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The molecular first hyperpolarizability (β) of a series of benzoate anions and their esters were measured by the hyper-Rayleigh scattering (HRS) in methanol solution. The effect of the presence of methanolic solvation on their β values were calculated and clearly correlates to the experimental β . The static β values of some of the benzoate anions were evaluated and found to be close to those of *p*NA irrespective of the cutoff wavelengths being shorter than 400 nm, and the absorption maximum shorter than those of corresponding esters. These new anions would be promising starting compounds for ionic crystalline second-harmonic generation (SHG) material of diode laser.

Introduction

Many organic compounds have been investigated intensively by theoretical and experimental methods, since organic materials have been proven to be potentially applicable for second-harmonic generation (SHG) devices that convert a laser beam into its double frequency. Moreover, organic materials exhibit some advantages compared to inorganic materials such as a large and fast nonlinear response, processibility, and greater resistance to optical damage.^{1,2} For blue lasers by frequency doubling of conventional diode lasers, materials are required to have an absorption cutoff wavelength (λ_{co}) shorter than 400 nm and a large second-order nonlinear coefficient ($\chi^{(2)}$). Though electrically-neutral π -conjugated compounds have been studied intensively, they are still insufficient for such an application. To achieve the noncentrosymmetric alignment, the use of ionic organic compounds is an important strategy,³⁻⁹ since they may be obtained by a variety of simple syntheses with appropriate counter ions. Through this approach, we have found that the co-crystal of hydroxystilbazolium with toluene-*p*-sulfonate (*p*TS) has a large SHG coefficient, d_{11} , of about 500 pm V⁻¹ at 1064 nm.⁵ The *p*TS salt of dimethylaminostilbazolium was reported to show an electro-optic (EO) coefficient r_{11} of about 400 pm V⁻¹ at 820 nm laser beam.⁹

Preparation of molecules with a large microscopic first hyperpolarizability (β) is needed to achieve large $\chi^{(2)}$ in bulk materials. Using the two-level model,¹⁰ the β is described by eqn. (1),

$$\beta = \left(\frac{3h^2}{2m} \right) \frac{E_{eg}}{(E_{eg}^2 - h^2\omega^2)(E_{eg}^2 - 4h^2\omega^2)} f \Delta\mu_{eg} \quad (1)$$

where E_{eg} is the transition energy between ground state and the excited state, f is the oscillator strength of the transition, $\Delta\mu_{eg}$ is the difference between ground-state and excited-state dipole moments, and ω is the in-put laser frequency of the 1064 nm beam. Increasing the β value of organic molecules is performed by introducing strong electron donor groups and acceptor groups and by elongation of the π -electron system, which act to enhance $\Delta\mu_{eg}$ and to reduce E_{eg} . For ionic compounds, the cation or anion parts are strong electron acceptors and donors, respectively. Therefore, introduction of any appropriate substituent at the *para*-position of the ion part gives rise to a large β . Through the establishment of the hyper-Rayleigh scattering (HRS) technique,¹¹⁻¹³ which measures the β values of ionic

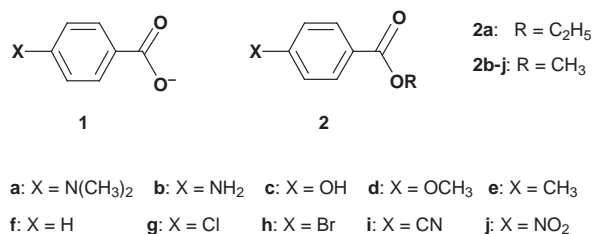


Fig. 1 Chemical structures of substituted benzoate anions and their esters used in this study.

species, their β values have been intensively examined.¹⁴⁻²⁰ We have found that substituted stilbazolium cations have extremely large β values for compounds with λ_{co} longer than 400 nm,^{14,15} while dimethylaminopyridinium cation, the compound with shorter π -conjugation and having λ_{co} shorter than 400 nm, has a static β value about 2.4 times larger than that of colored *p*-nitroaniline (*p*NA).¹⁶

Though cationic species have been intensively investigated as mentioned above, anionic species are less well studied. Recently, the *p*TS anion having a static β comparable to that of *p*NA has been reported.¹⁷ In this study we focus on a series of substituted benzoate anions to expand the study of β values of anionic species, and corresponding esters were also investigated. The β values of these compounds were evaluated by both semiempirical calculation and experimental method. The substituent and methanolic solvation effects on β values are reported.

