Theoretical Study on Second-order Nonlinear Optical Properties of Substituted Thiazole Derivatives

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On the basis of ZINDO program, we have designed a program to calculate the nonlinear second-order polarizability β_{ijk} and β_{μ} according to the SOS expression. The second-order nonlinear optical properties of 4-nitro-4′-dimethylamino-stilbene and a series of its thiazole derivatives were studied. The calculated results were that: When replacing a benzene ring in 4-nitro-4′-dimethylamino-stilbene by a thiazole ring, the influence on β values depends on the position of thiazole ring. When the thiazole ring connects with nitro group (acceptor), the β values increase significantly compared with corresponding stilbene derivatives. The β values of 2-(*p*-donor-β-styryl)-5-nitro-thiazole derivatives (2—7) are larger than those of 2-(*p*-nitro-β-styryl)-5-donor-thiazole derivatives (8—13) and 2-(*p*-donor-phenyl)-azo-5-nitro-thiazole derivatives (14—19). The 2-(*p*-donor-β-styryl)-5-nitro-thiazole derivatives (2—7) are good candidates as chromophores duo to their high nonlinearities and potential good thermal stability.

Keywords Thiazole derivatives, heterocyclic compounds, second-order polarizability, ZINDOS-SOS

Introduction

The design and synthesis of organic chromophores for use in electro-optic (EO) polymers are challenging but potentially useful areas of research that are currently receiving a great deal of attention.[1,2] The chromophore problem is challenging because the properties required for use in EO applications are to a large degree mutually exclusive.[3] But the materials to be used must not only have high nonlinearities, but also require good thermal and chemical stability and low optical loss (high-transparency). So, for organic nonlinear optical (NLO) chromophore to be practical, the trade-off between the nonlinearity and other properties must be minimized.

The tradeoff has been the nonlinearity-thermal stability, which has been received the most attention. In order for the nonlinear response to be stable during processing and operation, the chromophores need to be chemically stable at all temperatures that the system encounters. Achieving thermal stabilities of usual chromophores have been proven to be extremely difficult without compromising the molecule's nonlinearity. For example, addition of thermal stability in chromophore can in principle be achieved by replacing aliphatic structures by aromatic ones along the conjugation path of the molecules. However, additional aromaticity tends to decrease the hyperpolarizability. The decrease occurs because the intramolecular charge transfer that must occur in a useful chromophore would require the aromatic rings to adopt a quinoidal bonding pattern, which is clearly disfavored.[3] Miller and co-workers[4] developed a good method to minimize the tradeoff between nonlinearity and thermal stability. They used five-membered heterocyclic rings in place of classical aromatic and/or heteroaromatic substituents. Five-membered heterocyclic rings such as

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furans, thiophenes, pyrazoles and azole derivatives still constitute fully conjugated six-π-electron systems, a condition often associated with aromaticity, but are less aromatic than classical aromatic derivatives.[5,6] Consequently, the formation of quinodal structures in five-membered heterocycles is not quite as energetically costly. The five-membered heterocyles are often more electron-rich than classical six-membered aromatic carbocyclics, since the six π-electrons are distributed over only five atoms.

The studies of Moylan and co-workers[7] on 1,4,5-triaryl-substituted azole derivetives showed that the order of nonlinearities was thiazoles > oxazoles > imidazoles, although the measured differences were not very great. Dirk *et al*.[8] have also suggested that thiazole derivatives are good candidates as NLO chromophores. They conclude that replacing a benzene ring in a NLO chromophore by a thiazole ring can increase $\mu\beta$ by up to a factor of 3. In order to gain an insight into the enhanced effect of thiazole ring on the β values, we designed a series of thiazole derivatives and studied their NLO properties by using ZINDO/SCI aproaches combined with sum-over-states (SOS) expression.

