

Theoretical Studies on Electronic Spectra and Second-order Nonlinear Optical Properties of Barbituric Acid Derivatives Substituted with Schiff Base

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The structures of barbituric acid derivatives substituted with Schiff base were optimized using *ab initio* HF method at 6-31G basis set. Based on the optimized structures, the electronic spectra were obtained by INDO/CI method. The second-order nonlinear optical (NLO) coefficients β_{μ} were calculated according to the sum-over-states (SOS) formula. In addition, the effect of conjugation on electronic spectra and second-order NLO coefficients was investigated. The influence of exchange between C and N atoms as well as the substituted effect on the barbituric acid was discussed. It was indicated that the exchange between C and N atoms on Schiff base is important for enhancing the NLO coefficient of the whole molecule with donor and acceptor (D-A). Meanwhile significant changes in electron donation and acceptance were observed as substituents changes positions. Among the designed models, molecule **1b** has maximal β_{μ} value of 124.65×10^{-30} esu. About molecule **1b**, barbituric acid is considered as an accepted electronic group and the position of N atom on Schiff base is close to it.

Keywords INDO/CI, NLO, electronic spectra

Barbituric acid (BA) is a very important kind of compound in biological chemistry and medicine. It can be applied in abirritative medicine and antioxidants.¹ It is an important sort of raw material for organic synthesis.² It predicts the important reactive mechanism for organic synthesis.³ Some investigations for NLO properties of a series of BA derivatives have been reported by Feng and coworkers in the view of theory.^{4,5}

The Schiff base has extensive application in the fields of organic synthesis, leechdom^{6,7} and molecule pincers.⁸ Because Schiff base and its derivatives with structure of donor and acceptor (D-A) have the stability in ultraviolet,^{9,10} Schiff base becomes one of the focuses of theoretical investigation. They have extensive application in material science, photoelectricity and NLO.¹¹

The material exhibiting second harmonic generation responses, in particular those better NLO materials with D- π -A structure and real photoelectricity, have attracted much recent scientific interest.¹² Both BA and Schiff base are excellent candidates for gaining NLO property. However, BA derivatives with Schiff base substitution were seldom reported. Based on the idea of molecular tailor and our earlier theoretical investigation,¹³⁻¹⁵ the

NLO properties and electronic spectra were calculated on model systems in title.

Theoretic method and calculation models

INDO/CI method was proved to be better consistency in calculating organic conjugation UV-Vis spectrum. Molecular orbitals were obtained through INDO/CI method. Electronic spectra were gained according to oscillator strength and transition energy from calculation. Difference of calculating in spectrum is comparatively larger for BA using standard parameter of INDO in ordinary, so the parameter value of p- π that we summarized early is still applied by 0.415.

When a molecule is polarized in electric field, the dipole moment can be expressed:

$$\mu_i = \mu_i^0 + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \dots$$

In this equation, β_{ijk} is the first hyperpolarizability (second order effect) and γ_{ijkl} is the second hyperpolarizability (third order effect).

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The first hyperpolarizability β_{ijk} was generally acquired through the principle of second harmonic generation (SHG). β_{ij} was calculated as projection of the direction of dipole moment. Molecular polarizabilities were deployed using sum-over-states (SOS) of time-dependent perturbation theory, and the value β_{ijk} was calculated by addition.

A series of models were designed and calculated (Figure 1). Electronic spectra and NLO properties were studied through the exchange between C and N atoms in Schiff base, different substituents of *p*-benzene and different substitution position of the Schiff base on the BA.

Results and discussion

Firstly, the geometrical structures of systems **1a–4c** were chosen as models and optimized using HF method at 6-31G basis set level. The molecules were fixed in *xy* plane and *z* axis is perpendicular to the plane. Direction of *x* axis is consistent with that of dipole moment. All calculations were performed on PentiumIV 1.5G PC, using Gaussian98 package.

Total energy of the system, main bond lengths and distribution of net charge after optimization are listed in Table 1.

