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The important role of the bromo group in improving the properties of organic nonlinear optical materials

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Several kinds of bromo substituted organic conjugation compounds including chalcones, α-cinnamylideneacetophenones, benzophenones, stilbenes and diphenylacetylenes have been synthesized, and their powder second harmonic generation (SHG) efficiency, cut-off wavelength $\lambda_{\text{cut-off}}$ and thermal stability have been studied. Their molecular first-order hyperpolarizabilities β were investigated by CNDO/S-CI semiempirical calculation methods. The results reveal that the bromo group can obviously improve the molecular first-order hyperpolarizabilities and can effectively reduce the dipole–dipole interactions between the molecules. Thus the bromo group favors the acentric crystal structure, and therefore the SHG effect of the material. The transparency and the thermal stability of the materials can also be improved noticeably when the compounds are substituted with a bromo group. In conclusion, the bromo group is an excellent candidate group in designing effective organic second-order nonlinear optical materials.

1. Introduction

Much attention has been paid to organic nonlinear optical (NLO) materials due to their promising applications in optoelectronics technology[1,2] and the much larger nonlinear response, extremely fast switching time and convenient optimization routes through molecular engineering compared to the currently studied inorganic materials.[3–5] To have strong second-order NLO properties, the compound must possess a large first-order molecular hyperpolarizability, β, and also must crystallize in a noncentrosymmetric structure to have a nonzero $\chi^{(2)}$. Besides the strong nonlinear optical response the NLO materials must also fulfill some other requirements such as good transparency and high thermal stability *etc.*

It has been generally understood that the second-order molecular nonlinearity can be enhanced by large delocalized π-electron systems with strong donor and acceptor groups.[6,7] Since a large molecular hyperpolarizability β is the basis of a strong SHG response, organic molecules with long conjugation systems that usually exhibit large β values are certainly candidate molecules for NLO materials. Many highly nonlinear materials have been found according to this simple principle, such as 3-methyl-4-methoxy-4′-nitrostilbene (MMONS),[8] 4-bromo-4′-methoxychalcone (BMC),[9] *etc.*

A strong macroscopic second-order nonlinearity requires not only a large β value but also a noncentrosymmetric crystal structure. Unfortunately, only a few molecules with large β values crystallize in noncentrosymmetric style, and even fewer of them are useful for NLO materials. Many approaches have been tried to overcome this problem, *e.g.*, designing molecules with small ground-state dipole moments,[10] choosing pure enantiomers,[11] using inclusion complexes and introducing chirality[12] or an octupole[13] in the molecules. Recently, during our systematic search for NLO materials we have found that the highly conjugated organic compounds can easily be crystallized into noncentrosymmetric structures when their molecular conjugation systems are substituted with the bromo (Br) group. Thus these compounds not only have large β values but also usually have fairly strong powder second harmonic generation (SHG). That is to say, the bromo group is an effective group for the microscopic and macroscopic second-order nonlinearities. Moreover, the bromo group can also obviously improve the transparency and the thermal stability of the compounds.

In order to study the universality of the role of the bromo group in improving the properties of NLO materials, we have synthesized the bromo-substituted derivatives of chalcone, α-cinnamylideneacetophenone, benzophenone, stilbene and diphenylacetylene and studied their properties. Some derivatives with strong donor–acceptor groups were also synthesized to have a comparative study.

2. Experimental and calculation

2.1 Synthesis and measurements

Following the literature procedures we synthesized the derivatives of chalcone disubstituted with donor–acceptor substituents:[14] α-cinnamylideneacetophenone,[15] benzophenone,[16] some of the stilbenes[17] and diphenylacetylenes.[18]

Their powder SHG intensities were measured by the conventional technique of Kurtz and Perry,[19] using a Q-switched pulse Nd : YAG laser; the wavelength was 1064 nm, and the particle size of the samples was about 76–154 μm. Relative SHG intensities were detected by comparing the output power with that of the urea. $\lambda_{\text{cut-off}}$ values of the powder absorption spectra of the samples were measured using the photoacoustic spectrometry method.

