Second-order Nonlinear Optical Properties of a Series of Azulene Derivatives

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The first hyperpolarizabilities of a series of novel azulenic-barbituric acid chromophores have been studied by using 12 excitation wavelengths, ranging from 900 to 1907 nm. The dispersion relation of the first hyperpolarizabilities of chromophores holds the same tendency as the experimental results. In addition, the static first hyperpolarizability β_0 of molecules was calculated by means of the Sum-Over-States (SOS) expression and the two-level formula respectively. The results show that these molecules possess large static first hyperpolarizabilities and the β_0 value increases as the donor or acceptor strength enhances; the distorted degree of molecules has also an important influence on the β_0 value.

Keywords   the first hyperpolarizability, azulene derivative, ZINDO-SOS, structure, dispersion

Introduction

Over the past three decades, in nonlinear optical (NLO) phenomena, interest has increased tremendously because of their potential applications in both scientific and technological areas such as photocommunication, phototransformation and photocomputers.[1-6] A major feature of the research into materials capable of doubling the frequency of incident light [second harmonic generation (SHG)], a second order NLO property, is the determination of the first hyperpolarizability β. Organic chromophores with large and stable β are thus very important for the development of NLO devices. It has been shown that a large nonlinearity can be achieved either by employing hetero-aromatic rings in chromophores, whose aromatic stabilization energy is lowered upon charge separation,[7,8] or by using an extended polyene π-bridge system capped by strong electron acceptors and donors.[9] Much effort has been expended into finding the optimum combinations of acceptor and donor groups, such as acceptors nitro, cyano, sulfonyl, polycyanovinyl,[10-12] babituric acid[13] or dianonium salts[14] and donor units[15-17] principally diarylamines, alkoxyaryl groups, ferrocene,[18,19] 1,3-dithionle ring[15-17,20] or the TTF.[21-23] In spite of these different types of chromophores having been used, the development of more efficient donors, acceptors and conjugating moieties still tempts researchers for the NLO compounds.[24,25]

Azulene, a resonance-stabilized nonalternant aromatic hydrocarbon, is both unique and extremely effective as a π-electron donor-acceptor molecule. Azulene and its alkylated derivatives are quite unique in that the disruption of aromaticity on going from the neutral form is counterbalanced by the gain of resonance energy upon formation of the azulecylium carbocation. Therefore, as a consequence of this aromatic stabilization in both neutral and charge-separated forms, azulene and its alkylated derivatives can act as extremely potent electron donors and acceptors. The unique donor property of azulene has been exploited in the synthesis of azulenic retinal analogs which, upon incorporation into bacteriorhodopsin, form artificial bacteriorhodopsin pigments.[26] In this paper, we designed a series of chormophores, based on a babituric acid analog as the acceptor end of a D-π-A chromophore while an azulene analog as the donor end. Their equilibrium geometries, spectroscopies and first hyperpolarizabilities have been studied theoretically.

Methodology

A quantitative description of molecular NLO response is derived from a power series expansion of the molecular polarization upon interaction with an oscillatory external electromagnetic field [Eq. (1)].

$$P_i = \sum_j \alpha_{ij} E_j + \sum_{j \leq k} \beta_{ijk} E_j E_k + \sum_{j \leq k \leq l} \gamma_{ijkl} E_j E_k E_l + \cdots \tag{1}$$

where P_i is the molecular polarization induced along the ith axis, E_j, the jth component of the applied electric field. The coefficient α_{ij} is known as the linear molecular polarizability, and the coefficients β_{ijk} and γ_{ijkl} are termed molecular hyperpolarizabilities.

We used ZINDO-SOS method to gain the nonlinear second-order polarizabilities, which have been tested to be in excellent agreement with the experiment for a variety of molecules. The SOS expression for the individual components of the second-order susceptibility tensor has been given from perturbation theory [Eq. (2)]. [27,28]

$$\beta_{ijk}+\beta_{ikj}=\frac{1}{4\hbar^2}\left\{\sum_{\substack{n\neq n'\\n'\neq g\\n\neq g}}\left[\left(r_{gn'}^j r_{n'n}^i r_{gn}^k+r_{gn'}^k r_{n'n}^i r_{gn}^j\right)\left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}+\omega)}+\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}-\omega)}\right)+\right.$$
$$\left(r_{gn'}^j r_{n'n}^k r_{gn}^i+r_{gn'}^k r_{n'n}^j r_{gn}^i\right)\left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}-2\omega)}+\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}+2\omega)}\right)+$$
$$\left.\left(r_{gn'}^i r_{n'n}^j r_{gn}^k+r_{gn'}^i r_{n'n}^k r_{gn}^j\right)\left(\frac{1}{(\omega_{n'g}-2\omega)(\omega_{ng}-\omega)}+\frac{1}{(\omega_{n'g}+2\omega)(\omega_{ng}+\omega)}\right)\right]+$$
$$4\sum_{n\neq g}\left[r_{gn}^j r_{gn}^k \Delta r_n^i\left(\omega_{ng}^2-4\omega^2\right)+r_{gn}^i\left(r_{gn}^k \Delta r_n^j+r_{gn}^j \Delta r_n^k\right)\left(\omega_{ng}^2+2\omega^2\right)\right]\left(\frac{1}{(\omega_{ng}^2-\omega^2)(\omega_{ng}^2-4\omega^2)}\right)\right\}$$