Computational methodology

The fundamental relationship describing the molecular polarization induced by an external electric field can be expressed as a power series:

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

where p_i is the polarization induced along the ith molecular axes; E_j, the applied electric field in the jth direction; and, α, β, γ, the first-, second-, and third-order polarizability (or susceptibility) tensors, respectively. The basis of our treatment is the general quantum mechanical perturbation formula for the molecular nonlinear second-order optical susceptibility sum-over-states (SOS) expression that has been given by Teng and Garito:[9]

$$\beta_{ijk}(-2\omega,\omega,\omega) = \frac{1}{8\hbar^2}\left\{\sum_{\substack{n\neq n'\\ n\neq g\\ n'\neq g}}\left[\begin{array}{l}(r^i_{gn'}r^i_{n'n}r^k_{gn} + r^k_{gn'}r^i_{n'n}r^i_{gn})\cdot\left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}+\omega)}+\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}-\omega)}\right)\\ +(r^i_{gn'}r^j_{n'n}r^k_{gn} + r^i_{gn}r^k_{n'n}r^i_{gn})\cdot\left(\frac{1}{(\omega_{n'g}-2\omega)(\omega_{ng}-\omega)}+\frac{1}{(\omega_{n'g}+2\omega)(\omega_{ng}+\omega)}\right)\\ +(r^j_{gn'}r^k_{n'n}r^i_{gn} + r^k_{gn'}r^j_{n'n}r^i_{gn})\cdot\left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}-2\omega)}+\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}+2\omega)}\right)\\ +4\sum_n\left\{[r^j_{gn}r^k_{gn}\Delta r^i_n(\omega^2_{ng}-4\omega^2) + r^i_{gn}(r^k_{gn}\Delta r^j_n + r^j_{gn}\Delta r^k_n)(\omega^2_{ng}+2\omega^2)]\cdot\frac{1}{(\omega^2_{ng}-\omega^2)(\omega^2_{ng}-4\omega^2)}\right\}\end{array}\right]\right\} \quad (2)$$

Here, the subscripts i, j, and k are the Cartesian components; r_{ab} corresponds to the dipole integral involving the states a and b, and $\Delta r^i_n = r^i_{nn} - r^i_{gg}$ (g denote the ground state) is the difference of dipole moment between ground state g and excited state n; $\hbar\omega_{nn'}$ represents the electronic energies when an electron is transited from state n to n'; ω is the angular frequency of the applied electric field.

According to Eq. (2), 27 β_{ijk} components can be obtained, only the components along the direction of the dipole moment (β_μ) can be sampled by EFISH (electric-field induced second-harmonic generation) experiments. In order to compare our theoretical results with that of the EFISH experiments, β_μ is computed by Eq. (3):

$$\beta_\mu(-2\omega,\omega,\omega) = \sum_{j=1}^{3}\frac{\mu_i\beta_j}{\|\mu\|} \quad (3)$$

here, i and j run over the molecular Cartesian direction x, y, z; μ_i is the ith component of the dipole moment, $\|\mu\|$ is the norm of the dipole moment and β_i is defined by Eq. (4).

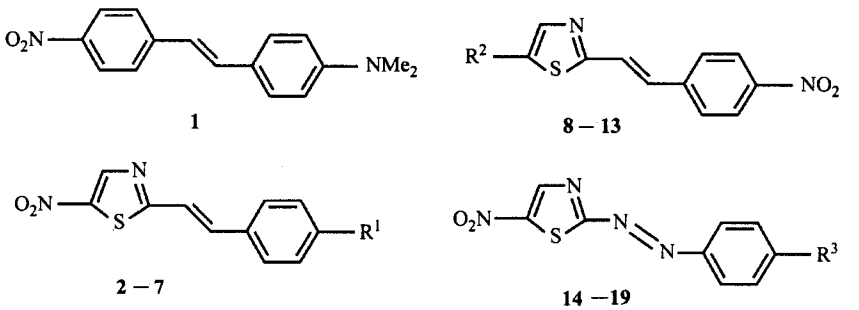
$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i\neq j}(\beta_{jii} + \beta_{iji} + \beta_{iij}) \quad (4)$$

Results and discussions

Optimization of the structures

We have designed a series of thiazole derivatives. Their structures are shown in Fig. 1. The geometric structures were fully optimized on the basis of the PM3 Hamiltonian in the MOPAC package. The PRECISE option was used as convergence criterion for PM3 calcula-

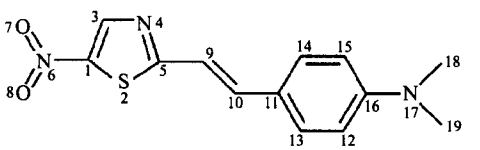
tion of geometry. Table 1 shows the optimized structure parameters of chromophore **3**.



