



Computational Study on the Second-Order Nonlinear Optical Properties of Coumarin Derivatives with N-*p*-Vinylphenyl Carbazole Chromophores

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Based on the density functional theory, a computational study was performed to investigate the second-order nonlinear optical properties of ten coumarin derivatives with N-*p*-vinylphenyl carbazole chromophores. All tested derivatives were divided into two groups, one with different substituent groups on carbazole (named as compounds **b1** to **b4**) and the other with the N-*p*-vinylphenyl carbazole substituent modified at different positions on coumarin (named as compounds **a** to **f**). The geometrical structure of these derivatives were first comprehensively optimized through density functional theory method at B3LYP/6-311G level. Then their static second-order nonlinear optical polarizabilities (β) were calculated at the same level and the molecular electric spectrum of each derivative was obtained *via* the time dependent density functional theory (TD-DFT). Computational results show that all these derivatives have large β_{tot} values and excellent transparence. However, as compared to compounds **a-f**, compounds **b1-b4** have longer conjugated bridges and larger β_{tot} values and show better planarity. It suggests that low transition energy, large $\Delta\mu_{\text{eg}}$ values and large charge transfer range play vital roles in the high second-order nonlinear optical response.

Keywords: Coumarin, Carbazole, Density functional theory, Second-order nonlinear optical property.

INTRODUCTION

With the development of laser technology, nonlinear optical materials, as key materials for photonic communication and digital memory, have been extensively applied to industry, national defense, medicine, research, *etc.*^{1,2}. Among them, organic nonlinear optical materials draw much more attentions than those inorganic and arouse extensive interests. Such organic materials were characterized for high first hyperpolarizability values (β), shorter response time, lower dielectric constants, and high photoelectric coefficients. On the other hand, they are more flexible due to their diverse modifiability and variable synthetic strategies³⁻⁵.

Theoretically, if high nonlinear optical responses were achieved, a second-order nonlinear optical molecule should have a large β value. However, for most organic molecules, their nonlinear optical properties are interdependently related with their spectral transmission properties. Molecules with larger β values generally possess longer maximum absorption wavelengths (λ_{max}) and shorter transparence ranges. The design of molecular materials with large β values, blue-shift absor-

ption and high thermo-stability has widely concerned⁶⁻⁸. It was reported that the introduction of heterocycles would significantly enhance nonlinear optical responses but slightly affect the transparence. The mechanism was attributed to the orientation relation between auxiliary donors (electron-excessive heterocyclic bridges) and auxiliary acceptors (electron-deficient heterocyclic bridges), which alternatively lead to the increase of β values.

Benefited from their unique optical characteristics, coumarins have been developed into an important type of nonlinear optical materials. Such organic compounds were characterized by high emissivity, light colour, excellent light transmittance, extended spectral range, high thermo-stability, *etc.*⁹⁻¹¹. In this study, a particular emphasis was devoted to coumarin derivatives modified with N-*p*-vinylphenyl carbazole chromophores. Such chromophores have conjugated rigid plane structures and electron-excessive heterocyclic rings, which could potentially promote the second-order nonlinear optical properties. The objective of this paper was to investigate the likely promotion *via* computations based on DFT and TD-DFT method.

COMPUTATIONAL DETAILS

Design of molecules: Two types of coumarin derivatives with *N-p*-vinylphenyl carbazole chromophores (Fig. 1), one with *N-p*-vinylphenyl carbazole substituent modified at different positions on coumarin (named as compounds **a** to **f**) and the other with different substituent groups on carbazole (named as **b1** to **b4**), were designed in this study. Compounds **a** to **f** were designed to investigate the influences of substituent positions on electron migration and consequential changes in second-order nonlinear optical responses. Compounds **b1** to **b4** were designed to investigate the influences of different substituent groups on the conjugated structure and second-order nonlinear optical properties.