(2)

where the summations are over the complete sets of eigenstates $|n>$ and $|n'>$ of the unperturbed molecular system. The quantities $r_{gn'}^i$ and $r_{nn'}^i$ are matrix elements of the ith components of the dipole operator between the unperturbed ground and excited states and between the two excited states, respectively; $\Delta r_n^i = r_{nn}^i - r_{gg}^i$ is the difference between the excited-state and ground-state energies. Although all 27 components in the dipolar direction (β_μ) are sampled by electric-field-induced second harmonic generation (EFISH) experiments, β_μ is given by

$$\beta_\mu=\left(\mu_x\beta_x+\mu_y\beta_y+\mu_z\beta_z\right)/\left(\mu_x^2+\mu_y^2+\mu_z^2\right)^{1/2} \quad (3)$$

where

$$\beta_i=\beta_{iii}+1/3\sum_{i\neq j}\left(\beta_{jii}+\beta_{iji}+\beta_{iij}\right)\quad i,j\in(x,y,z) \quad (4)$$

The all-valence ZINDO technique[29] was employed to provide the transition dipole moment and the transition energy needed in the SOS expression [Eq. (2)]. Standard parameters and basis functions were used. The ZINDO-SOS method is of proven reliability in the description of molecular NLO properties.[30,31] The second-order susceptibilities[4,32,33] and the third-order susceptibilities[6,34,35] of dozens of molecules have been reported in our previous work. In the computation, the 197 low-energy transitions were chosen to undergo CI mixing. The 197 states were found sufficient for effective convergence of the SOS procedure.

Results and discussion

Molecular design and structure optimization

Azulene taken as the donor in the conjugated systems was reported recently.[36,37] The results show that azulene can act as extremely potent electron donor. Recently, multi-substituent babituric acid and its derivatives have been studied by our group.[38,39] We discussed the NLO properties of these molecules and made the conclusion that babituric acid can serve as the acceptor in the organic conjugated systems. Herein, we present the combination of babituric acid with azulenylium through a conjugated bridge. The molecular structures of azulene derivatives are shown in Figure 1. Using the AM1 method (included in the Gaussian 98W program), the geometries of azulene derivatives were optimized. Except that the molecule **1** is the planar structure, other molecules all display out of plane distortions in structures. The main bond distances and a few selected bond angles are listed in Table 1 and the corresponding atom labels can be seen in Figure 2.

The bond length alternation (BLA) of the bridge part in molecules has been caculated. The BLA is defined here as the average of the difference in length between adjacent single and double bonds. We took molecules **1** and **2** as examples and compared their bond length alternations. From Figure 2 and Table 1, the following data were obtained. For the molecule **1**, the BLA value is equal to 0.0785 were obtained. In the molecule **2**, the BLA value is 0.0805. The comparison above foretells that the molecule **1** will show larger NLO response than molecule **2**, because the bond alternation of molecule **1** is in the scope corresponding to an optimized bond alternation for enhancement of quadratic and cubic NLO properties.[40] Marder *et al.*[40] considered various do-