Hyper-Rayleigh scattering (HRS) experiment

The chemical structures of the investigated compounds and their numbering are shown in Fig. 1. The substituted benzoate anions (**1a–1j**), in sodium-salt form, were synthesized from reaction of the corresponding benzoic acids with sodium methoxide in methanol. The crude product was purified by recrystallization from methanol, and the composition was confirmed by elemental analysis. Meanwhile, the neutral benzoate esters were purchased from Aldrich or Kanto Chemicals in the form of ethyl esters for **2a** and methyl ester for **2b–2j**, respectively, and were used without any further purification.

All the benzoate anions (**1**) and esters (**2**) were dissolved in methanol, and freshly prepared solutions were used for

measurement of absorption properties and the experimental evaluation of β . Solutions of about 1×10^{-2} M were used for determination of the absorption cut-off wavelength (λ_{co}) which corresponds to the wavelength of 99% transmittance. The more dilute solutions of about 4×10^{-5} M were used for measurement of absorption maximum wavelength (λ_{max}). The UV-VIS absorption properties were recorded by employing a Jasco V-570 spectrophotometer.

The β values of the compounds **1** and **2** were evaluated experimentally by use of the HRS technique. A Q-switched Nd:YAG laser at 1064 nm wavelength with 10 ns pulse width from Spectron LS-412 was irradiated on a quartz cuvette cell containing the freshly prepared solution. Concentration of the solution was changed successively in the order of $(0.12-1.2) \times 10^{20}$ molecules cm^{-3} , *i.e.* 0.02–0.2 M. All the solutions were filtered through filters with 0.1 μm pores to remove dust particles. The HRS experimental setup and determination method for β have been previously described in detail.^{11,12,14} The β value of 0.69×10^{-30} esu¹¹ for methanol, corresponding to 2.90×10^{-40} J⁻² C³ m³, was used as a reference. In this work, the β value obtained by the HRS (β_{obs}) was corrected for resonance effects using the two-level model to give those at zero frequency, namely the static β . Hereafter this static β is abbreviated to be β_{expt} , given by eqn. (2), where λ_{eg} is the absorption maximum of

$$\beta_{\text{expt}} = \beta_{\text{obs}} [1 - (\lambda_{\text{eg}}/\lambda)^2] [1 - 4(\lambda_{\text{eg}}/\lambda)^2] \quad (2)$$

the compound corresponding to the $\pi-\pi^*$ transition energy, and λ is the fundamental wavelength of the laser light.

Semiempirical calculation

Theoretically the β values of the compounds **1** and **2** were also evaluated using semiempirical calculation. The program system MOPAC 93²¹ provided on the SUNSPARC workstation system was employed for the calculation. The MNDO Hamiltonian and PM3 parametrization were used for optimizing geometric structures, calculating charge and dipole moment (μ) for the atoms. The EF and PRECISE options were also used as the optimization routine and a convergence criterion for the calculation of geometries, respectively.