2	R^1=NPh_2	**3**	R^1=NMe_2	**4**	R^1=$N(CH_2)_5$	**5**	R^1=OMe	**6**	R^1=OH
7	R^1=NEt_2	**8**	R^2=NPh_2	**9**	R^2=NMe_2	**10**	R^2=$N(CH_2)_5$	**11**	R^2=OMe
12	R^2=OH	**13**	R^2=NEt_2	**14**	R^3=NPh_2	**15**	R^3=NMe_2	**16**	R^3=$N(CH_2)_5$
17	R^3=OMe	**18**	R^3=OH	**19**	R^3=NEt_2				

Fig. 1 Structures of chromophores **1—19**.

Table 1 PM3 optimized molecular structure [some bond length (1×10^{-1} nm), bond angle (degree) and dihedral angle (degree)] of chromophore **3**



Entry	PM3	Entry	PM3	Entry	PM3	Entry	PM3
R(1,2)	1.744	R(10,11)	1.453	A(1,3,4)	113.9	A(13,12,16)	120.6
R(1,3)	1.389	R(11,13)	1.400	A(3,4,5)	112.1	A(12,16,17)	120.5
R(1,6)	1.484	R(12,13)	1.385	A(2,5,4)	113.6	A(16,17,19)	116.9
R(2,5)	1.753	R(12,16)	1.406	A(2,5,9)	125.9	D(3,1,6,7)	-0.07
R(3,4)	1.384	R(16,17)	1.439	A(1,6,7)	118.5	D(2,1,6,8)	-0.08
R(4,5)	1.349	R(17,18)	1.481	A(1,6,8)	119.8	D(3,4,5,9)	180.0
R(5,9)	1.445	R(17,19)	1.481	A(5,9,10)	123.5	D(4,5,9,10)	-179.6
R(6,7)	1.215	A(2,1,3)	111.2	A(9,10,11)	122.5	D(5,9,10,11)	180.0
R(6,8)	1.213	A(2,1,6)	126.4	A(10,11,13)	119.8	D(9,10,11,14)	0.03
R(9,10)	1.346	A(1,2,5)	89.2	A(11,13,12)	120.6	D(14,15,16,17)	-174.9

Electronic spectra

The electron spectra of chromophores **2—19** were obtained by single point calculation with INDO/SCI method using the above optimized geometries. INDO/SCI method has been proven to be especially effective in calculating electronic spectra of organic molecules.[10-12] The computing results are shown in Table 2. From Table 2, we can see that, for all these chromophores, there are two major absorption peaks. The transition energies (E_t) of 2-(*p*-donor-β-styryl)-5-nitro-thiazole derivatives (**2—7**) are slightly less than those of corresponding 2-(*p*-nitro-β-styryl)-5-donor-thiazole derivatives (**8—13**) and 2-(*p*-donor-phenyl)-azo-5-nitro-thiazole derivatives (**14—19**). For chromophores **14—19**, there are very weak absorption peaks in the visible range with oscillator strength between 0.007—0.009, which agrees well with the experiments.[4] The difference of the transition energy between computing results and experimental data maybe mainly due to solvent effects, since the experimental values were obtained in solvent and the calculated ones were for an isolated molecule in a vacuum.

Table 2 Transition energy (E_t) and oscillator strength (f) the studied chromophores

Chromophore	Calculated values						Observed values[a]
	E_t (cm^{-1})	f	E_t (cm^{-1})	f	E_t (cm^{-1})	f	E_t (cm^{-1})
2	24489	1.2872	51653	0.8217			20325 (in chloroform)
3	24692	1.1770	50885	0.4352			20921 (in chloroform)
4	24674	1.1913	50929	0.5254			
5	25356	1.1068	54360	0.5360			24631 (in *p*-dioxane)
6	25369	1.0977	51057	0.4562			
7	24653	1.1876	50751	0.3771			
8	24934	1.1191	50611	0.4438			
9	25534	1.0854	55597	0.3696			
10	24835	1.0943	47548	0.3126			
11	26708	1.1259	47695	0.3001			
12	26684	1.1201	47655	0.3117			
13	24879	1.0801	50582	0.5676			
14	19712	0.0072	29481	0.9721	52078	0.5622	17182 (in chloroform)
15	19399	0.0078	28297	1.0732	52254	0.4197	
16	19448	0.0087	28421	1.0827	52478	0.5422	
17	19323	0.0073	29033	0.9306	53253	0.3448	23582 (in *p*-dioxane)
18	19302	0.0072	29034	0.9152	54387	0.4677	
19	19410	0.0083	28127	1.1087	52373	0.5304	

[a] Experimental data from reference 4.