Design of computation: The DFT has become a popular method in calculating molecular properties such as molecular energies, ground state geometries, and optical transitions due to the high accuracy. The best DFT method achieves significantly greater accuracy than Hartree-Fock theory at only a modest increase in cost (far less than MP2 for medium size and larger molecular systems)¹²⁻¹⁴. It does so by including some of the effects of electron correlation much less expensively than traditional correlated methods. The geometries of all designed molecules were optimized by DFT methods at the B3LYP/6-311G level to minimize E. Corresponding parameters like the dipole moment (μ), and the static first hyperpolarizability (β_{tot}) were calculated by the same method.

On the other hand, to obtain the relationship between the electronic structure and second-order nonlinear optical properties of the molecules, the electronic absorption parameters, including wavelengths, oscillator strengths, and main assignment, were systematically investigated by using TD-DFT method on the basis of the optimized ground structures. TD-DFT is one of the most popular methods for the calculation of excitation energies in quantum chemistry due to its efficiency and accuracy. The calculation of the natural bond orbital (NBO)

analysis is performed at the B3LYP/6-311G level. All of the calculations in this work were carried out by using Gaussian 03 program package.

RESULTS AND DISCUSSION

Geometrical structures and charges distributions: Fig. 1 demonstrates the optimized geometrical structures of ten designed molecules in cartesian coordinate system. It is noteworthy that all these structures are nonplanar. The dihedral angle between the carbazole fragment and the styryl fragment, *i.e.* $\angle C10-N9-C12-C13$, ranges from 64° to 68° for compounds **a** to **f** while 49° to 58° for compounds **b1** to **b4**. On the other hand, the large dihedral angles between the styryl fragment and coumarin, *i.e.* $\angle C14-C15-C16-C17$ were only observed for compounds **d** and **e** (30° and 38° , respectively) while other angles were restricted within 4° . As a whole, the structural coplanarity of compounds **b1** to **b4** is relatively better than that of compounds **a** to **f**, which suggests the better conjugacy for compounds **b1** to **b4**. Among all designed molecules, compounds **d** and **e** are considerably poor in both coplanarity and conjugacy. It suggests that either the forms or the positions of substituents would lead to remarkable variation in conjugacy.

Atom charge is different from electron density, so it could not be observed by using quantum mechanics. As an absolute ordain, its results can reflect the static state atom charge distribution in the molecule to a certain extent. For a noncentrosymmetric molecule, the second-order polarizability caused by charge transfer (β_{CT}) of the whole system would generally get enhanced by the strong intramolecular charge transfer (CT). As a result, better nonlinear optical activities could be further achieved. In this paper, each designed molecule was artificially divided into three parts to evaluate the charge distribution, *i.e.* Part I for substituents (carbazole together with its substituents), Part II for styryl, and Part III for coumarin. The ground state charge distributions of all compounds, which obtained *via* natural bond orbital methods, were presented in Table-1. It is