By the finite-field (FF) method, *i.e.* through the treatment of an external electric field F , i component of μ is expressed as in eqn. (3),²¹⁻²³ where μ_{oi} is the permanent dipole moment and a_{ij} ,

$$\mu_i(F) = \mu_{oi} + a_{ij}F_j + \frac{1}{2!}\beta_{ijk}F_jF_k + \frac{1}{3!}\gamma_{ijkl}F_jF_kF_l + \dots \quad (3)$$

β_{ijk} and γ_{ijkl} are the tensor elements of the linear polarizability, the first and second hyperpolarizabilities of the molecule. The induced dipole moment is treated with time-dependent field by general treatment of the time-dependent coupled perturbed Hartree-Fock (TDHF) approach on MOPAC which has been described in detail by Dupuis and Karna.²⁴ The TDHF approach was performed by POLAR keyword. The frequency-dependent β values were calculated using eqn. (4):²⁵

$$\beta = \left(\frac{\epsilon}{\epsilon_0}\right) \sum_i \beta_i \mu_i / |\mu| \quad (4)$$

The calculated β values at zero frequency along the dipoles in the gas phase are expressed as β_{gas} . The values of β_{gas} for the investigated compounds have mostly been reported in our previous study.²⁶

Since the β value experimentally determined by the HRS is in methanolic solution, in this study, we employed a conductor-like screening model (COSMO)²⁷ by incorporating the relative permittivity (EPS) into the MOPAC calculation in order to approximate the effect of a solvent surrounding the solute structures. In this approach, the solute dipole is considered to

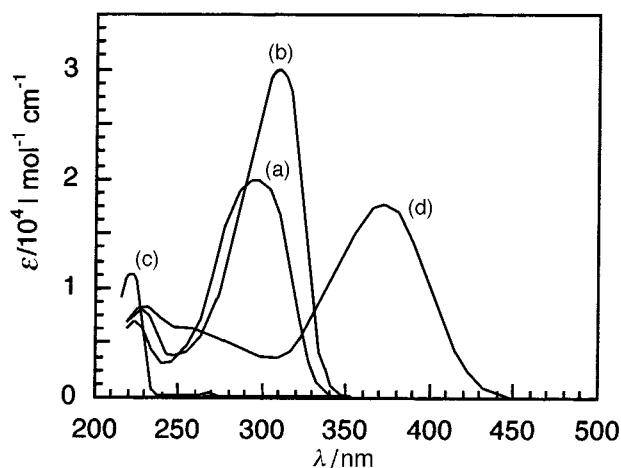


Fig. 2 UV-VIS absorption spectra of (a) dimethylamino benzoate (**1a**), (b) corresponding ester (**2a**), (c) *p*TS anion¹⁷ and (d) *p*NA.²⁶

be surrounded spherically by conductor-like continuum media of solvent molecules at van der Waals (vdW) distance, R_{solv} . Through the dipole-dipole and electrostatic interactions between solute and solvent molecules, energy and polarization of the solute are screened with scaling factor $F(\epsilon)$, which is given by eqn. (5), where ϵ is the relative permittivity of the screening solvent.

$$F(\epsilon) = \frac{(\epsilon - 1)}{(\epsilon + \frac{1}{2})} \quad (5)$$

In this calculation the relative permittivity (EPS) of 32.63 corresponding to the relative permittivity of methanol at 298 K has been employed. Since the value of R_{solv} itself is less crucial, in this application we have taken R_{solv} to be 1 Å. Hereafter, the COSMO calculated β values in the presence of methanol solvent along the dipoles are expressed as β_{meth} .

In order to analyse the calculated β values by the two-level model, μ_e and E_{eg} were also calculated both in the gas phase and in methanol by use of the multielectron configuration interaction (MECI)²¹ treatment implemented in the MOPAC program. This treatment was performed by MECI keyword. Keywords of 1SCF C.I. = 5 were added to consider a hundred microstate configurations between the two highest occupied and the two lowest unoccupied molecular orbitals. SINGLET and GEO-OK keywords were also added for only singlet states of interest and for overriding geometric safety checks, respectively. The band-gap energy (E_{eg}) is considered as the first singlet state of maximum oscillator strength, f . The excited state dipole moments (μ_e) were calculated by these keywords with additional ROOT = n and OPEN(2,2) keywords, where n is the number of the optimized singlet state.

