Articles

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

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The second-order nonlinear optical (NLO) properties of a series of benzothiazole derivatives were studied by use of the ZINDO-SOS method. These chromophores are formed by a donor-π-bridge-acceptor system, based on a nitro group connected with benzothiazole as the acceptor and a hydroxyl-functional amino group as the donor. For the purpose of comparison, we also designed molecules in which nitrobenzene is an acceptor. The calculation results indicate that benzothiazole derivatives exhibit larger second-order polarizabilities than nitrobenzene derivatives. In order to clarify the origin of the NLO response of these chromophores, their electron properties were investigated as well. The benzothiazole derivatives are good candidates for application in electro-optical device due to their high optical nonlinearities, good thermal and photonic stability.

Keywords   second-order nonlinear polarizability, benzothiazole derivatives, ZINDO-SOS

Introduction

Studies on materials with nonlinear optical (NLO) properties are of continuous interest[1-9] in modern science, and the design of new chromophores possessing large molecular second-order optical nonlinearity has been carried out for a long time. NLO effects are useful in manipulating the fundamental properties of laser light beams, such as in frequency doubling or tripling [second or third harmonic generation (SHG/THG)]. Besides extensive application for SHG and THG in high-power laser systems, NLO materials are of great importance to optoelectronic and photonic technologies relevant to applications such as optical computing. The D-π-A system is a major focus, and a variety of such compounds have been designed and synthesized with different acceptors (such as nitro, cyano, sulfonyl, polycyanovinyl,[10-12] babituric acid[13] and dianonium salts[14]) and donors[15-17] (principally diarylamines, alkoxyaryl groups, ferrocene,[18,19] 1,3-dithionle ring[15-17,20] and TTF[21-23]) separated by a π-conjugated linker. In spite of these different types of chromophores used, the development of more efficient donors, acceptors and conjugating moieties still tempts researchers for the NLO compounds.[24,25] Recently, we have synthesized a series of chormophores, based on a nitro group connected with benzothiazole as the acceptor and a hydroxyl-functional amino group as the donor in a donor-π bridge-acceptor chromophore. Experiments have demonstrated that the polymers of these chromophores have specific chemical stability, high solubility in aprotic polar solvents and high glass transition temperature. The NLO stability of these polyamides was also studied through the UV-visible spectra of their poled films (830 nm).[26]

In this paper, a series of chromophores with different donors, acceptors and structures was designed, and their equilibrium geometries, spectroscopies and first hyperpolarizabilities (β) were investigated theoretically.

Methodology

At the molecular level, NLO phenomena arise from subtle interactions between polarizable electrons within a material and the very strong electric field of a laser light beam. The resultant induced polarization response (P) of a molecule can be expressed as a power series in the applied field (E) according to the expression given in Eq. (1)

$$P_i = \sum_j \alpha_{ij} E_j + \sum_{jk} \beta_{ijk} E_j E_k + \sum_{jkl} \gamma_{ijkl} E_j E_k E_l + \cdots \quad (1)$$

With normal values of E, the quadratic and cubic terms in Eq. (1) can be neglected, and only linear optical behavior is observed. The coefficient α_{ij} is known as the *linear molecular polarizability* and is related to the refractive index of the material. However, under conditions where E approaches the magnitude of atomic field strengths, such as in a laser

beam, the $\sum \beta_{ijk}E_jE_k$ and $\sum \gamma_{ijkl}E_jE_kE_l$ terms in Eq. (1) become important and give rise to quadratic (second-order) and cubic (third-order) NLO effects, respectively. The coefficients β_{ijk} and γ_{ijkl} are termed molecular first and second hyperpolarizabilities, respectively.

In this calculation, we use INDO/2 (included in ZINDO) to optimize the geometry structure of the molecules; ZINDO is regarded as the effective method to calculate the UV-vis spectra. There are several approaches to calculate β,

such as coupled Hartree-Fock,[27] derivative Hartree-Fock[28] and correlated wave[29] *ab initio* procedures. But these methods can only be applied to limited size molecules now. The semiemperical calculation method——ZINDO has successfully handled large molecular systems with satisfactory accuracy.[19,30] We used ZINDO-SOS (which is shown below) method to obtain the nonlinear second-order polarizabilities, which have been demonstrated, to be in excellent agreement with the experiment for a variety of molecules.[31-35]

