Theoretical study on second-order nonlinear optical properties of unsymmetric bis(phenylethynyl)benzene series derivatives

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On the basis of ZINDO methods, according to the sum-over-states (SOS) expression, the program for the calculation of the second-order nonlinear optical susceptibilities β_{ijk} and β_μ of molecules was devised, and the structures and nonlinear optical properties of unsymmetric bis(phenylethynyl)benzene series derivatives were studied. The influence of the molecular conjugated chain lengths, the donor and the acceptor on β_μ was examined.

Keywords Unsymmetric bis(phenylethynyl) benzene series derivatives, second-order nonlinear optical susceptibility, ZINDO-SOS

Introduction

For wide application prospects in fields of light-communication, light-computer and light-energy conversion, synthesizing nonlinear optical materials having big β is a highly active high-tech field.[1-13] Second-order nonlinear optical properties of stilbene, Shiff bases, phenylazobenzene derivatives were studied widely.[14-16] Changing donor-acceptors, extending π-conjugated chain lengths could increase the value of β, but at the same time unavoidably resulted in the red-shift in their optical absorption of UV spectra and decreased transparency, thus limiting their application value.[17] The present paper concerned about unsymmetric bis(phenylethynyl)-benzene series derivatives, systematically studied the influence on their second-order nonlinear optical properties with extending π-conjugated chain lengths and with various substituents. The results show that electron push-pull groups substituted on the derivatives facilitate the second-order nonlinear optical susceptibility, extending conjugated areas increases the second-order nonlinear optical susceptibility while remaining good transparency.

Theoretical methodology

Nonlinear optical effects are the results of the interaction of Laser field with atoms or molecules constituting nonlinear optical media. Using perturb theory and density matrix method can induce out the sum-over-states (SOS) expression for second-order nonlinear optical susceptibilities β_{ijk}.[18] In principle, any kind of SCFMO + CI can be used to calculate the physical values in the expression. This paper is based on the INDO-CI method which proved to be especially effective in calculating UV-vis spectra of organic molecules.[19-21] This paper uses AM1[22] to optimize the geometric structures of the molecules concerned. AM1 has been proved to be a good method for reproducing geometric structures for organic molecules. We calculate the molecular orbitals by INDO-SCF, then process configuration interaction (CI) calculations to obtain the ground state and excited states, and the transition energies between states and corresponding oscillator strength (namely electronic spectra), finally compute β_{ijk} using program devised by ourselves.

β is a third-order tensor, while β_μ is its projector on

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the direction of dipole moment. β_μ is usually determined by the electric field induced second harmonic generation (EFISH) method. In order to compare with the experimental results, we use expression as follows to calculate β_μ:

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

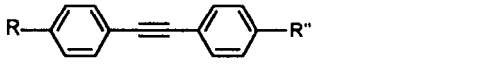
where

$$\beta_i = \beta_{iii} + 1/3\sum_{i\neq j}(\beta_{jii} + \beta_{iji} + \beta_{iij}) \quad i,j = (x,y,z) \quad (2)$$

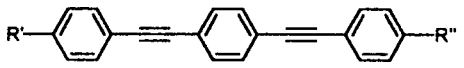
Results

Design of molecular structure and geometry optimization

24 kinds of molecules are studied in this paper, their molecular structures designed and numbered as:



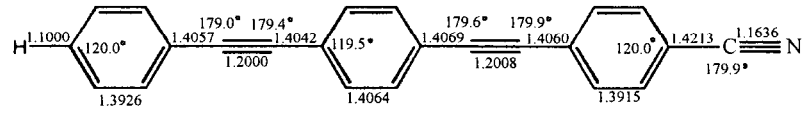
R =	H	CH_3	OCH_3	SCH_3	NH_2	$N(CH_3)_2$
R" = CN	1	2	3	4	5	6
R" = NO_2	13	14	15	16	17	18



R' =	H	CH_3	OCH_3	SCH_3	NH_2	$N(CH_3)_2$
	7	8	9	10	11	12
	19	20	21	22	23	24

This paper used molecules **1** and **13** as the initial molecules to carry on molecular design research. Groups $-CN$ and $-NO_2$ in molecules **1** and **13** are electronic pull groups. We changed electronic push groups at position *para* of the molecules to study the influence of electronic push groups on the second-order nonlinear optical properties, then increased π-conjugated chain lengths to study its influence on β.