Results and discussion

The investigated benzoate and ester compounds, **1** and **2**, exhibit cutoff wavelengths comparatively shorter than that of colored *p*NA. For example, Fig. 2 shows the UV-VIS absorption spectra of dimethylaminobenzoate (**1a**) and the corresponding ester (**2a**) together with those of the *p*TS anion and *p*NA. The λ_{max} of **1a** and **2a** are 297 and 309 nm, respectively, and they naturally have no absorption at 532 nm.

The values of λ_{max} and λ_{co} of all the compounds of **1** and **2** are listed in Table 1 together with their β_{gas} , β_{meth} and β_{expt} values and the Hammett σ_p constant.²⁸ For comparison, those of *p*TS anion and *p*NA are also included in Table 1. All of the benzoate compounds have λ_{max} within the UV region and most of them exhibited a cutoff wavelength shorter than 400 nm, except for **1a**, **1j** and **2j**. Benzoate anions have blue-shifted λ_{max} compared with the corresponding neutral benzoate esters,

Table 1 Hammett σ_p constant of each substituent, λ_{\max}/nm , $\epsilon_{\max}/10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $\lambda_{\text{co}}/\text{nm}$ of compounds **1** and **2** together with calculated β values/ 10^{-30} esu in gas phase and in methanol, and experimental β values/ 10^{-30} esu evaluated by HRS in methanol solution

Compound	σ_p	1						2					
		λ_{\max}	ϵ_{\max}	λ_{co}	β_{expt}	β_{gas}	β_{meth}	λ_{\max}	ϵ_{\max}	λ_{co}	β_{expt}	β_{gas}	β_{meth}
a	-0.83	297	2.0	420	17	0.8	4.6	309	3.0	375	35	8.3	9.4
b	-0.66	276	1.7	380	14	0.7	4.2	292	2.1	370	24	5.5	8.5
c	-0.37	252	1.3	325	13	1.4	1.3	259	2.2	338	20	1.7	4.0
d	-0.27	247	1.5	310	11	1.5	1.6	256	1.9	328	17	2.2	4.7
e	-0.17	233	0.5	340	9	2.4	0.6	239	1.5	330	9	1.2	3.0
f	0.00	224	0.7	340	6	2.3	0.2	229	0.7	300	5	0.5	1.4
g	0.23	232	0.5	330	8	0.9	2.5	240	1.6	360	17	4.5	5.6
h	0.23	238	0.4	330	7	2.0	0.1	245	2.5	300	9	0.8	2.3
i	0.66	238	0.8	375	10	5.0	1.6	239	2.0	375	6	0.6	0.9
j	0.78	270	1.3	425	14	5.2	2.5	261	1.6	430	9	0.3	0.7
<i>p</i> TS ^a		222	1.2	280	17	1.4	0.4						
<i>p</i> NA ^b		371	1.5	473	15	6.6	11.5						

^a Taken from ref. 17. ^b Taken from ref. 26.

except for the nitro derivative. The β_{expt} values of benzoate anions with donor substituents are smaller than those of the corresponding esters, while the opposite relation was found in strong acceptor substituted ones. Among the benzoate anions and esters, the β_{expt} values of **1a**, **1b**, **1j**, **2a–2d**, and **2g** range from about equal to, to twice as large as that of *p*NA. Especially, since esters of **2a–2d** have a π -conjugated structure with X being a strong donor and the ester a strong acceptor, β_{expt} values are much enhanced.

Ray and Das²⁹ have reported the β values of some substituted benzoic acids evaluated by the HRS method with addition of 1 M NaOH. By varying the dissociation constant they obtained the β value in ethanol solution and λ_{\max} in water of the corresponding benzoate anions. The values of β and λ_{\max} of all the anions reported by them are larger than those in this work. For example, they reported the β_{expt} and λ_{\max} for compound **1a** to be 23×10^{-30} esu and 310 nm, respectively. This difference between their and our data can be explained by different experimental conditions, since the difference in solvent¹³ and the pressure of NaOH increasing pH of solution must affect significantly the absorption and β .