nor-acceptor polyenes presenting maximal NLO response for bond alternations. This confirms that the BLA in the molecular structure is an essential parameter determining the NLO response of conjugated organic molecules. The absolute values of the maxima depend on the nature of donor/acceptor pair: in substituted polyenes with weak donors and acceptors, the neutral resonance form dominates the ground state and the molecule has a structure with a distinct alternation in the bond-length between neighboring carbon atoms, *i.e.* a high degree of bond length alternation. The contribution of the charge-separated resonance form to the ground state increases, but BLA decreases, when donor and acceptor substituents become stronger. According to this rule, we can gain the results above.
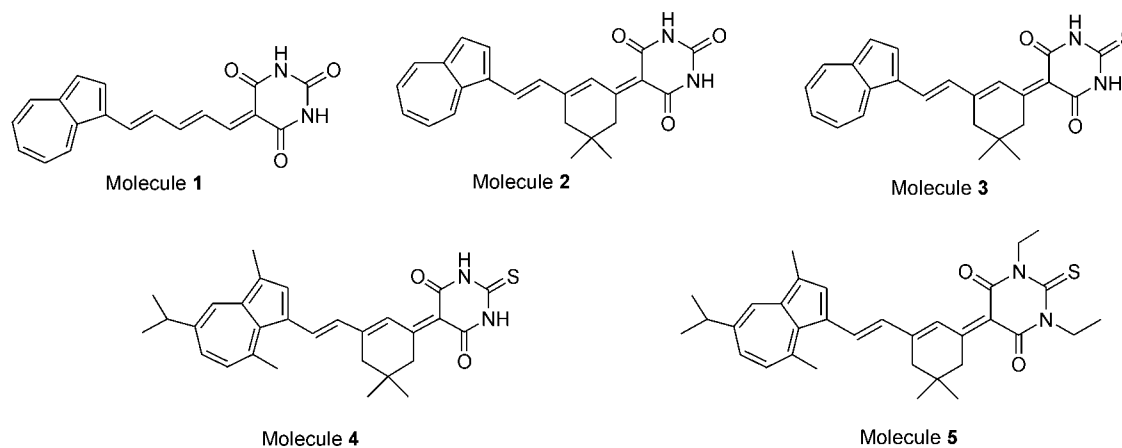

Molecule **1**   Molecule **2**   Molecule **3**

Molecule **4**   Molecule **5**

Figure 1 Molecular structures designed for compounds studied.

Table 1 Geometrical parameters for the compounds **1**—**5** from the equilibrium geometry [bond distance r (nm), bond angle θ (°), dihedral angel D (°)]

Parameter	Molecule **1**	Molecule **2**	Molecule **3**	Molecule **4**	Molecule **5**
$r(1)(2)$	1.4277	1.4543	1.4299	1.4308	1.4314
$r(1)(9)$	1.4008	1.3789	1.3990	1.4057	1.4053
$r(2)(3)$	1.4003	1.4079	1.3983	1.3964	1.3958
$r(3)(10)$	1.4599	1.4503	1.4614	1.4603	1.4606
$r(3)(11)$	1.4285	1.4309	1.4306	1.4358	1.4363
$r(4)(5)$	1.4101	1.4069	1.4114	1.4219	1.4222
$r(4)(10)$	1.3622	1.3642	1.3610	1.3706	1.3703
$r(5)(6)$	1.3652	1.3641	1.3641	1.3608	1.3605
$r(6)(7)$	1.4098	1.4111	1.411	1.4168	1.4171
$r(7)(8)$	1.3644	1.3611	1.3633	1.3679	1.3676
$r(8)(9)$	1.4061	1.4109	1.4073	1.4064	1.4066
$r(9)(10)$	1.4807	1.4799	1.4814	1.4839	1.4840
$r(11)(12)$	1.3520	1.3491	1.3496	1.3484	1.3479
$r(12)(13)$	1.4388	1.4486	1.4482	1.449	1.4497
$r(13)(14)$	1.3538	1.3589	1.3592	1.3586	1.3571
$r(14)(15)$	1.4338	1.4437	1.4432	1.4435	1.4461
$r(15)(16)$	1.3599	1.3738	1.3746	1.3745	1.3715
$r(16)(17)$	1.4839	1.4811	1.4792	1.4792	1.4782
$r(16)(21)$	1.4758	1.4795	1.4775	1.4776	1.4775
$r(17)(18)$	1.3963	1.3998	1.4031	1.4031	1.4109
$r(17)(22)$	1.2451	1.2457	1.2456	1.2456	1.2457
$r(18)(19)$	1.4044	1.4030	1.3941	1.3942	1.4059
$r(19)(20)$	1.4030	1.4018	1.3930	1.3931	1.4034
$r(19)(23)$	1.2485	1.2488	1.5872	1.5871	1.594