$$
\beta_{ijk} + \beta_{ikj} = \frac{1}{4\hbar^2} \left\{ \sum_{\substack{n,n' \\ n' \neq g \\ n \neq g}} \left[\begin{array}{l} (r^j_{gn'}r^i_{n'n}r^k_{gn} + r^k_{gn'}r^i_{n'n}r^j_{gn}) \times \left(\dfrac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \dfrac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)} \right) + \\[2ex] (r^i_{gn'}r^j_{n'n}r^k_{gn} + r^k_{gn'}r^i_{n'n}r^j_{gn}) \times \left(\dfrac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)} + \dfrac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} + \omega)} \right) + \\[2ex] (r^j_{gn'}r^k_{n'n}r^i_{gn} + r^k_{gn'}r^j_{n'n}r^i_{gn}) \times \left(\dfrac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \dfrac{1}{(\omega_{n'g} + \omega)(\omega_{ng} + 2\omega)} \right) \end{array} \right] + \\ 4\sum_{n \neq g} \left[r^j_{gn}r^k_{gn}\Delta^i_n(\omega_{ng}^2 - 4\omega^2) + r^i_{gn}(r^k_{gn}\Delta r^j_n + r^j_{gn}\Delta r^k_n)(\omega_{ng}^2 + 2\omega^2) \right] \left(\dfrac{1}{(\omega_{ng}^2 - \omega^2)(\omega_{ng}^2 - 4\omega^2)} \right) \right\} \quad (2)
$$

where the summations are over the complete sets of eigenstates $/n\rangle$ and $/n'\rangle$ of the unperturbed molecular system. The quantities $r^i_{gn'}$ and $r^i_{nn'}$ are matrix elements of the ith components of the dipole operator between the unperturbed ground and excited states and between two excited states, respectively; $\Delta r^i_n(r^i_{nn} - r^i_{gg})$ is the difference between the excited-state and ground state dipole moments. Although all 27 components of the β tensor can be computed, only the vector component in the dipolar direction (β_μ) is sampled by electric field-induced second-harmonic generation (EFISH) experiments. In order to compare with the experimental results, we followed the formula below to calculate β_μ:

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

where

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

The all-valence ZINDO technique[36] was employed to provide the transition dipole moments and the transition energies needed in the SOS expressions. Standard parameters and basis functions were used. 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

The designed molecular structures are shown in Fig. 1. For molecules **A** to **C** (nitrobenzene as the acceptor) and **D**

to **F** (benzothiazole as the acceptor), the bridge length changed in order, while all of them have the same donor—— hydroxy-functionl amino group. For the design of molecules **G**, **H** and **I**, **J**, we can not only compare the different donor effects, but also ulteriorly compare the different effects of benzothiazole and nitrobenzene on the NLO response.