Firstly we used AM1 to optimize the geometry. The results were shown in Fig. 1 with molecules **7** and **19** as examples. In calculating we set Z axis vertical to molecular plane, with X axis approximately along the direction of the permanent dipole moment.



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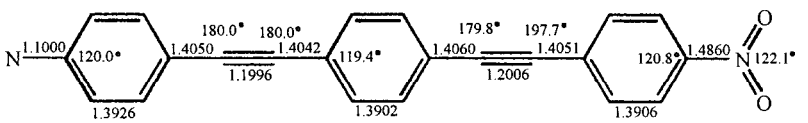

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Fig. 1 Optimized geometry for molecules **7** and **19**.

Electron spectra

We used INDO/CI to carry on spectroscopy calculations for molecules **1**→**24** at optimized structures. The results were shown in Table 1. The UV spectral absorption areas of these molecules are between 320—390 nm. The results calculated are in good agreement with the experimental data (shown in Table 1).[17] Only the wavelength (λ) and oscillator strength (f) of the maximum absorption peaks were shown in Table 1. The whole UV spectra were shown in Figs. 2 and 3 with molecules **12** and **21** as examples.

Table 1 UV-vis spectra of molecules

Substituents	No.	λ_{cal} (nm)	f	λ_{exp}[17] (nm)	No.	λ_{cal} (nm)	f	λ_{exp}[17] (nm)
- H	**1**	320.56	0.9338		**13**	343.7	0.9456	
- CH_3	**2**	2307.58	1.0451		**14**	344.4	0.6980	
- OCH_3	**3**	3330.13	0.8343		**15**	350.4	0.9817	
- SCH_3	**4**	4333.73	0.8128		**16**	348.4	0.9796	
- NH_2	**5**	5315.99	1.0692		**17**	360.8	1.0466	
- NMe_2	**6**	6330.56	1.1446		**18**	362.8	1.0440	
- H	**7**	327.48	1.8494		**19**	354.4	1.4653	
- CH_3	**8**	320.09	2.2622		**20**	353.0	1.4197	
- OCH_3	**9**	346.74	1.9044	340	**21**	363.1	1.7541	358
- SCH_3	**10**	341.59	1.8837	344	**22**	362.5	1.7527	362
- NH_2	**11**	337.69	1.8239	350	**23**	361.8	1.6797	370
- NMe_2	**12**	350.08	1.9645	376	**24**	368.4	1.8131	384

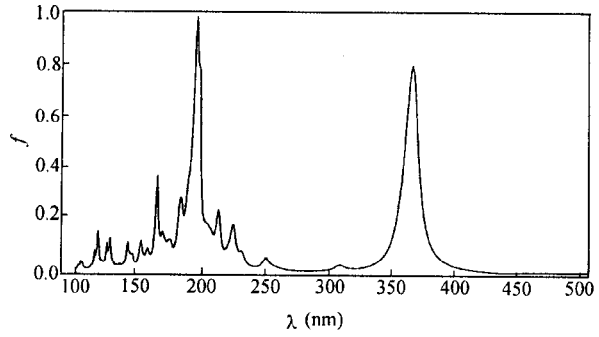

Fig. 2 UV-vis spectrum of molecule **12**.

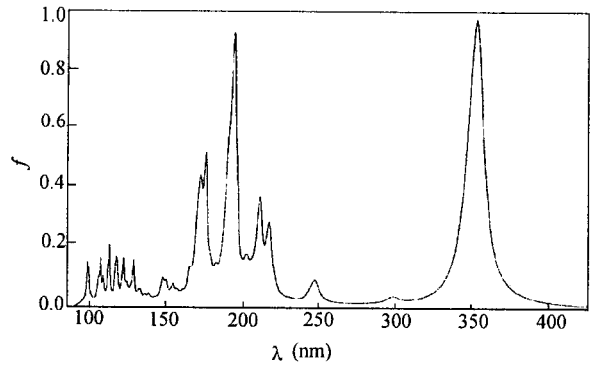

Fig. 3 UV-vis spectrum of molecule **21**.