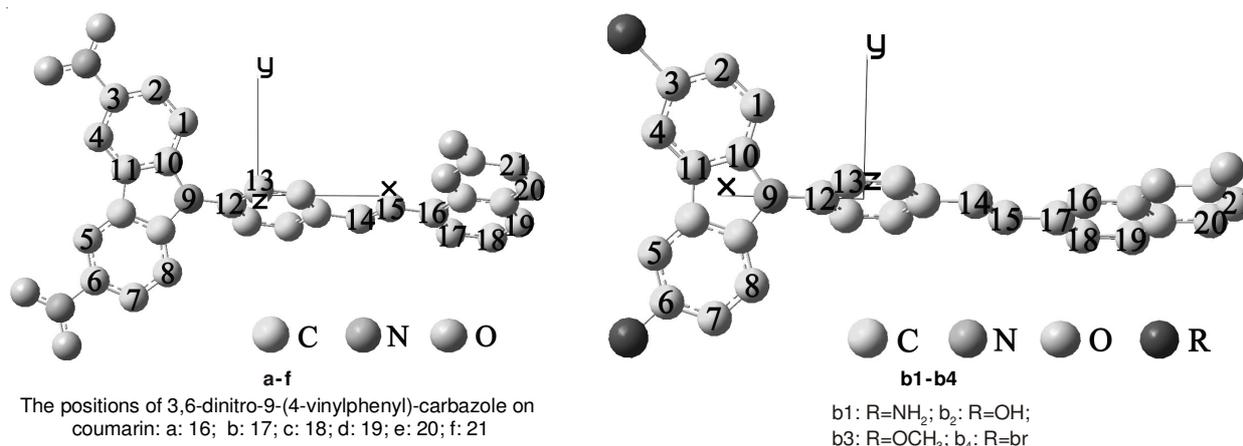


Fig. 1. Optimized geometry structures of the studied molecules at the B3LYP/6-311G level of theory showing the atom labeling scheme and Cartesian axes

TABLE-1
NATURAL BOND ORBITAL (NBO) CHARGE DISTRIBUTION (e) OF EACH PART

Molecule	a	b	c	d	e	f	b1	b2	b3	b4
I	-0.259	-0.247	-0.248	-0.247	-0.237	-0.247	-0.150	-0.183	-0.176	-0.214
II	0.285	0.272	0.249	0.260	0.293	0.289	0.220	0.239	0.235	0.255
III	-0.026	-0.027	-0.002	-0.016	-0.051	-0.042	-0.067	-0.053	-0.056	-0.042
Substituent on carbazole	-0.611	-0.608	-0.608	-0.608	-0.603	-0.611	-0.078	-0.450	-0.446	0.085

obvious that both Part I and Part III of each molecule are negatively charged and serve as electronic acceptors, while Part II are positively charged and serve both bridge and electronic donors. So all designed molecules could be structurally defined as the A- π -D- π -A type. In details, Part I contains much more negative charges than Part III, especially for compounds **a** to **f** which contain double nitril substituents. The substituents on carbazole play vital roles in the charge distribution and their effects could be sorted as nitril > hydroxyl > methoxy > amino > bromine atom.

Dipole moment (μ): For a given molecule, the dipole moment (μ) represents its polarity and has substantial impacts on the second-order nonlinear optical property. The values of μ were generally determined by the strength of donor/acceptor, as well as the entire charge distribution. Calculated values of μ for all designed molecules were listed in Table-2. Our results show that, with the positional variation of 3,6-dinitro-N-*p*-vinylphenyl carbazole substituent on coumarin, the values of μ for compounds **a** to **f** gradually increase following the order of **c**, **d**, **e**, **b**, **f**, to **a**. The fact should be attributed to the increasing difference in the charge distribution between Part I and Part II.

Our results also show that substituents modified on carbazole also exhibit different degrees of influences on μ . For compounds **b** and **b1** to **b4**, the value of μ reaches the largest when carbazole is substituted with nitril (*i.e.* compounds **b**) and decreases following the order of **b1**, **b4**, **b2**, to **b3**. Known as a vector, μ value is equal to the charges of positive center (or negative center) multiplied by the distances between two centers (*i.e.* $\mu = qL$). The distance is almost identical for molecules **b** and **b1** to **b4**, while the charge of Part II (positive center) of molecule **b** is obviously larger than molecules **b1** to **b4**. The value of μ could be modified by adjusting the ability of donor/acceptor.

Second-order nonlinear optical coefficient (β): In this paper, the first hyperpolarizabilities of all molecules were obtained at a static state. Results output from Gaussian03 yields 10 vector components of a $3 \times 3 \times 3$ matrix, including β_{xxx} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} , β_{yyz} , β_{xzz} , β_{yzz} , and β_{zzz} . For compounds **a** to **f**, their β_{xxx} and β_{xyy} components are much larger than the rest. On the other hand, the β_{xxx} components of compounds **b1** to **b4** are much larger than all the others. For all designed molecules, components in the z-axis yield slight contributions to β_{tot} due to the C1 symmetric molecular structure. The maximum value of β (Table-2) are derived in the x-axis. It reveals

that the intramolecular charge transfer mainly occurs in the x-axis and the xy-plane, which is caused by the offset of carbazole from coumarin in the xy-plane. Consequently, the second-order nonlinear optical responses would be much more remarkable in the x/y-axis than in the z-axis.