The equilibrium geometries were obtained by AM1. The optimized results show that all the molecules are coplanar, taking molecules **B** and **E** as examples, shown in Fig. 2. Comparing the bridge (that is azo part) length, in the molecule **E**, the single and double bond lengths are 0.1400 nm and 0.1255 nm, respectively, and the alternation of the bond length (BLA) are 0.01442 nm; while in molecule **B**, the single and double bond lengths are 0.14085 nm and 0.12495 nm, respectively, and the BLA is 0.01590 nm ($\Delta r = 0.01590$ nm). The comparisons above foretell that the molecule **E** will show larger NLO response than the molecule **B**, because the optimized bond alternation of molecule **E** is in the scope favouring enhancement of quadratic and cubic NLO properties.[37] In reference 37, Marder *et al*. correlated various donor-acceptor polyenes presenting maximal NLO response with bond length alternations. It is confirmed that the bond length alternation 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 (BLA). The contribution of the charge-separated resonance form to the ground state increases, and BLA decreases, when donor and acceptor substituents become stronger. According to this rule, we can obtain the results above.
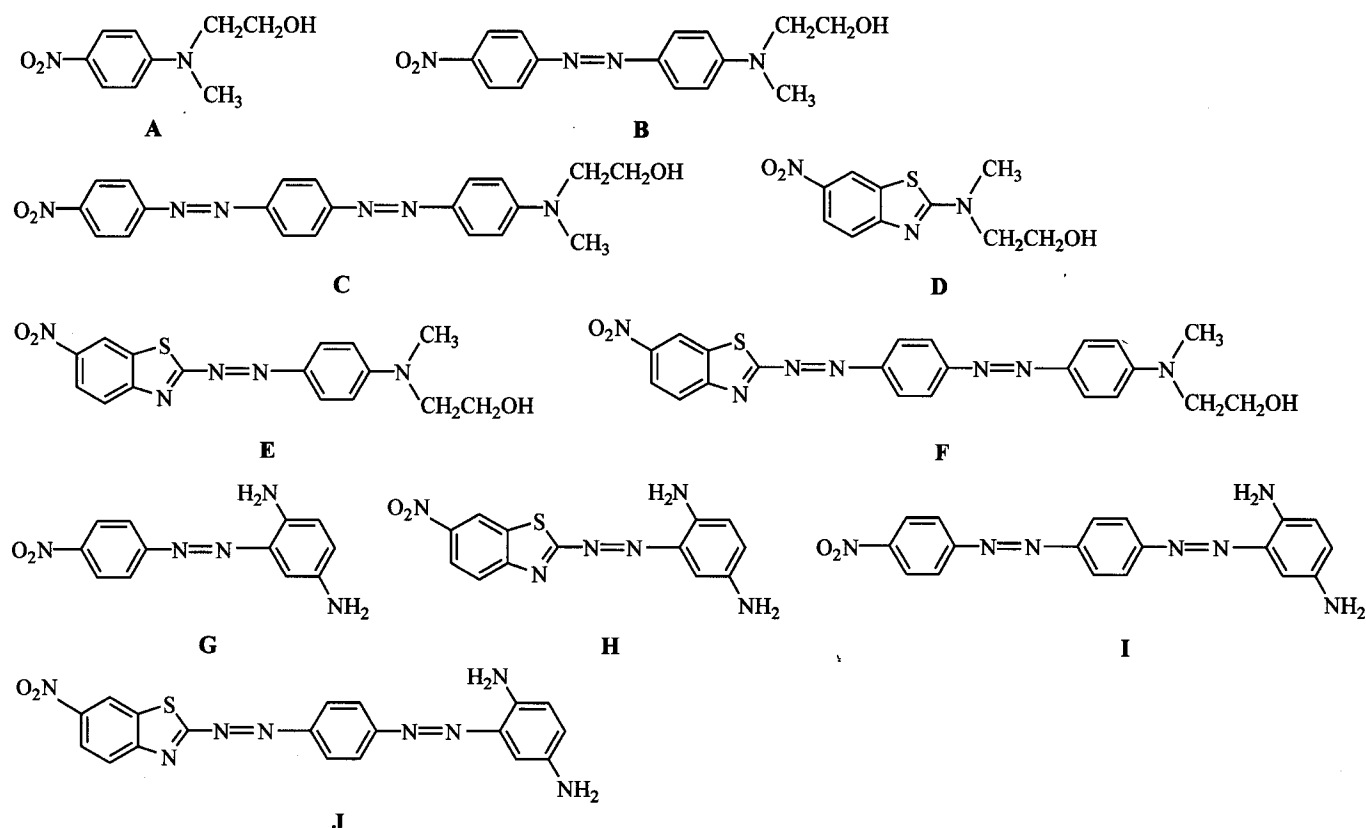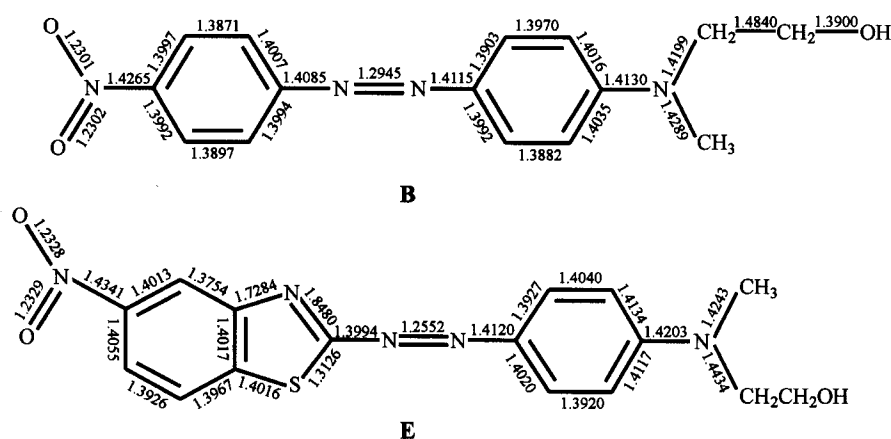
Fig. 1   Structures of chromophores **A—J**.