Continued

| Parameter	Molecule **1**	Molecule **2**	Molecule **3**	Molecule **4**	Molecule **5**
$r(20)(21)$	1.4007	1.4025	1.4059	1.4059	1.4132
$r(21)(24)$	1.2442	1.2442	1.2441	1.244	1.2442
$\theta(3)(11)(12)$	124.4	124.4	124.1	123.3	123.3
$\theta(10)(3)(11)$	125.0	126.6	124.9	127.6	127.6
$\theta(11)(12)(13)$	122.4	124.6	124.7	124.6	124.5
$\theta(12)(13)(14)$	122.8	119.9	119.9	120.0	120.2
$\theta(13)(14)(15)$	121.5	123.1	123.1	123.0	122.7
$\theta(14)(15)(16)$	127.1	122.9	122.9	122.8	122.4
$\theta(15)(16)(21)$	124.2	122.8	123.0	123.0	122.9
$D(3)(11)(12)(13)$	−179.9	−179.3			
$D(11)(12)(13)(14)$	−179.9	164.8			
$D(12)(13)(14)(15)$	−179.9	−176.5			
$D(13)(14)(15)(16)$	179.9	167.9			
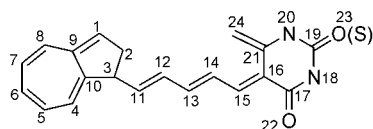
Figure 2   Atom labeling scheme for molecules studied in this paper.

Electronic spectra

Using the ZINDO/ SCI method, the electronic spectra of azulene derivatives were calculated. The calculated wavelength, oscillator strength and transition nature of the UV absorptions for molecules **1**—**5** are listed in Table 2 and the corresponding experimental values are given in parentheses for comparison. The calculations are in good agreement with the experiments. As can be seen in Table 2, from molecules **1**, **2** to molecules **3**, **4** and **5**, the O element in babituric acid is replaced by the S element, and the important excited state-the S_2 excited state turns into the S_3 excited state. In order to explore the source of the changing, the frontier orbital of molecules **2** and **3** (shown in Figure 3) is analyzed.

For molecule **2**, the second excited state comes from the electron transition from HOMO to LUMO. Figure 3 shows that the electron cloud on the HOMO concentrates on the azulene part, however, the electron cloud on the LUMO mainly concentrates on the conjugated bridge and the azulene part. Thus, the dominating charge-transfer takes place in the conjugated bridge and the azulene part. The same analytical method was used to deal with the molecule **3**. The third excited state of molecule **3** comes from the mixing of electron transition from HOMO-1 to LUMO and HOMO to LUMO. The charge-transfer chiefly takes place between the babituric part and the conjugated bridge. In a word, the difference of the charge-transfer orientation results in the changing of the important excited state. We chose molecule **5** as an example to have a look at the whole spectroscopy (shown in Figure 4).

The first hyperpolarizability

On the basis of the correct electronic spectra, we proceeded to calculate the nonlinear first hyperpolarizabilities β_μ (in following is called β for short) of molecules **1**—**5** by using the SOS method.

Table 2   UV-vis spectra of molecules

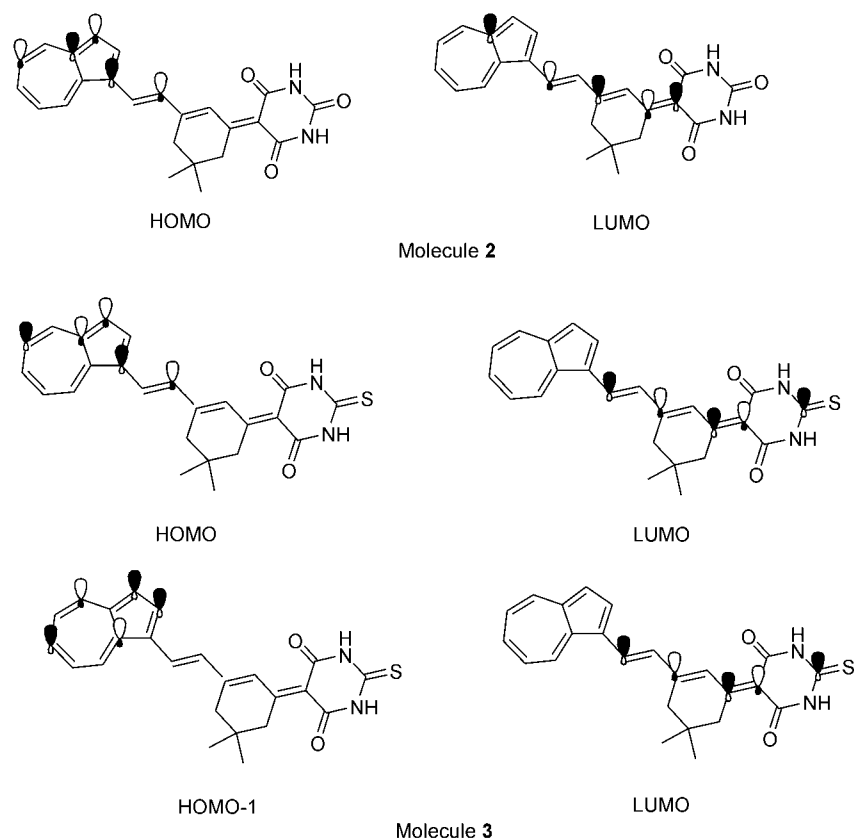| Molecule	λ /nm	f	Transition nature	Configurations and weight
1	669.1	0.77392	$S_0 \rightarrow S_2$	(HOMO,0)$\rightarrow$(LUMO,0) 64%
2	660.1	0.75290	$S_0 \rightarrow S_2$	(HOMO,0)$\rightarrow$(LUMO,0) 65%
3	669.1	0.69994	$S_0 \rightarrow S_3$	(HOMO,0)$\rightarrow$(LUMO,0) 53% (HOMO-1,0)$\rightarrow$(LUMO,0) 10%
4	671.7	0.65995	$S_0 \rightarrow S_3$	(HOMO,0)$\rightarrow$(LUMO,0) 43% (HOMO-1,0)$\rightarrow$(LUMO,0) 15%
5	654.2 (656)[37]	0.65854	$S_0 \rightarrow S_3$	(HOMO,0)$\rightarrow$(LUMO,0) 40% (HOMO-1,0)$\rightarrow$(LUMO,0) 15% (HOMO,0)$\rightarrow$(LUMO+2,0) 10%