Second-order polarizabilities

On the basis of geometrical optimization, the second-order polarizabilities (β_μ) were calculated by using ZINDO-SOS method.

In the sum-over-states Eq. (2), the summation is over the complete sets of eigenstates $|n\rangle$ and $|n'\rangle$ of the unperturbed molecular system. 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 n and n' increase, the energy differences between ground state and excited states will increase, *i.e.*, the denominator will increase more and more. It means the contribution for β_μ will become less and less; at last it will be negligible. How many excited states should be taken actually? There is not a common criterion for different molecules. Let us take chromophore **3** as an example.

In the INDO/SCI method, an active space of 14 occupied and 14 virtual orbital with 197 single-electron excitation configurations and the ground state were included. After configuration interaction (CI), 197 excitation states were obtained. We take the numbers of excited states from 1 to 197, and calculate β_{ijk} and β_0 ($\omega = 0$) for each different number of excited states and plot β_0 against the number of excited states N, as shown in Fig. 2. It is clear from Fig. 2 that β_0 converges when N equals 80.

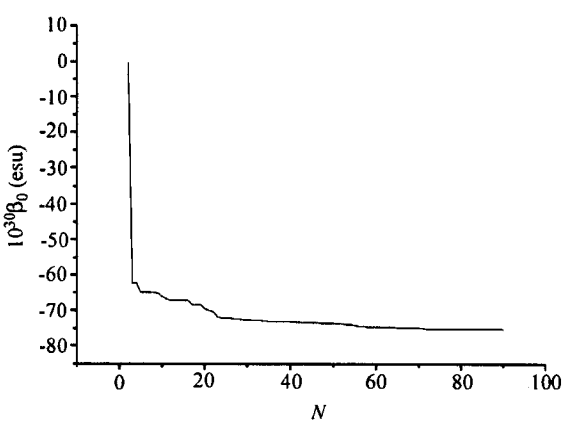


Fig. 2 Relationship between β_0 and N (the number of excited singlets) for chromophore **3**.

In this paper, for all β_0 and β_μ ($\omega = 1.907$ μm) results, the converged values are listed in Table 3. Table 3 also includes the β_μ (or β_0) values of 4-nitro-4′-dimethylamino-stilbene (**1**) and some experimental values for comparison.

Table 3 Calculated values of dipole moments (μ), second-order polaribilities, β_0, β_μ ($\omega = 1.907$ μm), $\mu\beta_0$ and $\mu\beta_\mu$ using INDO/SCI combined with the SOS expression

Molecules	μ (D)	β_0 (10^{-30} esu)	β_μ (10^{-30} esu)	$\mu\beta_0$ (10^{-48} esu)	$\mu\beta_\mu$ (10^{-48} esu)	T_d^a (℃)	$\beta_{\mu,exp}$
1	8.95	54.60	104.45[b]	488.0	933.9		73.0 ± 9.3 (in $CHCl_3$)[e]
		52[c]					
		50.3[d]					
2	9.76	90.30	110.97	880.3	1081.7	325	83.0 (in $CHCl_3$)[f]
3	10.11	75.25	93.49	759.7	944.0	253	93.8 (in *p*-dioxane)[f]
4	10.17	76.83	95.49	780.3	969.9		
5	8.84	55.59	67.99	490.8	600.3		
6	8.50	52.54	64.25	446.0	545.5		
7	10.21	76.73	95.40	782.5	972.8		
8	7.66	64.63	78.05	494.4	592.4		
9	8.54	54.60	66.49	465.7	567.1		
10	8.84	60.10	74.27	530.7	655.7		
11	7.61	45.49	54.40	345.7	413.5		
12	7.26	43.36	51.89	314.4	376.2		
13	8.96	60.98	75.14	545.7	672.3		
14	7.86	44.55	50.51	349.7	396.5	298	
15	9.36	47.98	56.26	448.5	525.9		
16	9.83	49.38	57.85	484.8	567.9		
17	7.93	34.70	40.19	274.8	318.3	328	
18	7.59	32.67	37.85	247.7	288.7		
19	9.70	51.50	60.57	499.0	586.8		

[a] Onset decomposition temperature measured by DSC at 20℃ min, the data from reference 4.
[b] The β_μ value were calculated when $\omega = 1.064$ μm.
[c] Experimental zero field result from reference 13.
[d] Calculated zero field result at the CNDOVSB level from reference 14.
[e] Frequency dependent result when $\omega = 1.064$ μm from reference 18. [f] Experimental data from reference 4.