In designing molecules of large β , it is worth clarifying the substituent effect. Since the electron-withdrawing or -donating ability of the attached substituent X at the *para*-position is represented by Hammett's σ_p , the correlation between β and σ_p is plotted in Fig. 3a and 3b for benzoate anions and esters, respectively. For benzoate anions the β_{gas} values decrease with decreasing σ_p , indicating that the carboxylate anion group takes the role of an electron donor. Therefore, a large β can be achieved by attaching a strong acceptor group at the *para*-position. In the case of benzoate esters, β_{gas} values decrease with increasing σ_p , indicating that the carboxylate ester is an electron acceptor and hence that strong donor groups lead to larger β values. Though in the case of benzoate esters all the β values tend to decrease with increasing σ_p , the β values of benzoate anions show a different tendency: the β_{gas} values tend to increase with increasing σ_p , whereas the β_{expt} and β_{meth} values are at a minimum value around $\sigma_p = 0$.

In the case of benzoate esters, β_{meth} is always larger than β_{gas} , whereas for benzoate anions no such clear tendency is seen. The discrepancy between β_{gas} and β_{meth} values must be due to an environmental effect,³⁰ *i.e.* solvent effect in the present study. In order to clarify the solvent effect, the origins of β , *i.e.* geometry and electronic structures of the benzoate anions in gas phase optimization and those in methanol optimization using the COSMO model were calculated. We found almost no significant difference in molecular structures of benzoate anions and esters in methanol-optimized geometry compared with those in gas-phase-optimized geometry. Table 2 displays geometric optimizations of bond lengths and torsion angles of

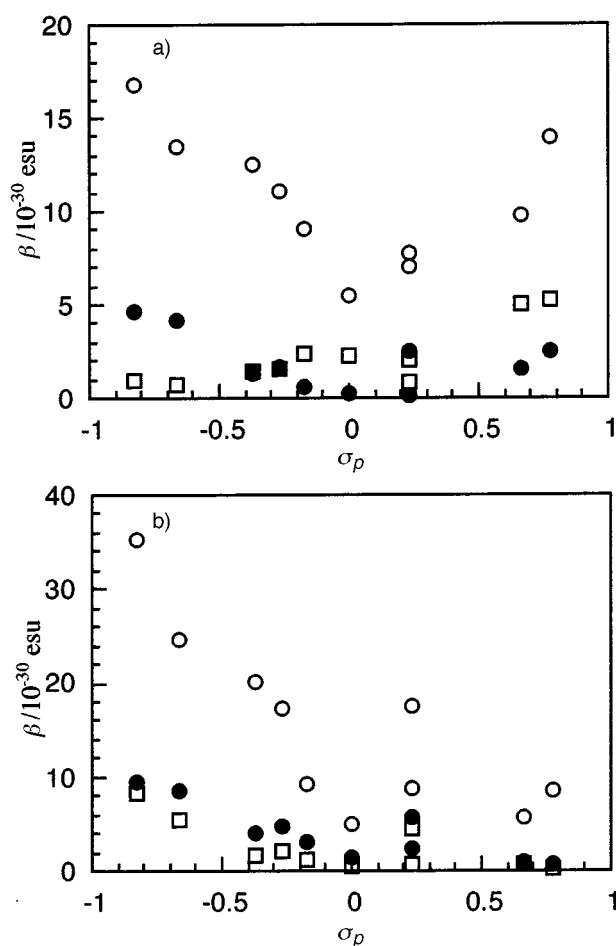



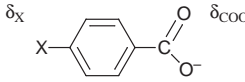
Fig. 3 The correlation between β values and σ_p for (a) benzoate anions and (b) benzoate esters; (\square) calculated values in the gas phase, (\bullet) calculated values in methanolic solution, and (\circ) experimental data.