HOMO   LUMO

Molecule **2**

HOMO   LUMO

HOMO-1   LUMO

Molecule **3**

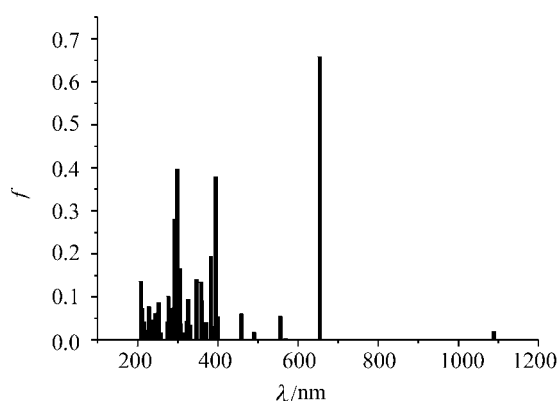**Figure 3** Partial frontier orbital of the HOMO-1, HOMO and LUMO for molecules **2** and **3**.

Figure 4 Spectroscopy of molecule **5**.

In the SOS expression [Eq. (2)] for β, the summation is over the complete sets of eigen states $|n>$, $|n'>$ of the unperturbed system. They have to be truncated in the practical calculation[4,41] for feasibility. In Eq. (2), the denominator of each term includes ω_{ng}, $\omega_{n'g}$. When n and n' increase, the energy differences between the ground state and the excited states will increase, *i.e.*, the denominator will increase more and more. This means the contribution for β will become less important when n and n' each a certain value. How many excited states should be taken actually? It depends on the different molecules. In the ZINDO/CI calculation, we took 14 occupied and 14 virtual orbitals and gained 197 con-

figurations including the ground state. We calculated the values of β for every number of exited states from 1 to 197 and plotted β against number N of excited singlets for all compounds. We took chormophore **1** as an example (shown in Figure 5). It is clear from Figure 5 that β converges when N equals to 40 for molecule **1**. As can be seen in Figure 5, the S_2 excited state is the most important one that significantly contributes to the first hyperpolarizability. The same method is applied to confirm the most important excited state of other molecules. Similar convergence trends were also obtained for the other molecules we studied.
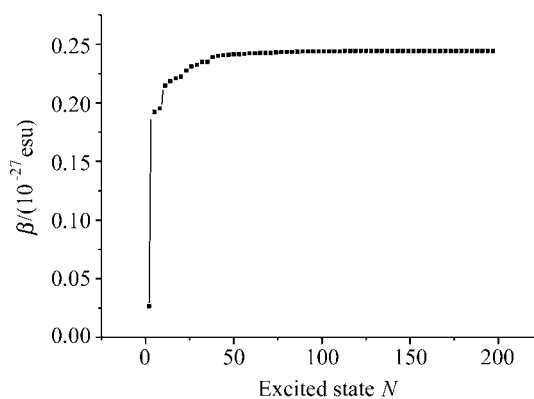

Figure 5 Relationship between β and number N of excited singlets for molecule **1**.