In Table-2, it was found that β_{tot} value of compounds **b1** to **b4** (ranging from 14 to 71 k) are about ten times higher than those of compounds **a** to **f**. The fact, as we presumed, should be attributed to the strong electron-accepting nitril groups modified on carbazole for compounds **a** to **f**. The molecular structures of all designed molecules, as mentioned before, all belong to the A- π -D- π -A type. At each end of any designed molecule, Part I (carbazole together with its substituents) and Part III (coumarin) act as the electronic acceptors, respectively. Since Part III is common for all designed molecules, the intramolecular charge transfer, to a large content, was thereby mainly determined by the charge distribution of Part I and partially by its position. For compounds **b1** to **b4**, the group of carbazole is modified with electron-donating substituents (amino, hydroxyl, methoxy, and bromine) which lower the electron-accepting capacity of Part I (Table-1). The order of corresponding β_{tot} values, *i.e.* **b1** > **b3** > **b2** > **b4**, is exactly consistent with that of electron-donating capacity as $-\text{NH}_2 > -\text{OCH}_3 > -\text{OH} > -\text{Br}$.

For a given molecule, the relation between its hyperpolarizability and its electronic transition in low-lying excited states could be briefly described by the two-level model as

$$\beta \propto \frac{\Delta\mu_{eg} f_{eg}}{E_{ge}^3} \quad (1)$$

where $\Delta\mu_{eg} = \Delta\mu_e - \Delta\mu_g$ is the change of dipole moment between the ground and excited (charge transfer) state, f_{eg} is the oscillator strength, and E_{ge} is the transition energy^{15,16}. All these factors are strongly correlated and vary with electronic properties of the donor/acceptor and the length of the conjugated bridge. With the aid of Gaussian 03, the electronic spectra of designed molecules were calculated by the TD-DFT method at the B3LYP/6-31G level. Several key characteristics, *e.g.* E_{ge} , the maximum absorption wavelength (λ_{max}), f_{eg} (> 0.1), $\Delta\mu_{eg}$, and the dominant transition, are listed in Table-3. It is noteworthy that, as compared to compounds **a** to **f**, compounds **b1** to **b4** (especially **b1**) all have much larger $\Delta\mu_{eg}$ values while relatively lower E_{ge} values. Following eqn. 1, the compound of **b1** was re-verified with the largest hyperpolarizability. However, it also has the largest λ_{max} (648.78 nm) among all

TABLE-2
MAJOR COMPONENTS OF SECOND-ORDER NONLINEAR OPTICAL COEFFICIENTS β_{tot} (a.u) AND DIPOLE MOMENTS μ (Debye) OF TEN MOLECULES

Molecule	β_{xxx}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	β_{tot}	μ
a	-1043.22	-550.26	-2896.46	861.36	201.70	236.80	42.89	-124.48	-29.70	3922.61	15.37
b	-1445.78	80.64	3147.75	51.02	-213.27	-8.58	11.90	-49.64	114.20	1719.21	10.65
c	-5502.52	-245.88	-3085.44	28.77	-374.92	-2.40	254.11	-29.24	-59.14	8348.90	6.36
d	-1094.00	98.18	-3016.93	-288.81	169.94	388.61	-55.67	3.27	36.38	4213.02	7.26
e	1988.99	223.22	-3192.27	-115.01	-60.27	-74.25	4.87	-21.21	13.48	1207.65	7.66
f	-276.30	343.63	3126.37	-153.18	337.54	-53.93	-134.47	49.91	100.87	2753.22	13.73
b1	70121.27	1016.78	404.10	95.48	967.36	44.99	-5.21	41.94	66.16	70538.77	7.50
b2	30177.33	-330.66	-196.76	-58.55	-334.73	-40.10	-19.44	-46.20	-67.69	29967.62	5.30
b3	-35612.06	-399.18	208.35	-59.18	389.83	38.79	22.02	-44.76	66.24	35388.93	5.17
b4	-14453.28	-21.89	361.35	-53.64	12.49	38.19	8.01	-46.27	71.18	14084.91	5.92