From Table 3 we can see that the β_0 value of chromophore **1** obtained in this paper agrees well with that of experimental data[13] and CNDOVSB calculated result.[14] So, the (SOS) program to calculate the second-order nonlinear polarizability β_{ijk} and β designed by ourselves is vilid.

Comparison of the molecular β values of chromophores **1**, **3** and **9** indicate that there are different influence on β values along with the different positions of thiazole ring when replacing a benzene ring in 4-nitro-4′-dimethylamino-stilbene (**1**) by a thiazole ring. When the thiazole ring connects with nitro group (acceptor), the β value and dipole moment increase significantly, *i. e.*, $(\beta_0)_3 > (\beta_0)_1$, $\mu_3 > \mu_1$. When the thiazole ring connects with NMe_2(donor), the change of β_0 values is not great and the dipole moment decreases slightly. The same order was found in other chromophores, *i. e.*, $(\beta_0)_2 > (\beta_0)_8$, $(\beta_0)_3 > (\beta_0)_9$, $(\beta_0)_4 > (\beta_0)_{10}$, $(\beta_0)_5 > (\beta_0)_{11}$, $(\beta_0)_6 > (\beta_0)_{12}$, $(\beta_0)_7 > (\beta_0)_{13}$ and $\mu_2 > \mu_8$, $\mu_3 > \mu_9$, $\mu_4 > \mu_{10}$, $\mu_5 > \mu_{11}$, $\mu_6 > \mu_{12}$, $\mu_7 > \mu_{13}$.

According to the Auxiliary Donor-Acceptor Effects theory,[15] the electron-excessive heterocyclic bridges act as auxiliary donor while connecting with electron donating group, and significantly enhancing NLO response. In chromophores **8**—**13**, the thiazole rings (electron-excessive ring) connect with the donor (NMe_2), hence, chromophores **8**—**13** were expected to have enhanced β values. However, it is found that chromophores **2**—**7** possess larger β values than chromophores **8**—**13**. The computing result is not according with the Auxiliary Donor-Acceptor Effects theory. In order to clarify the origin of the different NLO response between these chromophores, we investigate their electronic properties and frontier orbital properties, and take chromophores **3** and **9** as ex-

amples.

According to the two-level model,[16,17] the linkage between molecular β and the details of a low-lying charge-transfer transition can be described as

$$\beta \propto \Delta\mu_{eg} f / E_t^3 \quad (5)$$

where $\Delta\mu_{eg} = \mu_e - \mu_g$ is the difference of dipole moments between ground state and excited states, E_t the transition energy, and f the oscillator strength. The influence of substitution effects on β values can be analyzed from the three electronic properties.

For chromophores **3** and **9**, the second excited states are most important to β values due to their maximal oscillator strength. So, we only need to investigate the second excited states. The major excited configurations that constitute these two important excited states are listed in Table 4 and Table 5, respectively. It is found that a single, low-excited configuration, which can be described as HOMO→LUMO excitation, makes the dominant contribution to the intrinsic β values for these two chromophores. The contributions from other electronic configurations are very little and can be approximately neglected. So, we only investigate the HOMO→LUMO excited configuration.

Table 4 Major configurations that constitute the important excited state of chromophore **3** with the maximal oscillator strength

Configuration	Configuration coefficient	μ_e (D)	$\Delta\mu_{eg}$ (D)	E_t (eV)	f	Major transitions	$\Delta\mu_{eg} \cdot f / E_t^3$
184[a]	-0.9018	29.97	19.86	3.47	1.0620	HOMO→LUMO	0.5048
185	0.1061	29.75	19.64	4.58	0.3536	HOMO→LUMO+1	0.0723
171	0.2029	22.35	12.24	5.40	0.1561	HOMO-1→LUMO+1	0.0121
170	0.3281	22.54	12.43	4.54	0.1574	HOMO-1→LUMO	0.0209
143	-0.1055	32.34	22.23	7.02	0.0433	HOMO-3→LUMO+1	0.0003

[a] 184 means the 184th configuration. All the configurations with the absolute value of configuration coefficient larger than 0.1 are listed.