The first hyperpolarizability

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The calculated first hyperpolarizabilities of the molecules **1**—**5** are listed in Table 3 (λ＝1440 nm) and the corresponding experimental value is given in parentheses as comparison, which shows a good agreement between the calculation and experiment. From Table 3 it can be seen that from the molecule **1** to the molecule **2**, the β values decrease. As can be seen in Figure 1, on the basis of the molecule **1**, a 6-membered ring is added to the molecule **2**. As a consequence, the molecular plane takes distortion. The molecule **1** is planar, while the molecule 6-membered ring weakens the degree of planarity and the electron delocalization efficiency of the π-configuration system. The reason for this to allow the babituric acid part to bend down below the plane in order to reduce the repulsive interaction between it and the hexatomic ring part. The distorted structure results in the reduced conjugated degree, baffles the intermolecular charge transfer and decreases the β value. This result is in good agreement with foregoing forecasts in the *"Molecular design and structure optimization"* part. It is well known that in addition to optimizing the molecular β value in the design and synthesis of NLO chromophores, attention must also be paid to their thermal stability so that they will survive material processing and device fabrication.[42,43] Incorporating a 6-membered ring to the triene is to provide the configuration-locked geometry of *trans*-triene and prevent the thermally induced *cis-trans* isomerization process.[44,45] In Ref. 46, the reverse conclusion was made. The difference is resulted from the distinctness of ending groups: in this paper, the ending group-babituric acid connects with one double bond, which is prone to undergo distortion. Incorporating a 6-membered ring to the molecule makes the planar distortion. Nevertheless, it is thiophene analog linking with a single bond in Ref. 46 which has a well property of coplanarity. Incorporating a 6-membered ring to lock the *trans*-triene significantly improves the degree of planarity and the electron delocalization efficiency of the π-configuration system. Because the acceptor strength of molecule **3** is stronger than that of molecule **2**, the intermolecular charge transfer is increased and the β value is enhanced. The difference between the molecule **3** and the molecule **4** is that the azulene part becomes the multi-substituent azulene. CH_3 and C_3H_7 possess the push electron property and increase electron cloud density on the azulene. As a result, the donor strength of the azulene is enhanced and the β value is increased. We used C_2H_5 to substitute H on the N atom of the molecule **4** and it forms the molecule **5**. C_2H_5 possesses the push electron property and increases electron cloud density on the babituric acid ring. As a consequence, the accepting-electron ability of babituric acid is weakened and the β value is reduced.

In 1975 Oudar[1,47] developed the famous two-level approximation as shown bellow

$$\beta_\mu = \frac{3e^2\hbar^2}{2m} \frac{Wf\Delta\mu}{\left[W^2 - (2\hbar\omega)^2\right]\left[W^2 - (\hbar\omega)^2\right]} \tag{5}$$

Table 3 Values of β_μ and β_0 by the two ways

	β_μ (λ＝1440 nm) (10^{-28} esu)	β_0 Values obtained by SOS (10^{-28} esu)	β_0 Values obtained by Eq. (7) (10^{-28} esu)
Molecule **1**	15.438	2.446	1.651
Molecule **2**	12.336	2.288	1.555
Molecule **3**	17.576	2.930	1.880
Molecule **4**	19.000	2.991	1.928
Molecule **5**	11.967(13.091)[48]	2.534	1.657

where ω is the frequency of the laser field; $W = \hbar\omega_{ng}$ the transition energy from ground state to specific excited state, f the oscillator strength of the transition, and $\Delta\mu$ the difference of dipole moments between the excited state and ground state. Assuming

$$\beta_0 = \frac{3e^2\hbar^2 f\Delta\mu}{2mW^3} \tag{6}$$

which is the static (or intrinsic) first hyperpolarizability, then we have the following result:

$$\beta_\mu = \frac{\beta_0 W^4}{\left[W^2 - (2\hbar\omega)^2\right]\left[W^2 - (\hbar\omega)^2\right]} \tag{7}$$

From Eq. (5), it can be seen that the external field has no influence on β_0 value, which can reflect the molecular intrinsic properties. In this paper, we have obtained the value of β_0 by using the Eq. (7) (shown in Table 3). We can also gain the β_0 value by the SOS formula combined with Eqs. (2) and (3) as long as we make the value of ω to be zero (shown in Table 3). The β_μ value we used in Eq. 7 is the one when the frequency of external field ω is equal to 1440 nm. Comparing the values of β_0 by the two ways, it can be foun that there is difference between the β_0 by the two ways, but the trend is the same. The existing difference is understandable because the two-level formula only considers one important excited state and the ground state, so it is approximate. But from the data in Table 3, it can be found that the difference between the β_0 values by the two ways is not crucial. From the above result it is suggested that the two-level formula is a kind of reliable approximation. According to the two-level formula, the relatives between molecular β and the details of the most important excited state's charge-transfer can be described as

$$\beta \propto \Delta\mu_{eg} f / W^3 \tag{8}$$

where $\Delta\mu_{eg} = \mu_e - \mu_g$ is the difference of dipole moments between ground state and the excited state, W the transition energy, and f oscillator strength. While $\Delta\mu_{eg}$ is correlated with the charge transfer (Δq), so the influence of substitution effects on β can be analyzed

from the calculation of the charge transfer between the ground state and the most important excited state.