2.2 Calculation method

On the molecular level, the polarization induced by an external field $\boldsymbol{E}$ can be written as eqn. (1),

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

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 polarizability, first and second hyperpolarizabilities, respectively. An induced molecule in an electric field $\boldsymbol{E}$ can be considered as perturbation, the perturbing operator being

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$\boldsymbol{H'} = -e\boldsymbol{r}\cdot\boldsymbol{E}$, where $\boldsymbol{r}$ is the general coordinate of the molecule. According to perturbation theory and the Born–Oppenheimer approximation the hyperpolarizability tensor β_{ijk} can be expressed as[20] eqn. (2):

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

where i, j, k are the components of the cartesian coordinates, β_{ijk} is the component of the first-order hyperpolarizability tensor in the direction of (ijk), r^i_{gn}, r^i_{nn} represent the electron transition matrix element, as shown in eqn. (3).

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

$|g\rangle$ is the ground state wavefunction while $|n\rangle$, $|n'\rangle$ are the wavefunctions of molecular two different excited 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 molecular nonlinear optical hyperpolarizabilities β of the synthesized compounds at 1064 nm wavelength with the CNDO/S-CI program,[21] in which we used the perturbation theory and the β equation [eqn. (2)]. In terms of the calculated results, we have changed the tensors to vectors so that the calculated values are comparable with the experimental results. Thus the tensor β_{ijk} is changed to vector β_{vec} as given in eqn. (4).

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

3. Results and discussion

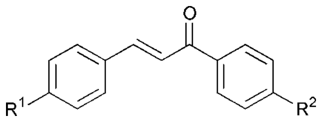
3.1. β value and powder SHG efficiency

13 Chalcone derivatives were studied and the results are listed in Table 1. The molecules substituted with bromo groups (**9**–**13**) have large molecular first-order hyperpolarizabilities β, which is comparable to that of the samples disubstituted with strong donor and acceptor groups (*e.g.* NH_2 and NO_2). However, the β values of the molecules substituted only with methoxy groups (OCH_3), *i.e.* compounds **2**, **7** and **8**, are relatively small. All the bromo substituted chalcones display fairly strong powder second harmonic generation, especially compounds **12** and **13**; their SHG intensity is about 20 times that of urea. However, compounds **1**–**4** have no SHG response yet. The strong donor–acceptor substitution is not effective for the macroscopic second-order nonlinearity of the materials.

α-Cinnamylideneacetophenone is another kind of molecule with a long conjugation system. We synthesized six α-cinnamylideneacetophenone compounds and studied their nonlinear optical properties and transparency. Table 2 lists the results. This kind of compound has very similar second-order nonlinearity dependence properties of the bromo group to the chalcones. The Br group can obviously improve the β values and the SHG activities of the compounds. The six α-cinnamylideneacetophenone samples studied have no or very weak SHG response except for the 2-bromo substituted derivatives; both of them show outstanding macroscopic nonlinear optical response.

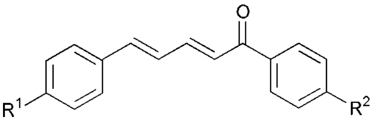
Our data clearly demonstrate that the bromo group favors microscopic nonlinearity, β value, and the macroscopic nonlinearity, SHG response. The bromo group should act as a good donor when the molecule is excited, as can be proven by the charge distributions in the 4-bromochalcone molecule of the ground and the first excited state calculated by the PM3 method. Fig. 1 shows the molecular structure of 4-bromochalcone. In this molecule there is a carbonyl group (C=O) as an acceptor and a bromo group (Br) as a donor. Thus, the contributing charge transfer direction should be from the

Table 1 The calculated and experimental results for chalcone derivatives



Compound	R^1	R^2	$\beta/10^{-30}$esu	SHG (×urea)	$\lambda_{\text{cut-off}}$/nm	T_m/°C	Solvent
1	H	H	19.22	0	435	58–59	Ethanol
2	H	OCH_3	24.82	0	440	106–107	Ethanol
3	NO_2	OCH_3	72.67	0	525	164–165	Ethanol
4	NO_2	NH_2	89.32	0	586	186–187	Ethanol
5	$N(CH_3)_2$	OCH_3	103.78	4	575	122–123	Ethanol
6	$N(C_2H_5)_2$	OCH_3	115.34	~2	535	111–112	Ethanol
7	OCH_3	H	46.70	8.5	440	73–74	Ethanol
8	OCH_3	OCH_3	46.78	8	440	100–101	Ethanol
9	Br	H	86.40	7	435	125–126	Ethanol
10	Br	Br	80.78	5.2	435	187–188	Acetone
11	Br	OCH_3	92.88	11	430	159–160	Ethanol
12	OCH_3	Br	55.16	20	435	145–146	Acetone
13	3,4-2OCH_3	Br	66.06	23.5	470	121–122	Acetone