Table 5 Major configurations that constitute the important excited state of chromophore **9** with the maximal oscillator strength

Configuration	Configuration coefficient	μ_e (D)	$\Delta\mu_{eg}$ (D)	E_t (eV)	f	Major transitions	$\Delta\mu_{eg} \cdot f / E_t^3$
184[a]	-0.8125	41.42	32.88	3.67	0.6588	HOMO→LUMO	0.4382
185	-0.5000	27.06	18.52	4.11	0.4885	HOMO→LUMO+1	0.1303
173	-0.1003	14.12	5.58	6.65	0.1027	HOMO-1→LUMO+3	0.0130
171	0.1020	13.91	5.37	5.46	0.0993	HOMO-1→LUMO+1	0.0033
170	-0.2052	28.17	19.63	4.77	0.4790	HOMO-3→LUMO	0.0866

[a] 184 means the 184th configuration. All the configurations with the absolute value of configuration coefficient larger than 0.1 are listed.

At first we compare the excitation dipole moments (μ_e) of the HOMO→LUMO excited configurations. It is very clear that $(\mu_e)_9 > (\mu_e)_3$. This can be explained by comparing their frontier orbital properties. Fig. 3 shows the molecular orbital diagram of the HOMO and LUMO of chromophores **3** and **9**, and the open circle and solid circle reflect the sign of the orbital coefficients of the p_z orbitals. From Fig. 3, we can see that, for chromophore **9**, the HOMOs are mainly centered on the thiazole ring and N atom in NMe_2 group, while the LUMOs are mainly on the NO_2 group and benzene ring, and hence can produce larger excitation dipole moment than that of chromophore **3**.

But there are three factors that determine the magnitude of β values. The oscillator strength and transition energy are also important for β values. Because the oscillator strength of chromophore **3** is larger than that of chromophore **9**, and the transition energy of chromophore **3** is less than that of chromophore **9**, so the value of $\Delta\mu_{eg} f / E_t^3$ of chromophore **3** is larger than that of chromophore **9**. Thus, chromophore **3** exhibits higher nonlinearity than chromophore **9**. Besides, the large β value of chromophore **3** can be explained by its longer conjugation length in HOMOs and LUMOs (see Fig. 3).

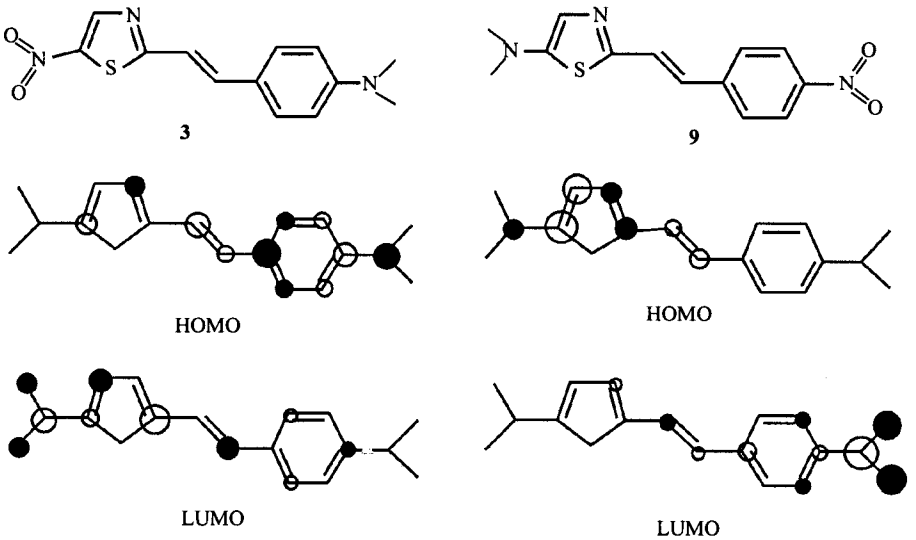


Fig. 3 ZINDO/SCI molecular orbital diagram of the HOMO and LUMO of chromophores **3** and **9**.