Second-order nonlinear optical susceptibility

In the SOS expression of β_{ijk}, it should include the full set of the nonperturbation system eigenfunctions, but in actual calculation only a limited set was used.[18] Taking molecule **21** for example, we selected the number of excited states from 1 to 197, calculated β_{ijk} and β_μ after each selection, then plotted β_μ against the number of excited states (Fig. 4) to obtain a converged value. β_μ values of other molecules were obtained in the same way. As shown in Fig. 4, it is fairly well converged when selecting about 120 excited states. β was taken as a shortcut for converged $|\beta_\mu|$. β was related with external field frequency. To compare with the experimental results, we used the Nd:YAG laser (used in Ref. 17) basic frequency (which is 1.064 μm). β_0 was the value of β at 0 frequency ($\omega = 0$, see below). β and β_0 were listed in Table 2. $\mu\beta$ was firstly obtained in EFISH experiments, so $\mu\beta$ and $\mu\beta_0$ were also listed in Table 2. By comparison of the calculation data with the experimental results we will find that they are not only at the same order but also change in the same trends.

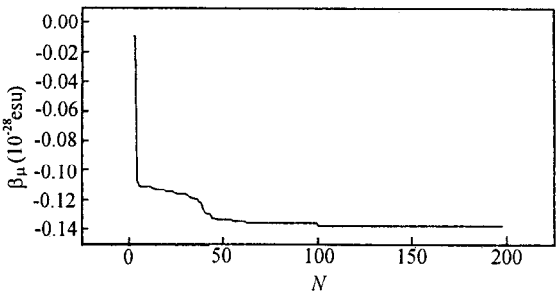

Fig. 4 β values plotted against numbers of excited states.

Two-state approximation

In the SOS expression of β_{ijk}, if only the ground state and the most important excited state are included, then the two-state approximate formula of β_μ can be ob-

tained:

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

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

Let $$\beta_0 = \frac{3e^2\hbar^2 f\Delta\mu}{2mW^3} \quad (4)$$

β_0 is called as static second-order nonlinear optical susceptibility.

So $$\beta_\mu = \frac{\beta_0 W^4}{[W^2 - (2\hbar\omega)^2][W^2 - (\hbar\omega)^2]} \quad (5)$$

Table 2 Values of μ (D_e), β (10^{-28} esu), β_0 (10^{-28} esu), $\mu\beta$ (10^{-46} esu), and $\mu\beta_0$ (10^{-46} esu)

No.	Substituents	μ	β_{cal}	$\mu\beta_{cal}$	$\beta_{0\,cal}$	$\mu\beta_{0\,cal}$	β_{exp}	$\mu\beta_{exp}$	$\beta_{0\,exp}$	$\mu\beta_{0\,exp}$
1	- H	5.34	0.365	1.947	0.249	1.331				
2	- CH_3	5.99	0.387	2.319	0.268	1.605				
3	- OCH_3	5.72	0.426	2.439	0.277	1.585				
4	- SCH_3	5.06	0.334	1.690	0.224	1.133				
5	- NH_2	6.89	0.492	3.388	0.330	2.246				
6	- NMe_2	6.61	0.544	3.593	0.347	2.292				
7	- H	5.53	0.816	4.513	0.495	2.739				
8	- CH_3	6.22	0.830	5.161	0.521	3.238				
9	- OCH_3	5.72	0.865	4.952	0.511	2.923	0.38	2.4	0.19	1.2
10	- SCH_3	5.21	0.705	3.674	0.429	2.236	0.29	2.5	0.15	1.3
11	- NH_2	7.10	0.992	7.080	0.615	4.393	0.47	4.2	0.20	1.8
12	- NMe_2	7.01	1.165	8.153	0.671	4.694	0.76	8.4	0.34	3.7
13	- H	7.19	0.599	4.310	0.368	2.647				
14	- CH_3	7.84	0.638	5.002	0.399	3.130				
15	- OCH_3	7.36	0.667	4.913	0.398	2.929				
16	- SCH_3	6.74	0.589	3.971	0.347	2.336				
17	- NH_2	8.90	0.960	8.551	0.540	4.802				
18	- NMe_2	9.06	1.023	9.268	0.514	4.657				
19	- H	7.51	1.153	8.695	0.676	5.074				
20	- CH_3	8.16	1.241	10.127	0.736	6.007				
21	- OCH_3	7.67	1.376	10.554	0.750	5.751	0.54	4.0	0.27	2.0
22	- SCH_3	7.09	1.217	8.629	0.670	4.752	0.51	3.8	0.24	1.8
23	- NH_2	9.12	1.633	14.893	0.906	8.260	0.57	6.8	0.26	3.1
24	- NMe_2	9.30	1.868	17.372	0.986	9.172	1.20	12.0	0.51	5.1