Table 2 The calculated and experimental results of the α-cinnamylideneacetophenone derivatives



Compound	R^1	R^2	$\beta/10^{-30}$esu	SHG (× urea)	$\lambda_{\text{cut-off}}$/nm	T_m/°C	Solvent
14	H	H	31.81	0	475	101–102	Ethanol
15	OCH_3	3-NO_2	85.04	weak	510	152–153	Ethanol
16	H	OCH_3	37.41	weak	500	116–117	Ethanol
17	NH_2	NO_2	128.66	weak	600	189–190	Ethanol
18	H	Br	77.67	7.4	450	131–132	Benzene
19	OCH_3	Br	103.20	10	460	150–151	Benzene

carbonyl group to the bromo group CO→Br. This is confirmed by the calculated results, which indicates the charge distribution of the Br radical is 0.005 in the ground state and 0.043 in the first excited state. At the same time that of the C=O radical is 0.365 (C), −0.326 (O) and 0.316 (C), −0.336 (O) in the ground and the first excited state, respectively.

Eqn. (5) shows the tensor components of β of 4-bromochalcone calculated using the CNDO/S-CI program (in 10^{-30} esu). Fig. 1 shows the coordinate system.

$$\beta_{xxx}=-28.23 \quad \beta_{yyy}=-57.92 \quad \beta_{zzz}=2.18 \quad \beta_{\text{vec}}=86.40 \qquad (5)$$

When considering the values of the calculated tensor components of β, we find that they are characteristically anisotropic. The out-of-(xy) plane component β_{zzz} is fairly weak, but inspection of the in-plane components shows that β_{yyy} is much larger than the other corresponding components. This reveals that the intramolecular charge transfer is predominantly along the y axis. If we neglect the small component β_{zzz} the vectors β_{xxx} and β_{yyy} can be combined into one vector, which is marked as β_{uuu}. The angle between the combined component β_{uuu} and the y axis is 26°. It is nearly the angle between the direction from the bromo to the carbonyl group, and the y axis (about 25°), which is just the direction of the intromolecular charge transfer we discussed above.

The ability of the molecular hyperpolarizability β to be reflected in the macroscopic nonlinearity depends on the orientation of molecules in the unit cell, that is, the crystal structure. Since a strong SHG response needs a noncentrosymmetric crystal structure the molecules designed for SHG should not be typical in that their ground state dipole moments are often large. In such a case the dipole–dipole interactions tend to favor crystal structures which are centrosymmetric so that dipoles may oppose one another or at the least bring the dipoles out of the required net alignment required for efficient SHG. Minimized dipole–dipole interaction often leads to required noncentrosymmetric crystallization, and as we have seen, small dipole moments of the ground state, in some instances, play an important role in bringing about a favorable orientation of the molecules in the crystal state for SHG response.

From the data in Table 3 we can see that the bromo substituted chalcone molecules usually have small ground state dipole moments μ_g while those of the other derivatives are much bigger. Especially, compounds **9** and **10**, in which there are no other substituents but bromo groups, have the lowest ground state dipole moments μ_g. The μ_g values of compounds **11**–**13** are also fairly small though they are a bit larger than those of compounds **9** and **10**. It seems that the substitution of the OCH_3 group in these molecules mainly contributes to the enlargement of the dipole moments. So it can be considered that the substitution of a Br group in a large conjugation system is propitious to the noncentrosymmetric crystal structure and therefore the SHG response to a certain extent, as has been confirmed by the experimental results. Since the bromo substituted compounds in Tables 1 and 2 exhibit strong SHG effects they must crystallize in noncentrosymmetric styles. The X-ray crystallographic studies tell us that the 4-bromo-4′-methoxychalcone is monoclinic, noncentrosymmetric space group P_c and m point group,[22] and 4-bromochalcone also belongs to the noncentrosymmetric m point group.[23] Besides the bromo substituted derivatives discussed above compounds **7** and **8** also crystallize in noncentrosymmetric crystal structures and exhibit strong SHG effects. Their crystal structures are noncentrosymmetric P_a and $P2_12_12_1$ space group,[24] respectively.

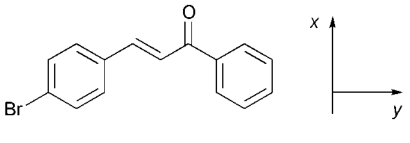


Fig. 1 The molecular structure and the coordinate system of 4-bromochalcone.

