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Theoretical study on the organic molecular second-order hyperpolarizability

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Abstract. The molecular second-order hyperpolarizabilities β of several series of substituted aromatic compounds have been calculated using the CNDO/S-CI method and perturbation theory. A systematical study was carried out and we found that there was a close relationship between the molecular structure and β. The β value usually increases with the strength of the substituents except for fluoro group. Chloro is amphiprotic in contributing to molecular nonlinearity. Of the donor groups Br, CH_3, OCH_3 and Cl are the best candidates according to S, which is defined as the criterion of choosing the groups in molecular designing for second-order nonlinear optical materials. The donor-acceptor para-disubstitution is the most effective comparing to the meta- or ortho-disubstitutions, and the contribution of the extending of conjugated system to β is dominant whereas that of the substitutions takes second place.

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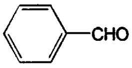
The current interest in finding organic nonlinear optical (NLO) materials is a result of the promising potential applications in optical information processing, telecommunications, and integrated optics [1], as well as the much larger nonlinear response, extremely fast switching time, and higher laser damage threshold compared to the currently studied inorganic materials. To have useful second-order nonlinear optical properties, the compound must possess a large second-order molecular nonlinearity and also be crystallized in a noncentrosymmetric structure to have a nonzero $x^{(2)}$.

Since optical nonlinear response of organic materials is related to both the magnitude of the molecular hyperpolarizability and the alignment of the molecules in the medium [2], the magnitude of the molecular second-order hyperpolarizability β should first be enhanced in order to increase the macroscopic nonlinearities of NLO materials. That is to say, the molecular hyperpolarizability β plays an important role in the NLO properties and a systematical study on β should be carried out.

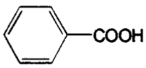
Generally, β increases when strong donor and acceptor groups are attached and π-conjugation is elongated [3, 4]. But very strong donor or acceptor groups and large-conjugated system usually cause redshift of the first electronic absorption peak [5] and therefore the transparency of the NLO materials will decrease, which is unexpected in application fields. However, it seemed that the small conjugated system is more suitable for the useful NLO materials, especially for the transparency. In the present work, we have chosen several kinds of compounds with fairly small conjugated molecular system and studied the effects of different substituents on the conjugated π-electron system.

The molecular structures of the compounds discussed in this manuscript

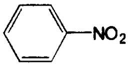

benzene



benzaldehyde



benzoic acid



nitrobenzene

1 Calculation method

In the dipolar approximation, the polarization induced in a molecule by an external field $\boldsymbol{E}$ can be written as

$$\boldsymbol{P} = \alpha \boldsymbol{E} + \beta \boldsymbol{EE} + \gamma \boldsymbol{EEE} + \cdots \ , \tag{1}$$

where the vector quantities $\boldsymbol{P}$ and $\boldsymbol{E}$ are related by the tensor quantities α, β, and γ, which are often referred to as the linear, second, third hyperpolarizabilities, respectively. In this formalism the even-order tensor β is zero in centrosymmetric media, so a lack of a center of inversion in the organic molecule is required for nonvanishing of β.

An induced molecule in an electric field $\boldsymbol{E}$ can be considered as perturbation, the perturbing operator is $\boldsymbol{H}' = -e\boldsymbol{rE}$, where $\boldsymbol{r}$ is a general coordinate of the molecule. According to perturbation theory and Born–Oppenheimer approximation the second-order hyperpolarizability tensor can be expressed as [6, 7]