β_0 is independent of external electric field (as expressed in Eq.(4)), so it can reflect the intrinsic nature of the molecule better. Usually β_μ is first obtained by experiments, then β_0 is calculated through Eq. (5).

β_0 can also be calculated using SOS expression of β_{ijk} and Eqs.(1) and (2), just letting $\omega = 0$ in the calculation. The β_0 values calculated by the two approaches were listed in Table 3. The results are in excellent agreement. It shows that "the most important excited state" really contributes to β_0 principally, and the two-state model is a good approximation.

Discussion

Donor's influence on β

We studied donor's influence on β by changing the donor substituents at the *para* position of *p*-cyano-bis(phenylethynyl)benzene and *p*-nitro-bis(phenylethynyl)-

benzene. By common organic chemistry knowledge, the sequence of the electronic contributing ability of the donors should be: $-H < -CH_3 < -OCH_3 < -SCH_3 < -NH_2 < -NMe_2$. It can be noticed from Table 1 that $\beta_6 > \beta_5 > \beta_3 > \beta_2 > \beta_1 > \beta_4$, $\beta_{12} > \beta_{11} > \beta_9 > \beta_8 > \beta_7 > \beta_{10}$, $\beta_{18} > \beta_{17} > \beta_{15} > \beta_{14} > \beta_{13} > \beta_{16}$, $\beta_{24} > \beta_{23} > \beta_{21} > \beta_{20} > \beta_{22} > \beta_{19}$. So the influence on β of changing the donor substitiuents obeys approximately the same rule of the common electrophilic substitution reactions of aromatics, whether the molecule is *p*-cyano- or *p*-nitro-bis (phenylethynyl)benzene and whether the conjugated area is increased or not, but the $-SCH_3$ is an exception. Thus we can conclude that electronic contributing groups attached to unsymmetry bis-(phenylethynyl)benzenes enhance the value of β. Good electronic push ability can increase the charge transfer in the molecule, thus enhances the value of β. We noticed that the values of β of molecules numbered **4**, **10**, **16** and **22** which have $-SH_3$ substitutent are somewhat low, which is not in agreement with their ordinary electronic push abilities. Experimental results also show the same thing, but Ref. 17 did not give a satisfactory explanation. In order to explain this, we calculated the charge distributions of molecules **9** and **10**, **21** and **22** which have similar structures. The charge distributions of the ground states and excited states of molecules **9**, **10** and **21**, **22** were shown in Fig. 5.

Table 3 Values of β_0 (10^{-28} esu) and $\mu\beta_0$ (10^{-46} esu)

	Calculated values from the SOS formula		Calculated values from two-state formula	
No.	β_0 (10^{-28} esu)	$\mu\beta_0$ (10^{-46} esu)	β_0 (10^{-28} esu)	$\mu\beta_0$ (10^{-46} esu)
1	0.249	1.331	0.245	1.306
2	0.268	1.605	0.249	1.605
3	0.277	1.585	0.293	1.678
4	0.224	1.133	0.232	1.172
5	0.330	2.246	0.325	2.240
6	0.349	2.292	0.374	2.475
7	0.495	2.739	0.558	3.084
8	0.521	3.238	0.555	3.454
9	0.511	2.923	0.619	3.528
10	0.429	2.236	0.499	2.595
11	0.615	4.393	0.684	4.786
12	0.671	4.694	0.801	5.600
13	0.368	2.647	0.518	3.723
14	0.399	3.130	0.561	4.401
15	0.398	2.929	0.552	4.064
16	0.347	2.336	0.483	3.255
17	0.540	4.802	0.733	6.520
18	0.514	4.657	0.697	6.315
19	0.676	5.074	0.923	6.932
20	0.736	6.007	1.015	8.283
21	0.750	5.751	1.014	7.775
22	0.670	4.752	0.906	6.424
23	0.906	8.260	1.219	11.119
24	0.986	9.172	1.322	12.296