From Table 3 we can see that the β values of chromophores **14**—**19** are less than those of chromophores **2**—**7** and **8**—**13**. This maybe due to the stopping action of N atom in the middle bridges of 2-(*p*-donor-phenyl)-azo-5-nitro-thiazole derivatives (**14**—**19**) to the charge transfer from donor to acceptor. The little dipole moments of chromophores **14**—**19** compared with those of chromophores **2**—**13** are a good testimony. In order to clarify the electronic origin of different NLO response between these two kinds of chromophores, we calculated the Mulliken charge populations of chromophores **6** and **18**. The computing results are shown in Fig. 4.

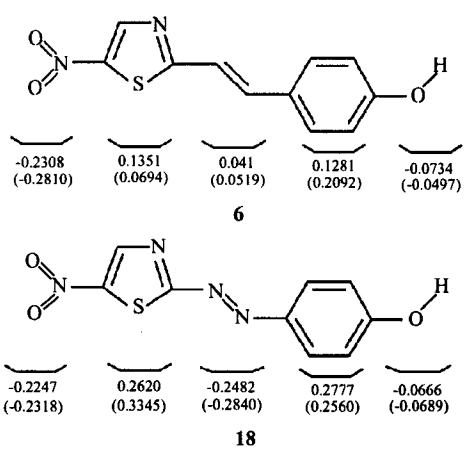


Fig. 4 Mulliken charge populations of the ground state and the excited states (in parentheses) (for chromophore **6**, the second excited state; for chromophore **18**, the forth excited state).

For chromophore **6**, the total charge of NO_2 group in ground state is − 0.2308 and in excited state is − 0.2810, and the total charge transfer is 0.0502. For chromophore **18**, the total charge of NO_2 group in ground state is − 0.2247 and in excited state is − 0.2318, and the total charge transfer is 0.0131. Thus, the total charge transfer of chromophore **6** is larger than that of chromophore **18**, and hence chromophore **6** exhibits larger nonlinearity than chromophore **18**. Besides, we can compare the values of $\Delta\mu_{eg}$ (the difference of dipole moments between excited and ground states), E_t (transition energy) and f (oscillator strength) of chromophores **6** and **18**. For chromophore **6**, the $\mu_g = 8.50$ D, $\mu_e = 16.04$ D, $\Delta\mu_{eg} = 7.54$ D, $f = 1.0977$, $E_t = 3.145$ (eV) and $\Delta\mu_{eg}f/E_t^3 = 0.266$. For chromophore **18**, the $\mu_g = 7.59$ D, $\mu_e = 14.29$ D, $\Delta\mu_{eg} = 6.70$ D, $f = 0.9152$, $E_t = 3.60$ eV and $\Delta\mu_{eg}f/E_t^3 = 0.131$. According to the two-level model,[16,17] we can understand why the β value of chromophore **6** is larger than that of chromophore **18**.

The static second-order polarizability (β) values of chromophores **2**—**7** increase in the order of **6** < **5** < **3** ≈**4** ≈**7** < **2**, similar to the electron donor power of the substituent R^1(OH < OMe < NMe_2 ≈ $N(CH_2)_5$ ≈ NEt_2 < NPh_2). The β values of **8**—**13** also increase in the similar order of **12** ≈**11** < **9** < **10** ≈**13** < **8**. But for chromophores **14** —**19**, the order of β values changes and chromophore **19** corresponds to the largest β value. The reason for this difference is not clear. It is probably due to the changes of bridge atoms.

To be used for electrooptical application the NLO chromophores should also have enough thermal stability. As far as thermal stability is concerned, the higher decomposition temperatures (> 250℃) of chromophores **2**, **3**, **14** and **17** from Table 3 reflect their better thermal stability.

Conclusions

In summary, we have studied a variety of NLO chromophores containing thiazole ring. The examples include 2-(*p*-donor-β-styryl)-5-nitro-thiazole (**2**—**7**), 2-(*p*-nitro-β-styryl)-5-donor-thiazole derivatives (**8**—**13**) and 2-(*p*-donor-phenyl)-azo-5-nitro-thiazole (**14**—**19**). The β values of chromophores **2**—**7** are larger than those of chromophores **8**—**13** and **14**—**19**. It does not agree with the Auxiliary Donor-Acceptor Effects theory. The 2-(*p*-donor-β-styryl)-5-nitro-thiazole derivatives (**2**—**7**) are good candidates as chromophores duo to their high nonlinearities and potential good thermal stability.

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