$$\begin{aligned}\beta_{ijk}+\beta_{ijk}=\frac{-e^3}{4\hbar^2}\Bigg[&\sum_{n\neq g}\sum_{n\neq n}\sum_{n'\neq g}\left(r^j_{gn}r^i_{n'n}r^k_{gn}+r^k_{gn'}r^i_{n'n}r^j_{gn}\right)\\ &\times\left(\frac{1}{(\omega_{ng}-\omega)(\omega_{ng}+\omega)}+\frac{1}{(\omega_{ng}+\omega)(\omega_{ng}-\omega)}\right)\\ &+\left(r^i_{gn'}r^j_{n'n}r^k_{gn}+r^i_{gn'}r^k_{n'n}r^j_{gn}\right)\left(\frac{1}{(\omega_{ng}+2\omega)(\omega_{ng}+\omega)}\right.\\ &\left.+\frac{1}{(\omega_{ng}-2\omega)(\omega_{ng}-\omega)}\right)+\left(r^j_{gn'}r^k_{n'n}r^i_{gn}+r^k_{gn'}r^j_{n'n}r^i_{gn}\right)\\ &\times\left(\frac{1}{(\omega_{ng}-\omega)(\omega_{ng}-2\omega)}+\frac{1}{(\omega_{ng}+\omega)(\omega_{ng}+2\omega)}\right)\\ &+4\sum_n\left[r^j_{gn}r^k_{gn}\Delta r^i_n\left(\omega^2_{ng}-4\omega^2\right)\right.\\ &\left.+r^i_{gn}\left(r^k_{gn}\Delta r^j_n+r^j_{gn}\Delta r^k_n\right)\left(\omega^2_{ng}+2\omega^2\right)\right]\\ &\times\frac{1}{(\omega^2_{ng}\omega^2)(\omega^2_{ng}-4\omega^2)}\Bigg]\,. \end{aligned} \tag{2}$$

Here $i,\ j,\ k$ are the components of cartesian coordinates, β_{ijk} is the component of the second-order hyperpolarizability tensor in the direction of (ijk), $r^i_{gn},\ r^i_{nn'}$ represent the electron transition matrix element:

$$r^i_{gn}=\langle g|r^i|n\rangle\ ,\quad r^j_{nn'}=\langle n|r^i|n'\rangle\ . \tag{3}$$

$|g\rangle$ is the ground state wavefunction while $|n\rangle$, $|n'\rangle$ are the wavefunctions of two different excited molecular states. ω_{ng}, $\omega_{n'g}$ are the molecular transition frequencies from the excited to the ground state and ω is the external field frequency. The change of the dipole moment between excited and ground state is $e\Delta r^i_n$, $\Delta r^i_n=r^i_{nn}-r^i_{gg}$.

We calculated the second-order hyperpolarizabilities of the chosen compounds with the CNDO/S-CI quantum chemistry program [8], in which we used the perturbation theory and (2) to calculate the β values. In terms of the calculated results, we have changed the tensor to vector so that the calculated values are comparable with experimental results. Thus the tensor β_{ijk} is changed to vector β_{vec} as follows, and the semi-empirical parameters of related atoms are given in [9].

$$\begin{aligned}&\beta_{\mathrm{vec}}=(\beta_x^2+\beta_y^2+\beta_z^2)^{1/2}\ ,\\ &\beta_i=\frac{1}{3}\sum_k(\beta_{ikk}+\beta_{kik}+\beta_{kki})\ ,\quad i,k=x,y,z\ .\end{aligned} \tag{4}$$

2 Results and discussion

2.1 Substitution dependence of β

In order to investigate the effect of different acceptor groups on second-order hyperpolarizability we calculated five benzene (C_6H_6) derivatives substituted with different acceptors, and the results are listed in Table 1. The calculated results reveal that the enhancement of β increases with the strength of the acceptor groups. For example, the nitrobenzene ($C_6H_5NO_2$) has the largest β whereas that of benzoic acid ($C_7H_6O_2$) is fairly small. Perhaps this is the result of the accepting-electron abilities of the acceptors.