Compounds **1**–**4** have large β values but no powder SHG response, which shows that their crystal structures must be centrosymmetric. This prediction is in accordance with the X-ray crystallographic measurements. The chalcone crystal belongs to the *Pbcm* space group[25] and 4′-methoxylchalcone is *Pbca* space group.[26] The centrosymmetric structures have a close relationship with their large ground state dipole moments.

Y. Wang *et al.* reported that the bromo derivatives of stilbene and diphenylacetylene[27] showed strong powder second harmonic generation though there was polymorphism. We have studied some other derivatives substituted with strong donor–acceptor groups, such as NH_2–NO_2, NMe_2–NO_2 *etc.* and the results together with three compounds cited from reference 27 are listed in Table 4. Like the chalcones and the α-cinnamylideneacetophenones the bromo group is more effective than the strong donors in enhancing the macroscopic nonlinearity in these two series of compounds. For example, when the nitrostilbene is substituted with a Br radical as R^2 (compound **23**), the SHG efficiency of the relevant compound is up to 177 times that of urea. But when the same position is substituted with NH_2, NMe_2 or OCH_3 group then the relevant samples (compounds **20**–**22**) show very weak or no powder SHG response. Compound **24** has a much stronger macroscopic nonlinearity than compound **22** because the R^1 substituent is Br not NO_2. 4-Bromo-4′-nitrodiphenylacetylene **28** has a very similar molecular structure to 4-bromo-4′-nitrostilbene **23** and displays a very strong powder SHG effect while the other diphenylacetylene samples exhibit very weak or no powder SHG response.

We synthesized six benzophenone compounds and list the powder SHG efficiency and cut-off wavelengths of the solid samples in Table 5 . The bromo substituted compounds show an obvious SHG effect while the derivatives **29**–**31** have zero

Table 3 The calculated ground state dipole moments μ_g of the molecules in Table 1

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
μ_g/D	2.70	3.86	4.74	5.87	4.68	5.05	2.45	3.48	2.12	1.58	3.21	3.09	2.26

SHG values. Compound **31** was found to be SHG active in the case of rapid crystallization in ethanol or dichloromethane.[28] 4-Aminobenzophenone also has a fairly strong SHG response: compared to compound **29** the nitro substitution at the 4′-position does not obviously favor the noncentrosymmetric crystal structure and the macroscopic second-order nonlinearity.

The above study apparently demonstrates that the substituents are the main factors that determine the crystal structures and therefore the macroscopic second-order nonlinearities. The bromo group can greatly increase the probability of forming an acentric crystal structure while strong donor and acceptor substituents, such as NH_2, NMe_2, NO_2 *etc.*, easily lead to centric molecular packing in the crystals.

3.2. The transparency of the material

Good transparency is also one of the important properties for a useful second-order nonlinear optical material, and so it is necessary to shorten the cut-off wavelength of transmission in designing excellent NLO materials. From the $\lambda_{\text{cut-off}}$ values in Tables 1 and 2 we can clearly see that the bromo substituted compounds usually have much shorter cut-off wavelengths compared to the strong donor–acceptor substituted derivatives. The $\lambda_{\text{cut-off}}$ of compounds **9**–**12** in Table 1 is 430–435 nm, which is almost 150 nm shorter than that of compounds **3**–**6**. Compound **11** has the same structure as compound **5** except for the Br and $N(CH_3)_2$ group, but the difference in their cut-off wavelengths is up to 145 nm. 3,4-Dimethoxy-4′-bromochalcone (**13**) has a longer $\lambda_{\text{cut-off}}$ because two OCH_3 groups are present in its benzene ring. When there is only one OCH_3 group in the molecular structure (*e.g.* **12**) the cut-off wavelength will be shortened greatly. Compounds **2**, **7** and **8** are only substituted with the methoxy group and also have fairly short $\lambda_{\text{cut-off}}$, which shows the OCH_3 group is of course a good candidate for improving the transparency of the materials.

The α-cinnamylideneacetophenone derivatives have very similar transparency properties to the chalcones. The bromo compounds **18** and **19** (see Table 2) have better transparency than the compounds whose substituents are NO_2, NH_2 and OCH_3 *etc.* Moreover, the substitution of a Br group potentially produces a strong hypsochromic shift in the stilbenes and diphenylacetylenes (Table 4). 4-Bromo-4′-nitrostilbene (**23**), 4-bromo-4′-methoxystilbene (**24**) and 4-bromo-4′-nitrodiphenylacetylene (**28**) have much shorter cut-off wavelengths. A comparative study of these compounds with the others in Table 4 shows that the bromo group indeed plays a very important role in improving the transparency of the materials.