TABLE-3
COMPUTED TRANSITION ENERGY (E_{gc} IN eV), ABSORPTION WAVELENGTHS (λ IN nm), OSCILLATOR STRENGTHS (f_{eg}), $\Delta\mu_{eg}$, AND MAJOR CONTRIBUTIONS OF THE CRUCIAL EXCITED STATES FOR TEN MOLECULES

Molecule	E_{gc} (eV)	λ (nm)	f_{eg}	$\Delta\mu_{eg}$	Major contributions (%)
a	3.251	381.35	0.496	1.132	HOMO \rightarrow LUMO + 1 (63.14)
b	3.250	381.53	1.070	0.9498	HOMO \rightarrow LUMO + 1 (67.83)
c	3.276	378.45	0.329	0.7142	HOMO \rightarrow LUMO + 1 (68.43)
d	3.197	387.80	0.127	1.6196	HOMO \rightarrow LUMO (69.03)
e	3.268	379.39	0.170	2.1239	HOMO \rightarrow LUMO (65.49)
f	3.127	396.51	1.108	0.7923	HOMO \rightarrow LUMO + 1 (68.49)
b1	1.911	648.78	0.298	6.3556	HOMO \rightarrow LUMO (70.57)
	2.957	419.26	0.203		HOMO \rightarrow LUMO + 1 (69.55)
b2	2.374	522.29	0.324	5.5759	HOMO \rightarrow LUMO (70.36)
	3.385	366.31	0.936		HOMO-2 \rightarrow LUMO (52.15)
b3	2.294	540.59	0.323	5.7417	HOMO \rightarrow LUMO (70.39)
	3.323	373.15	0.485		HOMO \rightarrow LUMO + 1 (63.85)
b4	2.839	436.71	0.454	6.5332	HOMO \rightarrow LUMO (70.08)
	3.476	356.72	0.969		HOMO-1 \rightarrow LUMO (69.82)