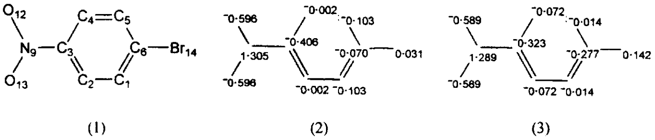
Table 1. The calculated β values of benzene derivatives ($\times 10^{-30}$esu)

Acceptor	CHO	COOH	$COCH_3$	CN	NO_2
β	6.34	4.78	5.55	8.67	10.72

Table 2 lists the β values of some disubstituted aromatic compounds, including benzaldehyde (C_7H_6O), benzoic acid, nitrobenzene, and their para-substituted derivatives. In these donor–acceptor systems the nitro (NO_2), carboxy (COOH), and aldehyde (CHO) groups act as acceptor radicals and various donor groups are attached on the para-position so that the contributions of different donors to the hyperpolarizabilities β are comparable. From the results we can see that when the conjugation system is para-substituted by F group β will decrease, which reveals that F group is not a good donor and can reduce the intromolecular charge transfer, as well as the molecular nonlinearity. Here Cl is an amphiprotic group, its contribution to β is different when the para-position of the molecular conjugation system is attached to a different acceptor group. When the substituted acceptor is very strong, the Cl group acts as a strong donor and can improve the hyperpolarizability obviously. But when the acceptor is relatively weak (for example carboxy group), the improvement of β is very small. The β values of the other compounds are improved greatly with the increasing of the electron-donating ability of their donors, of which the Br group is the best one.

In order to understand the origin of the large β values of the Br-substituted compounds, the charge distribution of p-bromonitrobenzene was calculated. Figure 1 shows the molecular structure and the net charge distribution in the ground and the first excited states. The charge on the Br group in the first excited state is much more than that in the ground state, which indicates that Br is a strong electron donor. On the other hand, the NO_2 group is a strong electron acceptor and so the intromolecular charge transfer is from NO_2 to Br group along the $N_9 \rightarrow$ Br direction. It is this charge asymmetry that gives rise to a large second-order hyperpolarizability. Besides the good electronic property the p-bromonitrobenzene has fairly good planar molecular structure, which supplies an excellent electron tunnel and the molecular electron transfer is more improved. That is, the large molecular nonlinearity of the Br-substituted compounds is the result of the strong molecular charge transfer.

A useful NLO material needs not only strong nonlinearity but also good transparency [5, 10], so the cut-off wavelength should be considered carefully when we design an effective



(1) (2) (3)

Fig. 1. The molecular structure of p-bromonitrobenzene (1), and the charge distribution of the ground (2) and the first excited state (3)

Table 2. β values of the para-disubstituted molecules D-C_6H_4-A* ($\times 10^{-30}$esu) *A-acceptor, D-donor

	H	F	Cl	Br	OH	NH_2	CH_3	OCH_3	$NHCH_3$	$NHCOCH_3$
CHO	6.34	4.24	7.88	21.24	7.74	10.03	8.24	10.06	13.94	11.77
COOH	4.78	3.26	4.16	17.02	8.04	9.58	7.40	9.07	9.33	15.48
NO_2	10.72	8.73	15.76	27.02	12.82	18.01	14.32	16.16	19.89	21.66

Table 3. λ values of different donor groups (unit: nm)

	Br	CH_3	Cl	OCH_3	OH	$NHCOCH_3$	NH_2	NR_2
λ(p)	15	10	10	25	25	45	58	85
λ(m,o)	2	3	0	7	7	20	13	20

NLO material. To solve this problem we define:

$$S = \Delta\beta/\lambda = (\beta_s - \beta_u)/\lambda \,, \tag{5}$$

here β_s is the second-order hyperpolarizability of a substituted molecule, and β_u is that of a unsubstituted molecule, so $\Delta\beta$ is the substituent contribution to the molecular second-order hyperpolarizability, λ (unit: nm) is the redshift wavelength caused by the studied group attached on the benzene ring. So S includes the substituent contribution to the molecular nonlinearity and the substituent effect on the transparency of the material. Table 3 lists the λ values of different donors and p, m, o refer to para-, meta- and ortho- substituted position, respectively.

We can give an order of the donors above according to their S values approximately: Br > CH_3 > Cl > OCH_3 $\approx$ $NHCOCH_3$ > NH_2 $\approx$ $NHCH_3$ > OH. Considering nonlinear properties and cut-off wavelength, Br, Cl, CH_3, and OCH_3 groups are the best candidates for useful NLO materials. Thus S may act as the standard of choosing groups in designing suitable nonlinear molecules.