For a certain molecular conjugation system its substituents can greatly affect the transparency, as well as the nonlinearity. Of these groups the Br favors short absorption edges but some other radicals, such as NH_2, $N(CH_3)_2$, OH and so on, often cause a fairly strong red-shift of the absorption edges.[29] Compounds **33** and **34** have no obviously shorter $\lambda_{\text{cut-off}}$ than the other compounds because of the substitution of an OH group in the molecular system.

Besides the second-order nonlinearity and transparency the Br group can obviously improve the thermal stability of various compounds. The melting point values of the chalcones, α-cinnamylideneacetophenones and benzophenones are listed in Table 1, Table 2 and Table 5, respectively. Considering the chalcones substituted by Br or OCH_3, we find that the compounds substituted with a Br group have higher melting points. The substitution of one Br radical can contribute approximately 60 °C to their melting points, as can be seen by the comparison of the melting point of compound **1** with **9**, compound **2** with **11**, compound **7** with **12** and compound **9** with **10** (Table 1).

The improvement of the melting points of the α-cinnamylideneacetophenones is less than that of the chalcones after Br is introduced into the molecules. The contribution of Br to the melting point becomes less with the extending of the conjugation system. It probably results from the lower contribution of Br to the molecular mass of the larger molecule. For homologues the melting point generally increases with the augmentation of the molecular weight if we neglect the other intermolecular interactions, such as the hydrogen bond interaction. The NO_2–NH_2 compounds often have high melting points because there are often strong intermolecular hydrogen bond interactions that can strengthen the intermolecular link and improve the thermal stability.

4. Conclusion

We have synthesized various kinds of bromo substituted large conjugation compounds and studied their molecular hyperpolarizabilities β, powder SHG efficiency, cut-off wavelengths

Table 4 The powder SHG data of stilbene and diphenylacetylene derivatives

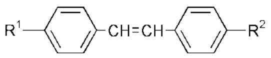
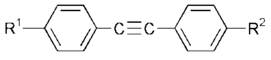
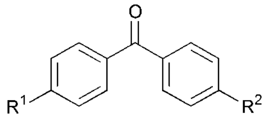
Compound	R^1	R^2	SHG/10^{-30}esu	$\lambda_{\text{cut-off}}$/nm	Solvent
					
20	NO_2	NH_2	0	590	Dioxane
21	NO_2	NMe_2	0	580	Dimethyl sulfoxide
22	NO_2	OCH_3	0.6	520	Dioxane
23	NO_2	Br	177	460	Toluene[29]
24	Br	OCH_3	7	480	Ethyl acetate[29]
					
25	NO_2	NH_2	0	580	Dioxane
26	NO_2	OCH_3	0.1	500	Dioxane
27	NO_2	NMe_2	0	570	Dimethyl sulfoxide
28	NO_2	Br	114	450	Chloroform[29]

Table 5 The SHG properties and cut-off wavelength of benzophenone derivatives



Comp.	R^1	R^2	SHG/ 10^{-30}esu	$\lambda_{\text{cut-off}}$/nm	T_m/°C	Solvent
29	NH_2	NO_2	0	430	146–147	Ethanol
30	2-OH	2-OH	0	430	59–60	Ethanol
31	OCH_3	NO_2	0	390	119–120	Chloroform
32	NH_2	H	14	420	123–124	DMF
33	OH	Br	6	400	190–191	Ethanol
34	OH	2-Br	4.8	420	114–115	Ethanol

and thermal stability. In order to have a comparative study some other compounds were also synthesized and studied.

The electronegativity of Br is 2.96 (Pauling value) and so it has relatively good electron donation ability. The Br group can effectively reduce the ground state dipole moment of the molecule, and therefore the dipole–dipole interaction between the molecules. Minimized dipole–dipole interaction often leads to a noncentrosymmetric crystal structure and thus the bromo group usually can improve the probability of forming noncentrosymmetric crystal styles. So the Br group is effective for the macroscopic second-order nonlinearity, powder SHG response. Furthermore, the Br group can obviously improve the transparency and the melting points of the materials. The results reported in this paper provide the information that the Br is an excellent candidate group in designing effective second-order nonlinear optical materials.

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