　　We should specify the most important excited state through the figure of β versus N, for the molecules **1**—**5**, the most important excited states are 2, 2, 3, 3, 3 states respectively, which can also learned from Table 2. Hence, we only studied the most important excited states of molecules **1** and **2**. Figure 6 shows the detailed account of the charge distribution. For the molecules **1** and **2**, the charge on the azulene part of the ground state is －0.159, －0.169, respectively. This indicates the azulene part acts as the acceptor in the ground state. However, the azulene part acts as the donor in the excited state because the charge on the azulene part of the excited state is 0.107, 0.060 respectively. Such result is related to the donor-acceptor property of the azulece part. For the babituric acid part, not only in the ground state but also in the excited state, it serves as the acceptor. For the molecule **1**, the charge transfer on the azulene part between the ground state and the important excited state is [0.107－(－0.159)]＝0.266 while for the molecule **2** that is [0.060－(－0.169)]＝0.229＜0.266. From the relationship above, one can infer that the first hyperpolarizability β of the molecule **1** is larger than that of the molecule **2**. Analyzing the babituric acid part, we can draw the same conclusion. This conclusion is in good agreement with the foregoing calculated results.
By means of the SOS expression, we calculated the first hyperpolarizabilities of molecules **1**—**5** using 12 excitation wavelengths, ranging from 900 to 1907 nm and

protracted dispersion curves of molecules. The curves are shown in Figure 7. The β value is related to the frequency of the external field, and this relationship is called dispersion relationship. The value of β enhances as the frequency of the external field ω increases. When the ω value reaches a certain resonance frequency, the β value becomes very large. The resonance frequency is that when ω (or 2ω) is equal to ω_{ng}, the denominator will appear zero and so the β value will become infinite. When the ω value exceeds the resonance frequency, the β value will decrease as the ω value increases. In Ref. 48, the dispersion curve of the molecule **5** has been studied, and our result is basically coincided with the experiment result. When the relationship between the molecular structure and the β value was studied, we did not include damping factor in the calculation. This makes the β value approach infinity on resonance frequency. But the theoretical calculation is valid on the off-resonance region, and forexample at 1440 nm, $\hbar\omega$ is 0.86 eV, corresponding 6944 cm^{-1}, which is on the off-resonance region.

Conclusions

　　In this paper, five azulenic-barbituric molecules with and without a configuration-locked trans-triene bridge for enhanced thermal stability have been designed. ZINDO calculations were carried out to investigate the geometries, electronic structures, UV-vis spectra and
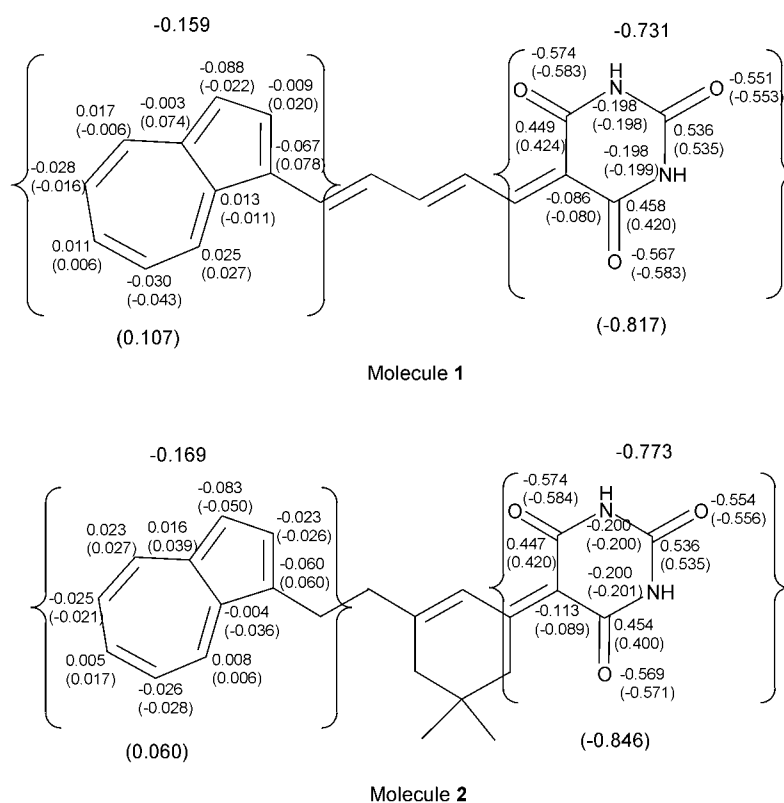