Since the intromolecular electron transfer usually occurs from a donor to an acceptor the molecular second-order hyperpolarizability β should be anisotropy [11]. The following are the calculated results of p-methylnitrobenzene and Fig. 2 shows its molecular structure and coordinate system.

μ_x	μ_y	μ_z	μ
0.24	6.74	0	6.74(D)

β_{xxx}	β_{yyy}	β_{zzz}	β
0.75	14.30	0	14.32($\times 10^{-30}$esu)

The molecule lies in the (xy) plane and we chose the acceptor (NO_2)-donor (CH_3) axis as y axis, the noncoplanar hydrogen atoms of methyl group are neglected. β_{zzz} and μ_z are zero because the z axis is perpendicular to the molecular plane and so there is no charge transfer along this direction. β_{yyy} and μ_y are much larger than the components along the x axis and their directions are the same as the charge transfer direction ($NO_2 \rightarrow CH_3$). The calculated results reveal that nearly all the contributions to β and μ are from their y components, if we neglect β_{xxx} then the second-order hyperpolarizability β of p-methylnitrobenzene can be considered one dimensional to a good approximation along the y axis. That is to say, intromolecular charge transfer is indeed the origin of molecular second-order nonlinearity and they have the same direction.

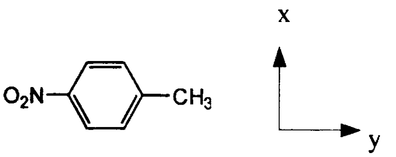


Fig. 2. Molecular structure and coordinate system of p-methylnitrobenzene

2.2 *Substituent location effect*

For disubstituted aromatic compounds, the molecular second-order hyperpolariability must be different because of the different substituted location of the radicals. We calculated β of the benzaldehyde, benzoic acid, and nitrobenzene derivatives and studied the substituted location dependence of β when the donors of these molecules was attached on para-, meta-, and ortho-position, respectively. Table 4 gives the β values of these derivatives.

Of the donors in Table 4, F and Cl groups are different from the others. β of ortho-substituted molecules by F is the largest whereas the para-substituted ones is the smallest. The changes of β of the Cl-substituted molecules are more complicated. When the acceptor is fairly strong (for example NO_2 or CHO), β(p) is larger than the others and β(m) is relatively weak. But when the acceptor is weak (for example COOH). β(o) is the biggest and β(m) is very small. From the other results in Table 4, one can immediately note that β values of all para-disubstituted molecules are biggest, then the meta-disubstituted benzenes, and finally the ortho-disubstituted ones. In other words, we can draw a conclusion from these data that the para-disubstituted molecules with various donor–acceptor combinations usually have strongest molecular nonlinearities except for F and Cl groups. F and Cl groups have their own characteristics.

Table 4. Calculated β values of the chosen aromatic molecules ($\times 10^{-30}$esu)

	F	Cl	Br	OH	NH_2	CH_3	OCH_3
Benzaldehyde derivatives							
p	4.24	7.88	21.24	7.74	10.03	8.24	10.06
m	6.20	3.69	9.92	8.47	7.86	7.53	9.32
o	7.02	3.89	7.97	6.81	4.48	5.28	8.58
Benzoic acid derivatives							
p	3.26	2.16	17.02	8.04	9.58	7.40	9.07
m	5.33	0.44	7.83	7.73	7.10	6.44	8.21
o	6.26	6.01	9.12	4.05	3.69	4.47	7.40
Nitrobenzene derivatives							
p	8.26	15.76	27.02	12.82	18.01	14.32	16.16
m	8.71	5.85	12.28	11.51	12.77	11.34	12.55
o	11.08	6.10	12.03	8.86	9.83	10.55	9.85

Table 5. β values of the multisubstituted benzaldehyde molecules ($\times 10^{-30}$esu)

Substituted locations	3,4	2,4	2,3,4	2,3,4,5	2,3,4,5,6
OH	6.88	8.27	5.77	6.11	5.80
CH_3	9.38	6.98	9.02	10.49	11.25
OCH_3	12.59	8.62	42.03	34.99	55.36

2.3 Multisubstitution effect

Here the multisubstituted molecules refer to the benzaldehyde molecules with two or more donors. To understand the contributions of multisubstitutions to the molecular nonlinearity we calculated the benzaldehyde derivatives substituted with two or more OH, CH_3 or OCH_3 donors. Table 5 gives the calculated results.