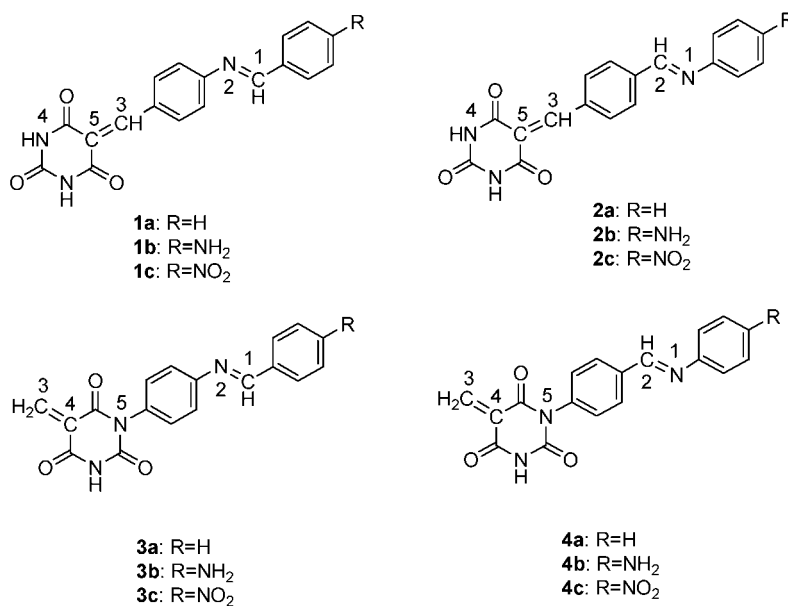


Figure 1 Calculation models of BA derivatives.

Table 1 Total energy (a.u.) and net charge (e) in the systems **1a–4c**

System	Energy/a.u.	Bond length/nm		Net charge/e		
		C(1)=N(2)	C(3)=C(4)	C(4)	N(2)	C(1)
1a	-1076.7456	0.12686	0.13604	-0.105	-0.62	0.15
1b	-1131.7583	0.12729	0.13622	-0.104	-0.641	0.161
1c	-1280.0953	0.12654	0.13578	-0.108	-0.605	0.142
2a	-1076.7442	0.12645	0.13590	-0.105	-0.594	0.123
2b	-1131.7547	0.12652	0.13604	-0.104	-0.584	0.16
2c	-1280.0956	0.12665	0.13566	-0.108	-0.61	0.144
3a	-1076.7021	0.12663	0.13301	-0.265	-0.609	0.136
3b	-1131.7135	0.12691	0.13302	-0.265	-0.627	0.147
3c	-1280.0539	0.12642	0.13306	-0.262	-0.594	0.128
4a	-1076.7015	0.12652	0.13303	-0.264	-0.603	0.137
4b	-1131.7108	0.12651	0.13302	-0.265	-0.593	0.122
4c	-1280.0549	0.12681	0.13306	-0.262	-0.618	0.156

The systems were divided into three groups of isomeric compounds: the systems **1a**–**4a** have no substituent on the benzene; the systems **1b**–**4b** have amino on *para* position of benzene; the systems **1c**–**4c** have nitro on *para* position of benzene. It can be seen from Table 1 that Schiff base substitutes on the different position of BA, the energy of substitution on C atom is lower than that on N atom, and the energy difference is about 0.04 a.u.. For substitute of Schiff base on the same position of BA, the energy difference is about 0.001 a.u. when C and N atoms were exchanged on characteristic bond C=N. When the discussed systems were synthesized by the Schiff base and BA, the product is probably the mixture of systems **1** and **2** or **3** and **4**.

The change of the bond length of ethylene is obvious. C=N bonds of systems **1** and **2** are longer than those of systems **3** and **4** by about 0.002 nm. It shows that the ability of accepting electron is increased for ethylene, when the position of substituent exchanges between C and N atoms. At the same time, net charge distribution on C atom of BA shows the same phenomena, and its value is reduced about 0.16 e.

Frontier molecular orbitals

It is necessary that FMO should be discussed when NLO properties were researched. The FMO of **1b** are showed in Figure 2 and the energies of HOMO and LUMO of system **1a**–**4c** are presented in Table 2.