Fig. 2   Optimized structures of molecules **B** and **E** (unit: 0.1 nm)

Electronic spectra

The calculated wavelength and oscillator strength (only for some large absorption peaks) of molecules **A—J** are shown in Table 1. The experimental data of chromophores **D**, **E** and **F** are listed as well. The table shows that the calculated and experimental results are in a good agreement and it can be concluded that there are three or four excited states showing large oscillator strength for these series of chromophores. As shown in Table 1, the UV-vis spectral absorption wavelengths redshifts as the bridge lengths of the chro-

mophores increase. Molecule **F** is used as an example to study the whole spectroscopy. As shown in Fig. 3, there is an exicited state, which has the largest oscillator strength and it will give the main contribution to the NLO response.

The second-order polarizabilities

On the basis of optimized geometries and correct electronic spectra, the first polarizabilities β_μ (hereinafter called β for short) of molecules **A—J** were calculated by using Sum-Over-States (SOS) method.

Table 1 UV-vis spectra of chromophores A—J

| Chromophore	Transition	λ_{cal} (nm)	Oscillator strength (f)	λ_{cal} (nm)	Chromophore	Transition	λ_{cal} (nm)	Oscillator strength (f)	λ_{cal} (nm)
A	1→4	406	0.4089		F	1→5	465	1.7781	466
	1→10	226	0.8099			1→39	213	0.6298	
	1→11	222	0.4381			1→47	204	0.8200	
B	1→5	401	0.5496		G	1→5	427	0.2877	
	1→23	214	0.5523			1→6	380	0.3107	
	1→24	209	1.1993			1→19	230	0.6481	
						1→26	210	0.8374	
C	1→6	394	1.0242		H	1→4	484	0.4770	
	1→29	224	0.9740			1→6	414	0.4152	
	1→39	206	1.3996			1→26	224	0.5240	
D	1→4	427	0.5577	419	I	1→6	407	0.4843	
	1→12	237	0.5738			1→7	382	0.4578	
	1→13	225	0.3572			1→29	228	1.3804	
						1→39	206	1.3814	
E	1→5	453	1.3108	437	J	1→5	501	1.1242	
	1→19	237	0.3136			1→7	438	0.6055	
	1→24	217	0.6046			1→43	209	0.6017	
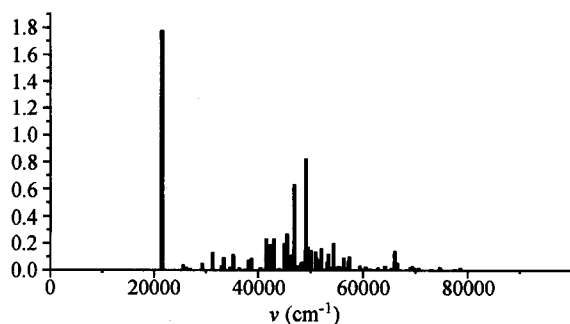
Fig. 3 Spectroscopy of molecule F.

In the Sum-Over-States expression,[39] the summation is over the complete sets of eigenstates $/n\rangle$ and $/n'\rangle$ of the unperturbed molecular system and it must be truncated in practical calculations. It is possible from the theoretical analysis: in SOS expression, the denomination of each term includes ω_{ng} and $\omega_{n'g}$; when the n and n' increase, the energy differences between ground state and excited states will increase accordingly, *i. e.*, the denominator will become more and more. It means that the β will become less and less; at last it will be negligible. How many excited states should be taken actually? It depends on the different chromophores. In the SOS calculation, all electronic states are included which are generated by singly exciting all electrons in the 14 highest occupied MOs to the 14 lowest unoccupied MOs with respect to the ground state (all together 197 configuration states). We calculated the values of β for every number of excited states from 1 to 197 and plot β against N. Chromophore E is used as an example, shown in Fig. 4. It is clear from Fig. 4 that β converges when N equals to 60 for E.
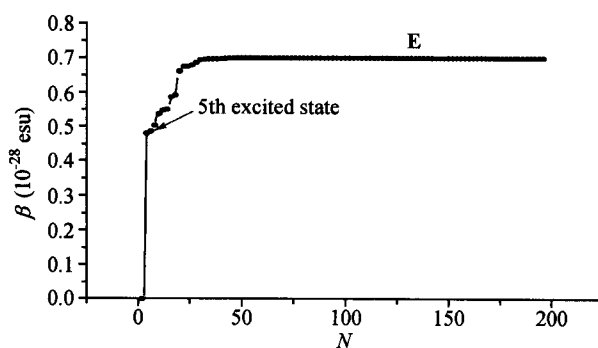
Fig. 4 Relationship between β and N (the number of excited singlets) for chromophore E.