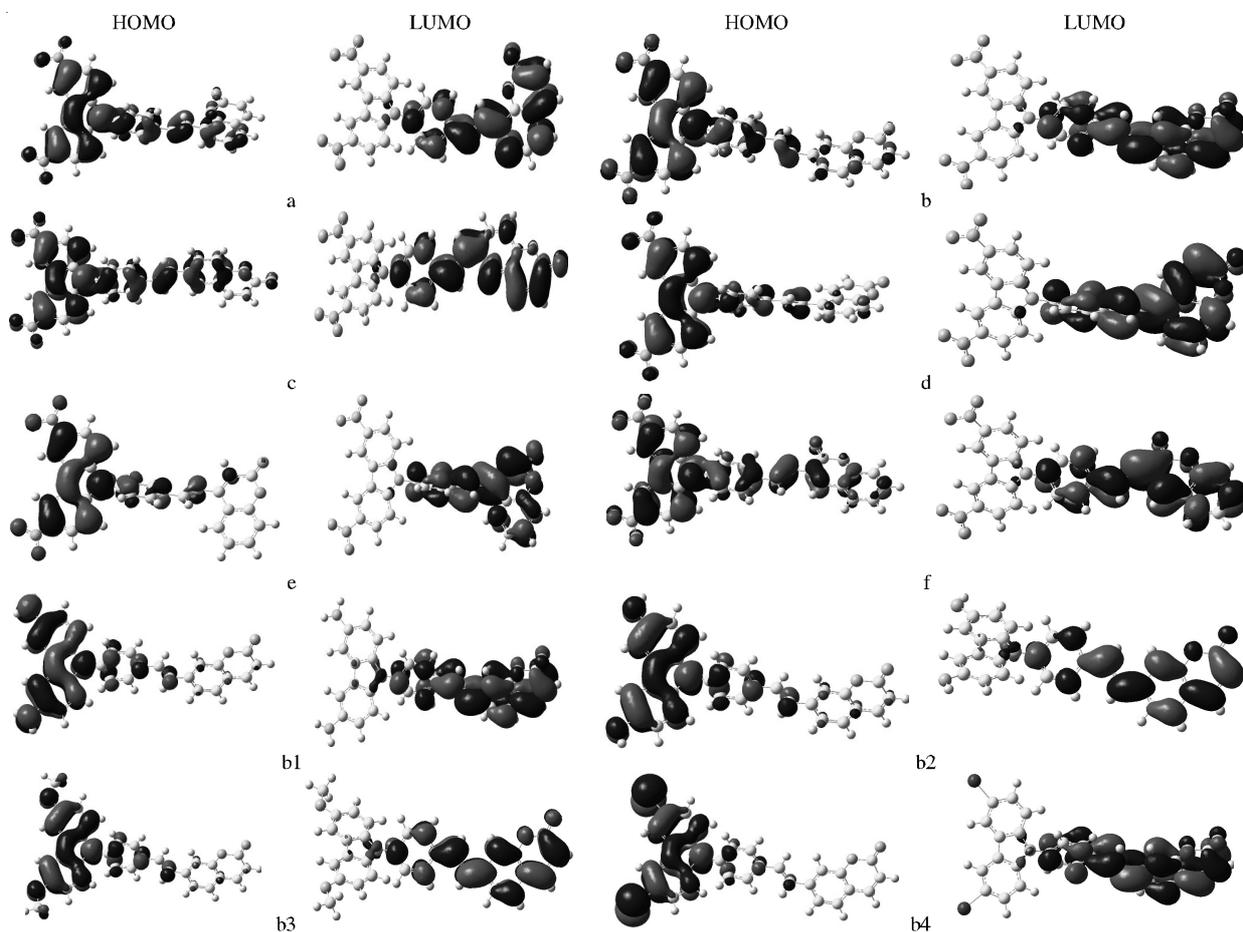


Fig. 2. Frontier molecular orbitals

designed molecules, which indicates poor light transmittance. For all the other molecules, their λ_{max} (350-400 nm) values are restricted within the ultraviolet band and indicate excellent light transmittance.

The frontier molecular orbitals, especially HOMO and LUMO, have determinant influences on the intramolecular charge transfer and corresponding photophysical properties of compounds¹⁷. The TD-DFT calculations show that excited

transitions of all molecules mainly comprise the HOMO \rightarrow LUMO, HOMO \rightarrow LUMO + 1 transitions and also some deeper layer orbitals transitions. As shown in Fig. 2, both HOMO and LUMO are π -orbitals. For all designed molecules, electrons at the LUMOs were densely located on the styryl and coumarin. On the contrary, the distribution of electrons at the HOMOs is quite different: those of compounds a to f are dispersed in almost the whole molecule, while those of com-

pounds **b1** to **b4** are densely concentrated around carbazole and a spot of around the styryl substituent. It is obvious that the charge transfer within compounds **b1** to **b4** mainly occurs from modified carbazole groups to the styryl and then to coumarin. The electron-donating substituents on carbazole of such molecules (**b1** to **b4**) significantly enhanced the CT extent and remarkably promoted the second-order nonlinear optical properties.

Conclusion

Based on DFT method, the second-order nonlinear optical properties and relative parameters of some N-*p*-vinylphenyl carbazole coumarin derivatives were theoretically investigated. The following conclusions are drawn:

- All ten designed molecules could be structurally characterized as the A- π -D- π -A type.
- The substituents on carbazole, as well as the position of carbazole on coumarin, could change the conjugacy of molecules. Better conjugacy was observed for compounds **b1** to **b4**.
- The positional variation of carbazole substituents presents remarkably affects on β_{tot} .
- Compounds **b1** to **b4** have larger β_{tot} values than **a** to **f**. The fact can be explained as an altogether result of their low transition energy, large $\Delta\mu_{\text{eg}}$ values and large CT extent.
- By introduction of electron-donating substituent (*e.g.* NH₂, OH *etc.*) to carbazole, β_{tot} value of the title coumarin is remarkably enhanced. The second-order nonlinear optical properties of them are thereby promoted.

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