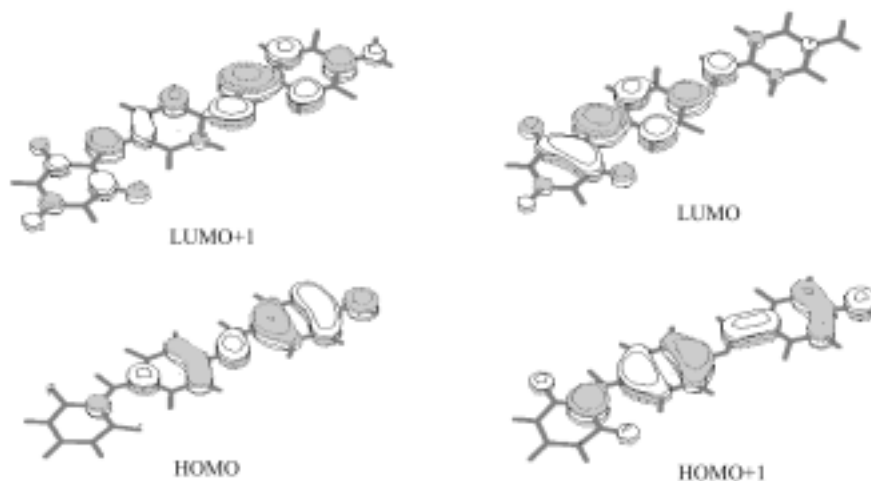


Figure 2 Frontier molecular orbitals of **1b** calculated with HF/6-31G.

Table 2 Energies of HOMO and LUMO of systems **1a**–**4c**

System	LUMO	HOMO	System	LUMO	HOMO
1a	0.00850	−0.30951	3a	0.03128	−0.29512
1b	0.01497	−0.28105	3b	0.03427	−0.26808
1c	−0.01093	−0.33184	3c	0.01528	−0.31812
2a	0.08048	−0.30916	4a	0.03004	−0.29529
2b	0.01087	−0.27606	4b	0.03280	−0.26412
2c	−0.01265	−0.33501	4c	0.01742	−0.32152

The electron cloud distributions of the HOMO and LUMO are quite different from each other. The components of HOMO mainly concentrate on aniline while those of LUMO dominantly concentrate on BA. The NLO properties will enlarge obviously due to remarkable charge transfer in process of electronic excitation of such a molecule, which will be proved by following calculation. Maximal absorption of molecule **1b** for the transition from HOMO to LUMO is 471 nm and corresponding oscillator strength is 1.13.

The energy differences of systems **1b**–**4b** that contain amino are less. Contrarily, the energy differences of systems **1c**–**4c** that contain nitro are larger. It shows that electronic transition is very easy for the systems containing amino. The systems including nitro are contrary.

The electronic spectra of the molecules were calculated by INDO/SUM. Three maximal wavelengths λ and corresponding oscillator strength f of the systems are listed in Table 3.

(1) The influence of different substituted group on electronic spectra

For the system **1**, the maximal absorption shows red shift according to the change from the acceptor to donor when different substitute groups were introduced into them. The regularity is: $\lambda_{1b} > \lambda_{1c} > \lambda_{1a}$. It is the reason why electron is easier to transfer when the group as donor was introduced into the system.

Table 3 Electronic spectra of systems **1a–4c**

System	λ/nm	f	System	λ/nm	f
1a	457	1.02	3a	363	0.84
	234	0.57		221	0.51
	231	0.39		238	0.47
1b	471	1.13	3b	377	0.92
	236	0.93		239	0.72
	233	0.49		227	0.49
1c	450	1.24	3c	452	0.66
	231	0.72		212	0.62
	212	0.67		225	0.60
2a	410	1.02	4a	361	0.81
	230	0.68		214	0.63
	215	0.39		239	0.60
2b	459	1.08	4b	381	0.53
	238	0.36		241	0.50
	240	0.34		216	0.67
2c	456	1.14	4c	461	0.68
	230	0.53		227	0.81
	233	0.45		224	0.60

(2) The influence of position change between the C and N atoms in the Schiff base on the electronic spectrum

There are some changes in electronic spectra of system **2** in comparison with system **1**. Wavelength of maximal absorption shows blue shift between **2c** and **2a**. It is the reason of this kind of phenomenon that positions of the C and the N atoms in the Schiff base were exchanged. It makes intramolecular direction of dipole moment of C=N contrary to that of whole system after exchanging. On the respect of ability of electronic transfer, the nitro is stronger than the BA, and it shows that $\lambda_{1a} > \lambda_{2a}$, $\lambda_{1b} > \lambda_{2b}$, but $\lambda_{1c} < \lambda_{2c}$.