The calculated NLO susceptibilities of chromophores A—J are listed in Table 2 (λ = 830 nm). The results shown in Table 2 suggest that with the increase of the π bridge, the first hyperpolarizability increase quickly, indicating that the length of the conjugated π-electron system is an important factor contributing to the nonlinear optical susceptibility.

From Table 2 it can be seen that for molecules **B** and **E**, **G** and **H**, **I** and **J**, the rated values of β_E/β_B, β_H/β_G, β_J/β_I of first hyperpolarizabilitis are 1.90, 1.55 and 1.96, respectivlely. These show that the benzothiazole derivatives exhibit much larger second-order polarizabilities than nitrobenzene. The enhancement of the NLO response of the benzothiazole derivatives is due to the atoms S and N, with large electronegativity and lone electron pair, which induce the enhancement of the electron-withdrawing ability and electronic delocalization, and then increase NLO response. We will give further explanation in the following section.

Table 2   Values of μ, β_μ, β_0, $\mu\beta_\mu$ and $\mu\beta_0$

Chromophore	μ (D)	β_μ ($\lambda = 0.83\mu m$) (10^{-28} esu)	β_0 (10^{-28} esu)	$\mu\beta_\mu$ (10^{-46} esu)	$\mu\beta_0$ (10^{-46} esu)
A	10.00	3.201	0.3365	32.01	3.365
B	10.11	5.265	0.5606	53.23	5.668
C	10.73	8.154	0.9285	87.49	9.963
D	10.22	4.329	0.5145	44.24	5.258
E	11.73	7.001	0.9519	82.12	10.757
F	9.86	10.28	1.673	101.36	16.496
G	7.65	4.055	0.4426	31.02	3.386
H	8.97	6.283	0.8972	56.36	8.048
I	9.01	6.120	0.6754	55.14	6.085
J	10.97	12.01	2.065	131.75	22.65

In 1975 Ouder[39,40] developed the famous two-level approximation as shown bellow:

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

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

Assuming

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

which is called static second-order NLO polarizability, then we have the following result:

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

From Eq. (5), it can be seen that β_0 is independent of external field, which can reflect the molecular intrinsic properties. The value of β_μ is often measured in experiment, so according to Eq. (5), the value of β_0 can be obtained.

The value of β_0 can also be obtained by the SOS formula combined with Eqs. (2) and (3) as long as we make the value of ω to be zero. Table 3 shows the value of β_0 by the two ways. The corresponding values are in good agreement with each other, which indicates that the most important excited state is indeed the main contribution to β_0, proving the reliability of the two-level formula.
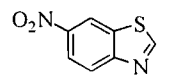
According to the two-level formula, the relationship between molecular β and the details of the most important excited state's charge-transfer transition can be described as
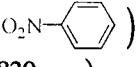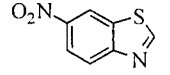
$$\beta \propto \Delta\mu_{eg} f / W^3 \qquad (8)$$

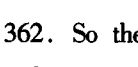where $\Delta\mu_{eg}(\mu_e - \mu_g)$ is the difference of dipole moments

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), 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_μ versus N. For the molecules A—J, the most important excited states are 3, 4, 5, 4, 4, 4, 4, 3, 5, 4 states respectively, shown in Table 1. Hence, we only study the most important excited states of chromophore B (the fifth state) and E (the fifth state). The benzothiazole derivatives involve the atoms S and N, with large electronegativity (Pauling electronegativity: N, 3.04; S, 2.58; C, 2.55) and lone electron pair, which leads to the enhancement of electron-withdrawing ability and electron delocalization. From Fig. 5 we can see the electron density in the ground state. The electron-accepting moiety of molecule

E (O_2N——S——N) has larger electron density (-0.159)

than that of molecule B (O_2N——◯) (-0.121), while in the outer field ($\lambda_{field} = 830$ nm), owing to the stronger delocalization of benzothiazole derivatives, a series of relative derivatives have a further charge transfer: the electron density of the electron-accepting moiety for molecule

E (O_2N——S——N) is -0.468, and that of molecule

B (O_2N——◯) is -0.362. So the charge transfer of molecule B between the ground and main excited state (the fifth excited state) is 0.241, meanwhile, that of molecule E (the fourth excited state) is 0.309. Furthermore, the larger the charge transfer, the larger the difference of dipole moment between the ground and the main excited state ($\Delta\mu_{eg}$). So benzothiazole derivatives have larger NLO susceptibilities than nitrobenzene derivatives. Both the calculation and experiment[26] indicate that the benzothiazole derivatives have large NLO coefficients showing that they are good candidates for NLO chromophores.

