	0.0022	30.24	8.16	0.00
$S_0 \rightarrow S_{10}$	0.0479	47.05	8.21	0.01

$$\beta^{\text{TLM}} = \frac{3\hbar^2 e^2 f \Delta\mu_{0 \rightarrow i}}{2m_e \Delta E_{0 \rightarrow i}^3} \quad (4)$$

where \hbar is the reduced Planck constant, e and m_e are the charge and mass of the electron, $\Delta E_{0 \rightarrow i}$ is the excitation energy from the ground state S_0 to the charge transfer excited state S_i , f is the corresponding transition oscillator strength, $\Delta\mu_{0 \rightarrow i}$ is the difference of dipole moments between S_0 and S_i .

By using TLM we calculated the β value from the ten transitions between ground state S_0 and low-lying excited states S_i for derivative **9** and the results were displayed in Table 4. We found that the β value of $S_0 \rightarrow S_1$ transition is quite larger than that of $S_0 \rightarrow S_i$ transition ($i = 2-10$). Derivatives **1–8** show the similar results with that of derivative **9**. This confirms that the first excited state dominates the β value for the studied systems, so we can use TLM to semi-quantitatively/quantitatively study β of hemicyanine dye derivatives.

4. Conclusions

In this work, we investigated the first hyperpolarizability, absorption spectra and molecular frontier orbital properties of hemicyanine dye derivatives with different electron donor groups by using quantum chemistry calculations. We found that the charge transfer from HOMO to LUMO is determined by electron donor and electron acceptor group, and the first excited state transition is responsible for the molecular second-order NLO properties of studied hemicyanine dye derivatives. Our results show that there exists a linear relationship between the static first hyperpolarizability and the HOMO–LUMO energy gap for hemicyanine dye

derivatives with the different electron donor groups. In addition, we also found the linear effect of charge transfer magnitude $\Delta\mu$ on the first hyperpolarizability β . Our results may be helpful to understand the structure–optical nonlinearity relationship in organic NLO materials.

Acknowledgements

This work was supported by the Fundamental Research Funds for the Central Universities (CUMT) (Grant No. 2013XK04), and the National Science Foundation of China (Grant Nos. 61372048, 11347123). We are also grateful to the Advanced Analysis and Computation Center of CUMT for the award of CPU hours to accomplish this work.

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