(3) The influence of Schiff base substitute on the electronic spectra

Comparing the isomeric compounds **3a** and **1a**; **3b** and **1b**; **4a** and **2a**; and **4b** and **2b**, shows red shift. For the isomeric compounds of **3c** and **1c**, **4c** and **2c**, it shows blue shift. The BA is regarded as acceptor due to

three carbonyls on the BA when Schiff base group substitutes on the C atom of BA. Although there are three carbonyls on the BA, the BA is regarded as donor because of a couple of lone paired electrons on the N while Schiff base group substitutes on the N atom of BA, lone paired electrons of N counteract the role of pulling electron of BA in the molecules **3a**, **3b**, **4a** and **4b**. It is obviously that red shift phenomena were shown. But it is contrary for molecules **3c** and **4c** containing stronger acceptor group on the benzene of another aspect of the system.

Second order NLO coefficients

β_{ijk} and β_{ii} were calculated for each configuration of molecule **1b** from 1 to 197. The curve of the first hyperpolarizability was drawn about relation between β and the number N of excited singlet states for system **1b** (Figure 3). It is convergent when N arrived on the one hundred and the fortieth point. It is reasonable to adopt 196 excited states in the paper. The values of β_{ii} are arranged in Table 4, when frequency of electronic field is 0 in the process of calculation.

The values of dipole moment are in direct proportion with those of NLO coefficient basically. The maximal β is about 124.65×10^{-30} esu for whole systems. Based on standard of NLO coefficient, 10×10^{-30} — 100×10^{-30} esu is relatively big. All of the systems above are in accord with this standard. For the systems **1** and **2**

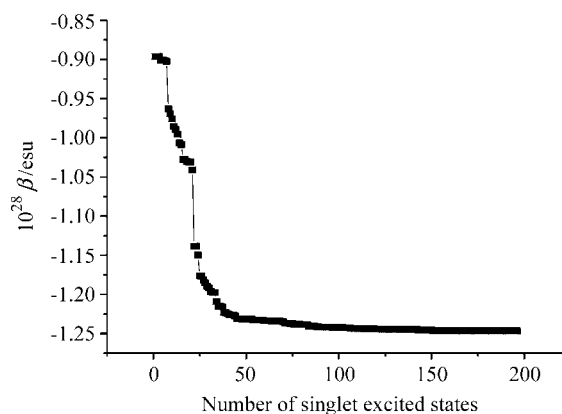


Figure 3 Relationship between β and number of singlet excited states for system **1b**.

Table 4 Calculated μ and β values of systems **1a–4c**

System	$\mu/(10^{-30} \text{ C.M})$	$\beta/(10^{-30} \text{ esu})$	System	$\mu/(10^{-30} \text{ C.M})$	$\beta/(10^{-30} \text{ esu})$
1a	24.48619	89.613	3a	6.71129	10.617
1b	32.02972	124.65	3b	6.80368	22.711
1c	18.65718	36.856	3c	23.40278	59.34
2a	19.15886	46.737	4a	11.21039	20.24
2b	25.79743	71.529	4b	11.43654	19.794
2c	14.38357	53.489	4c	30.55137	96.976

and molecules **3c** and **4c**, their transparent nature are in the visible light and it is not very conformable. For the molecules **3a**, **3b**, **4a** and **4b**, although their maximal absorptions are in the ultraviolet region, their NLO coefficients are not good as the former.

Conclusions

When Schiff base substitutes on the C atom of the BA, substituted group containing pushing electronic group will get favored NLO coefficient such as **1b**, while substitution reaction happened on the N atom of the BA, contrary to the former is pulling electronic substitution group is favored of getting better NLO coefficient such as **4c**.

In order to get better NLO coefficient, the structure of donor-acceptor of C=N is consistent with that of the whole molecule. When Schiff base substitution happens on different atom on BA, substitution on C atom is better than that on N atom. It is the appropriate choice for the molecules **3c** and **4c** in order to get the wavelength of molecular maximal absorption in the ultraviolet region.

Among the whole systems, molecule **1b** has maximal NLO coefficient by 124.65×10^{-30} esu and maximal absorption by about 471 nm.

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