In molecule **9**, the charge on $-CH_3$ in the ground state is -0.037, in the excited state is -0.094. The change of charge (ΔQ) is 0.094. In molecule **10**, the charge on $-SCH_3$ in the ground state is -0.033, and in the excited state is -0.026. The change of charge (ΔQ) is 0.007. In molecule **21**, the charge on $-OCH_3$

in the ground state is -0.131, in the excited state is -0.038. The change of charge (ΔQ) is 0.093. In molecule **22**, the charge on $-SCH_3$ in the ground state is -0.032, in the excited state is -0.026. The change of charge (ΔQ) is 0.006. The change of charge in molecule **9** is greater than that of molecule **10**, and the change of charge in molecule **21** is greater than that of molecule **22**. So β value of molecule **9** is greater than that of molecule **10**, and β value of molecule **21** is greater than that of molecule **22**. We also calculated the dipole moments (μ) of molecules **9** and **10**, **21** and **22** in the ground state and excited state (μ_g and μ_e respectively). The dipole moment of molecule **9** in the ground state is $\mu_g = 5.72$, and in the excited state is $\mu_e = 11.68$, and the difference between μ_g and μ_e is $\Delta\mu = (11.68 - 5.72) = 5.96$. The dipole moment of molecule **10** in the ground state is $\mu_g = 5.21$, and in the excited state is $\mu_e = 8.53$, and the difference between μ_g and μ_e is $\Delta\mu = (8.53 - 5.21) = 3.32$. In molecule **21**, μ_g is 7.67, μ_e is 15.30, $\Delta\mu$ is 7.63. In molecule **22**, μ_g is 7.09, μ_e is 12.30, $\Delta\mu$ is 5.21. As expressed in the two-state model formula Eq. (3), β increases when f and $\Delta\mu$ increase and W decreases (λ increases). As shown in Table 1, $f_9 > f_{10}$, $\lambda_9 > \lambda_{10}$, $f_{21} > f_{22}$, $\lambda_{21} > \lambda_{22}$, and more important $\Delta\mu_9 > \Delta\mu_{10}$, $\lambda_{21} > \lambda_{22}$, so the β value of molecule **9** should be greater than that of molecule **10** and the β value of molecule **21** should be greater than that of molecule **22**, judged by Eq. (3). Thus the experimental and computational results have been explained micromechanically.