compounds of **1b** and **2b** in the gas phase and in methanol for representative examples. In the geometry of **1b** in methanol, only an increase in C4–C7 bond length of about 0.04 Å and a decrease in H–N1–C1–C6 torsion angles of about 2° were observed, while the other bond lengths and angles are almost the same. For compound **2b**, there are no such significant changes in bond lengths and only a decrease in H–N1–C1–C6 torsion angles of about 3° was observed. Irrespective of the similarity in geometric structures, the solvation significantly changes charge distribution on benzoate anions and esters. Charge on carboxylate anion part (δ_{COO}) and charge on substituent part (δ_{X}) calculated for ground and excited states in the

Table 2 The calculated bond lengths and torsion angles of compounds **1b** and **2b** in the gas phase and in methanol optimization


Bond length/Å	In gas phase		In methanol	
C1–C2	1.399	1.402	1.403	1.404
C2–C3	1.389	1.387	1.403	1.404
C3–C4	1.394	1.396	1.398	1.400
C4–C5	1.394	1.397	1.397	1.398
C5–C6	1.389	1.402	1.387	1.386
C6–C1	1.399	1.403	1.403	1.404
C7–C4	1.540	1.496	1.423	1.425
C7–O1	1.254	1.264	1.483	1.478
C7–O2	1.254	1.264	1.217	1.228
C1–N1	1.441	1.430	1.370	1.359
			1.411	1.417

Torsion angle/°	In gas phase		In methanol	
H1–N1–C1–C6	31.3	29.9	24.4	28.9
H2–N1–C1–C2	121.1	123.3	126.6	124.0

Table 3 The calculated ground state and excited state charge distribution of compounds **1** in the gas phase and in methanol together with the corresponding dipole moments


	Ground state						Excited state					
	In gas phase			In methanol			In gas phase			In methanol		
	δ_x/eec	δ_{COO}/eec	μ_g/D	δ_x/eec	δ_{COO}/eec	μ_g/D	δ_x/eec	δ_{COO}/eec	μ_g/D	δ_x/eec	δ_{COO}/eec	μ_g/D
a	0.039	-0.779	16.2	0.102	-0.961	20.8	0.182	-0.314	9.0	0.398	-0.980	25.4
b	0.072	-0.779	11.7	0.145	-0.962	17.1	0.136	-0.276	4.6	0.572	-0.977	24.2
c	-0.072	-0.778	11.4	-0.037	-0.960	16.3	-0.067	-0.154	3.3	0.043	-0.980	18.0
d	-0.080	-0.774	12.9	0.039	-0.960	17.8	-0.062	-0.149	4.2	0.055	-0.980	20.9
e	0.038	-0.780	11.7	0.089	-0.960	16.6	0.018	-0.359	2.5	0.123	-0.998	18.0
f	0.078	-0.780	9.6	0.125	-0.964	14.1	0.069	-0.388	8.0	0.133	-0.997	14.8
g	-0.017	-0.770	12.6	0.061	-0.950	17.1	-0.035	-0.356	6.0	0.733	-0.989	25.4
h	-0.098	-0.767	15.9	0.001	-0.952	20.9	-0.292	-0.217	6.4	-0.058	-0.998	23.2
i	-0.196	-0.760	8.8	-0.182	-0.949	12.5	-0.247	-0.188	3.4	-0.257	-0.951	11.1
j	0.046	-0.746	8.9	0.049	-0.942	12.6	-0.095	-0.230	4.7	-0.765	-0.946	9.9