To our surprise, the results in Table 5 show that the second-order polarizabilities β have not yet been improved obviously because of the multisubstitution of the OH or CH_3 groups. Some of the β values even decrease comparing to that of the para-disubstituted molecules. So it is not effective to improve the molecular nonlinearity through the multisubstitution of OH or CH_3 donors. On the contrary, OCH_3 multisubstituted compounds have fairly bigger β values, especially for the 2,3,4-trisubstituted and the 2,3,4,5,6-penta-substituted ones. It is effective to improve the molecular nonlinearity through the multisubstitution of OCH_3 group.

Table 6 lists the β values of the p-hydroxybenzaldehyde ($C_7H_6O_2$) derivatives. These molecules are the derivatives of p-hydroxybenzaldehyde substituted with one or two CH_3 or OCH_3 groups. As we have discussed previously, CH_3 and OCH_3 groups are effective in improving the second-order hyperpolarizability, but the results show that the β values have not been enhanced obviously after p-hydroxybenzaldehyde is substituted by CH_3 or OCH_3 group, some of them even become smaller than that of p-hydroxybenzaldehyde. It seemed that the β values of the molecules in Table 6 were determined by OH donor, which is inactive in improving the molecular nonlinearity. The CH_3, OCH_3 donors have few contributions to β when a hydroxy group exist in a molecule.

2.4 Carbonyl location and conjugated system dependence of β

It is well known that the conjugated donor–acceptor-substituted molecules have generally large hyperpolarizabilities because the delocalized π-electrons give rise to charge transfer. In order to ascertain the relationship between the molecular conjugation system and the second-order hyperpolarizability β we have calculated the (values of some unsaturated carbonyl compounds and the results are listed in Table 7.

Table 6. β values of the multisubstituted p-hydroxybenzaldehyde ($\times 10^{-30}$esu)

Substituted locations of CH_3	2	3	2,3	3,5	2,6
β	6.64	8.86	7.85	9.90	7.03
Substituted locations of OCH_3	2	3	2,3	3,5	2,6
β	6.98	6.20	7.76	6.58	9.52

Table 7. β values of the unsaturated carbonyl compounds ($\times 10^{-30}$esu) p-R_1–C_6H_4–$(CH{=}CH)_n$–CO–C_6H_4–R_2-p′

Series	R1	R2	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$
1	H	H	8.59	19.66	31.81	50.70	84.04
2	OCH_3	H	25.66	49.89	97.93	159.45	250.45
3	NH_2	NO_2	39.98	78.24	128.66	190.04	279.66
4	OCH_3	NO_2	58.53	101.62	152.98	234.70	345.39

The carbonyl group in the molecule acts as an acceptor and the whole conjugated system was disturbed, which can produce a large hypsochromic shift of cut-off wavelength of transmission. Of these kinds of compounds some excellent NLO matericals such as BMC (4-bromo-4′-methoxy chalcone) were found [12, 13], and this is just the reason why we investigate these kinds of compounds in the present work. We studied four series of unsaturated carbonyl compounds substituted with different groups at their two benzene rings, and the corresponding four teams of data can be fitted by least-square method as following, respectively:

Series	Equation
1	$\ln\beta = 0.482n + 2.495$
2	$\ln\beta = 0.572n + 3.320$
3	$\ln\beta = 0.477n + 3.804$
4	$\ln\beta = 0.438n + 4.128$

From the results we can see that β increases rapidly with the extending of the molecular conjugated system and the relationships between β and n (the number C=C in the molecular system) of these four series of compounds are very similar. The molecules, except for series 1, are substituted with OCH_3, NO_2, or NH_2 radicals at their benzene rings, these radicals can improve the β values obviously when the number n is certain for every molecule. But the changes of β caused by these radicals are much weaker than that of the extending of the molecular conjugation system, that is the increase of n, as can be easily noted from the data in Table 7. So it can be concluded that the contribution of the extending of the conjugation system to β is dominant and that of the substitution takes second place.