Table 3   Values of β_0 and $\mu\beta_0$ by the two ways

Molecule	Values obtained by SOS		Values obtained by Eq. (8)	
	$\beta_0(10^{-28}$ esu)	$\mu\beta_0(10^{-46}$ esu)	$\beta_0(10^{-28}$ esu)	$\mu\beta_0(10^{-46}$ esu)
A	0.3365	3.365	0.1044	1.044
B	0.5606	5.668	0.2676	2.705
C	0.9285	9.963	0.6231	6.686
D	0.5145	5.258	0.1866	1.907
E	0.9519	10.757	0.9414	11.043
F	1.673	16.496	1.8015	17.163
G	0.4426	3.386	0.1748	1.337
H	0.8972	8.048	1.4933	13.386
I	0.6754	6.085	0.1773	1.597
J	2.065	22.65	3.4924	38.311
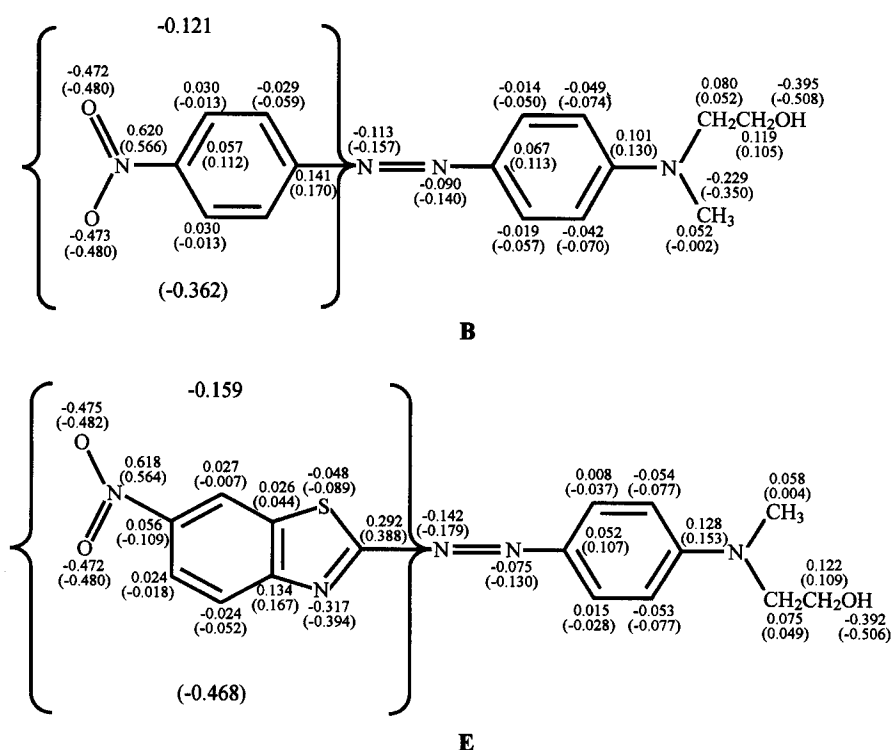
Fig. 5   Ground and excited states (shown in the parentheses) charge distribution of chromophores **B** and **E** (unit: e).

Conclusion

The second-order nonlinear optical properties of a series of benzothiazole derivatives and nitrobenzene derivatives have been studied. From above discussions the following results can be concluded:

(1) With the bridge length increasing, the second-order susceptibility becomes larger, which is in agreement with other experiments and calculations.

(2) Because of the large electronegativity and lone electron pairs of S and N atoms, the NLO susceptibilities of benzothiazole derivatives are almost twice as large as those of nitrobenzene derivatives, and they keep good transparency showing that they are the good choice for the NLO materials.

For electro-optical application, the NLO chromophores should also have good thermal and photo stability. The experimental data indicate that benzothiazole derivatives have high melting point as well as good transparency insuring that they are good candidates for the application.

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