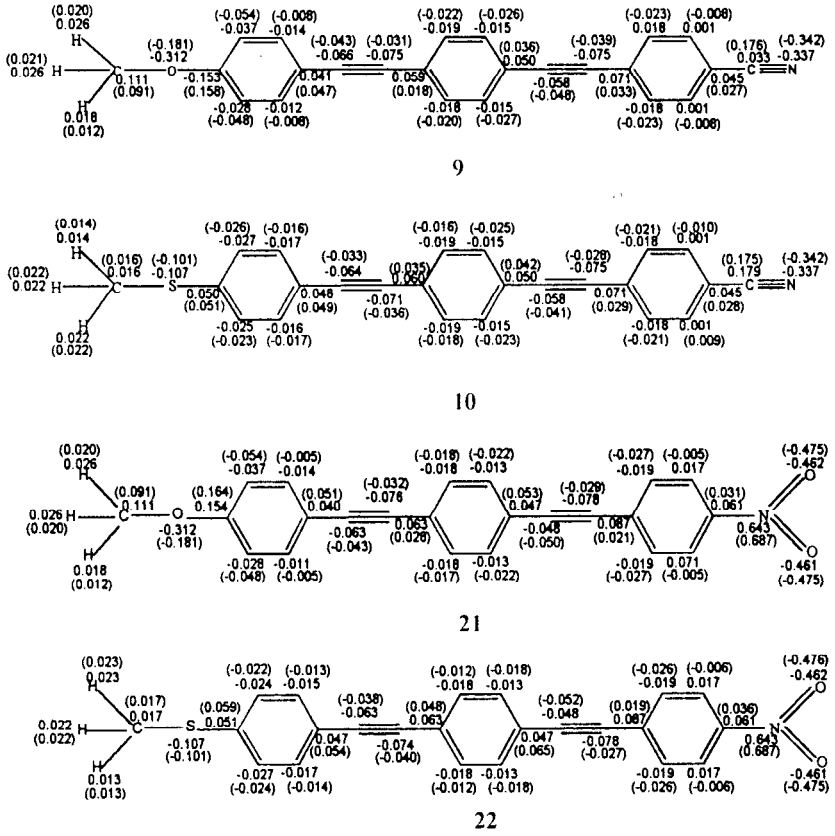

Fig. 5 Charge distributions of the ground state and excited state of **9**, **10** and **21**, **22**.

Influence of acceptor on β

The present paper studied two kinds of acceptors: $-CN$ and NO_2. The calculated results are: $\beta_{13} > \beta_1$, $\beta_{14} > \beta_2$, $\beta_{15} > \beta_3$, $\beta_{16} > \beta_4$, $\beta_{17} > \beta_5$, $\beta_{18} > \beta_6$, $\beta_{19} > \beta_7$, $\beta_{20} > \beta_8$, $\beta_{21} > \beta_9$, $\beta_{22} > \beta_{10}$, $\beta_{23} > \beta_{11}$, $\beta_{24} > \beta_{12}$. It shows that the β values of the molecules attached by $-NO_2$ are all greater than the β values of the counterpart

molecules attached by $-CN$, in a pronounced order.

By common organic chemistry knowledge, the electronic withdrawing ability of $-NO_2$ is greater than that of $-CN$. We can conclude that acceptors attached to unsymmetric bis(phenylethynyl) benzene series derivatives facilitate β. Substituents with greater electronic withdrawing ability can further increase the charge transfer in the molecules, thus enhancing the β values.

Influence on β of extending conjugated areas

β values increase when conjugated chains are elongated, as indicated in Table 2. It shows the same rule for all the substituents, that is: $\beta_7 > \beta_1$, $\beta_8 > \beta_2$, $\beta_9 > \beta_3$, $\beta_{10} > \beta_4$, $\beta_{11} > \beta_5$, $\beta_{12} > \beta_6$, $\beta_{19} > \beta_{13}$, $\beta_{20} > \beta_{14}$, $\beta_{21} > \beta_{15}$, $\beta_{22} > \beta_{16}$, $\beta_{23} > \beta_{17}$, $\beta_{24} > \beta_{18}$. It can be explained by the fact that f and λ all increase when conjugated chains are elongated, as shown in Table 1: $f_7 > f_1$, $\lambda_7 > \lambda_1$, $f_8 > f_2$, $\lambda_8 > \lambda_2$, $f_9 > f_3$, $\lambda_9 > \lambda_3$, $f_{10} > f_4$, $\lambda_{10} > \lambda_4$, $f_{11} > f_5$, $\lambda_{11} > \lambda_5$, $f_{12} > f_6$, $\lambda_{12} > \lambda_6$, $f_{19} > f_{13}$, $\lambda_{19} > \lambda_{13}$, $f_{20} > f_{14}$, $\lambda_{20} > \lambda_{14}$, $f_{21} > f_{15}$, $\lambda_{21} > \lambda_{15}$, $f_{22} > f_{16}$, $\lambda_{22} > \lambda_{16}$, $f_{23} > f_{17}$, $\lambda_{23} > \lambda_{17}$, $f_{24} > f_{18}$, $\lambda_{24} > \lambda_{18}$.

It is worth noting from Table 1 that β values are greatly enhanced when conjugated chains are elongated, while the red-shift of the maximum absorption peaks is not very big; even for the molecule **24** the longest wave length is only 368.4 nm, still in UV section. It indicates that these molecules have big nonlinear optical susceptibilities and remain good transparency when the conjugated chains are elongated. It is the main advantage of these molecules to be nonlinear optical materials.

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