The electron-accepting ability of the carbonyl group is much weaker than that of nitro group, but the carbonyl group lies in the molecular-conjugated system and so it can greatly influence the charge transfer of the delocalized π-electron,

Table 8. β values of the molecules p-R_1–C_6H_4– $(CH{=}CH)_n$–CO–$(CH{=}CH)_m$–C_6H_4-R_2-p′ ($\times 10^{-30}$ esu)

R1	R2	$n=4$ $m=0$	$n=3$ $m=1$	$n=2$ $m=2$	$n=3$ $m=0$	$n=2$ $m=1$	$n=2$ $m=0$	$n=1$ $m=1$
H	H	84.04	37.87	30.21	50.70	23.24	31.81	14.51
OCH_3	H	250.45	189.29	144.04	159.45	119.24	97.93	65.66
NH_2	NO_2	179.66	207.80	182.81	190.04	138.13	128.66	92.60
OCH_3	NO_2	345.39	288.04	225.53	234.70	193.46	152.98	117.37

and therefore the molecular nonlinearity, as can be proved by the calculated β values in Table 8.

For the same kind of substituted compounds their β values are different with the change of the carbonyl location. To simplify the problem, we express the carbonyl location through different n and m values. When the carbonyl is located on the end of the conjugation system ($m = 0$), the molecular second-order hyperpolarizability shows the maximum value. But with the moving of the carbonyl group to the middle of the conjugated molecule the β value decreases until it is minimum while the carbonyl group lies in the middle of the molecule ($m = n$). With the moving of the carbonyl to the middle of the molecular system the distance of the charge transfer becomes shorter and shorter, which is the main reason that the β values decrease. The change of β is about $30\text{–}60 \times 10^{-30}$ esu per C=C double bond distance moved. All of the results and discussions above show that the carbonyl group has the greatest contributions to molecular nonlinearity when it is located on the end of the molecule. On the other hand, when the two benzene rings were attached acceptors or donors the carbonyl group should be near to the substituted acceptor. Such molecular structure can give rise to fairly strong molecular nonlinearity, which is the basis of a useful NLO material.

3 Conclusion

We have calculated the molecular second-order hyperpolarizabilities β of several series of substituted aromatic compounds, including benzene derivatives, benzoic acid derivatives, benzaldehyde derivatives, and the unsaturated carbonyl compounds using the CNDO/S-CI method and perturbation theory, and a systematic study has been carried out. β values usually increase with the strength of the acceptors and donors. But fluoro generally reduce the intromolecular charge transfer and therefore the molecular nonlinearity, and chloro is an amphiprotic group in contributing to the microscopic nonlinearity. Considering the nonlinearity and the transparency we defined S as the criterion for choosing the substituents in molecular designing for NLO materials. Of the donor groups, Br, CH_3, OCH_3, and Cl are the best candidates according to the investigations above. Furthermore, the substituted location dependence of β of the disubstituted molecules is also obvious and the calculated results reveal that the donor–acceptor para-disubstituted molecules are the most effective structure whereas the ortho-disubstituted ones are weakest. For the molecular nonlinearity of the multisubstituted compounds the multisubstitutions of OH and CH_3 are not effective, but the trisubstitution and the pentasubstitution of OCH_3 can improve β values greatly. When an OH group attached on the benzene ring the CH_3, OCH_3 donors will have few contributions to β, and it seemed that the OH donor can determine the molecular β values.

Besides the substitution effect the carbonyl location and conjugated system dependence of β also play an important role in the second-order NLO materials. The corresponding calculated results tell us that β increases rapidly with the extending of the conjugated system and when the carbonyl is located on the end of the conjugation system the molecule exhibits the largest second-order hyperpolarizability. The systematical investigations of the second-order hyperpolarizabilities in this paper are expected to be useful for designing effective NLO crystal materials.

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