Figure 6　Ground and excited state (shown in the parenthesis) charge distributions of molecules **1** and **2**.
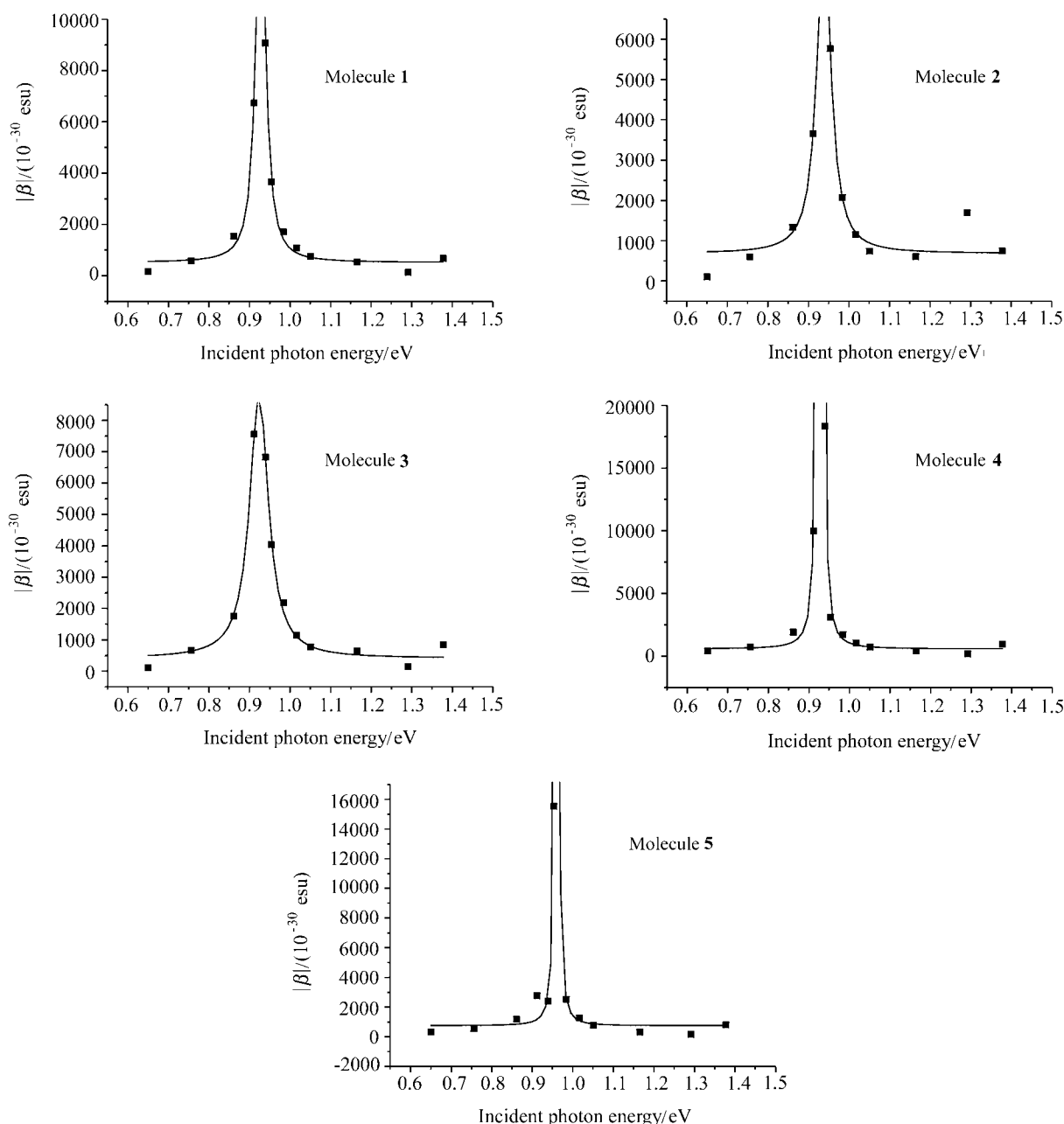
Figure 7 Dispersion curves of molecules **1**—**5**.

charge-transfer interactions and to evaluate the first hyperpolarizabilities for these molecules. The caculated values of β are largish (228×10^{-30}—299×10^{-30} esu), the β_0 value increases as the donor or acceptor strength enhances, and the distorted degree of molecules has also an important influence on the β_0 value. The dispersion relationship of molecules has the same trend as the experimental result. That is, the azulenic-barbituric molecules are promising candidates for the second-order NLO materials.

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