gas phase as well as in methanol are summarized in Table 3 together with their dipole moments. The corresponding data for benzoate esters are displayed in Table 4, where δ_{carb} represents net charge on the alkoxy carbonyl group. For benzoate anions in the ground state of the gas phase, the net charge on δ_{COO} of around $-0.77e$ indicates that a portion of $-1e$ charge on this part is transferred; *i.e.* this part is an electron donor as was mentioned above. In methanol geometry, the minus charge on δ_{COO} increases up to around $-0.95e$. It is remarkable that the methanol solvation causes only a little charge to be transferred from the carboxylate anion to the other side. Hence, the ground state dipole moments of all benzoate anions are enhanced in methanol. In the excited state, the dipole moments in the gas phase of all benzoate anions are smaller than those in the ground state resulting in less polarization. On the contrary, for methanol geometry, δ_{COO} values in the excited state are more negative, in the range of $-0.004e$ to $-0.046e$, than those in the ground state. This additional negative charge of δ_{COO} is accompanied with an additional negative charge of δ_x for strong acceptor groups and an additional positive charge of δ_x for other groups. Therefore, the excited state dipoles (μ_e) of the strong acceptor groups (**1i**, **1j**) are reduced and those of other groups are enhanced, in general, compared with μ_g .

For benzoate esters, the net charge on the carboxylate ester moiety of $-0.02e$ to $-0.04e$ in gas phase geometry increases to -0.04 to $-0.06e$ in the methanol geometry. A little negative net charge on δ_{carb} indicates that the carboxylate ester is a weak electron acceptor in the gas phase as well as in the methanol geometry. This may not be surprising, since benzoate esters are electrically neutral compounds, thus there is no net charge on this system to be transferred by solvation. However, methanol solvation is seen to increase significantly both the negative net charge of strong acceptor groups and the positive net charge of strong donor groups. Namely, solvation enhances the withdrawing ability of acceptor groups as well as the donating ability of donor groups. Therefore, the methanol solvation gives rise to a unique enhancement in μ_g of the benzoate esters of around 1.3 D on average. In the excited state, for gas phase geometry, the negative charge of δ_{carb} increases in the range of $-0.02e$ to $-0.13e$ compared to that in ground state, while, the positive charge δ_x of donor groups increases, and that of acceptor groups decreases, except for chloro derivatives. As a result, μ_e of esters with strong donors, **2a** and **2b**, becomes larger than the corresponding μ_g . Even in the methanolic environment, a similar tendency was found in the excited state though the μ_e values of most of the compounds are increased.

Table 4 The calculated ground state and excited state charge distribution of compounds **2** in the gas phase and in methanol together with the corresponding dipole moments

	Ground state						Excited state					
	In gas phase			In methanol			In gas phase			In methanol		
	δ_x/eec	$\delta_{\text{carb}}/\text{eec}$	μ_g/D	δ_x/eec	$\delta_{\text{carb}}/\text{eec}$	μ_g/D	δ_x/eec	$\delta_{\text{carb}}/\text{eec}$	μ_g/D	δ_x/eec	$\delta_{\text{carb}}/\text{eec}$	μ_g/D
a	0.113	-0.038	2.9	0.120	-0.062	4.3	0.504	-0.165	9.5	0.664	-0.248	12.5
b	0.149	-0.038	2.9	0.166	-0.064	4.4	0.424	-0.109	6.6	0.615	-0.235	11.8
c	-0.020	-0.038	1.5	-0.028	-0.063	2.5	0.035	-0.140	3.7	0.060	-0.260	9.6
d	-0.021	-0.038	1.7	-0.029	-0.061	2.7	0.104	-0.140	4.6	0.057	-0.248	8.7
e	0.077	-0.038	2.3	0.092	-0.060	3.6	0.116	-0.138	4.1	0.144	-0.243	7.1
f	0.106	-0.038	2.0	0.126	-0.059	3.3	0.104	-0.127	3.1	0.142	-0.283	6.7
g	0.078	-0.026	1.6	0.075	-0.054	2.6	0.395	-0.135	5.8	0.733	-0.174	10.3
h	0.009	-0.026	1.5	0.011	-0.052	2.5	-0.012	-0.140	2.2	0.194	-0.157	4.7
i	-0.152	-0.026	2.6	-0.176	-0.049	3.9	-0.170	-0.078	1.9	-0.177	-0.130	3.1
j	0.115	-0.019	4.3	0.056	-0.042	5.6	0.054	-0.045	4.8	-0.070	-0.089	6.6

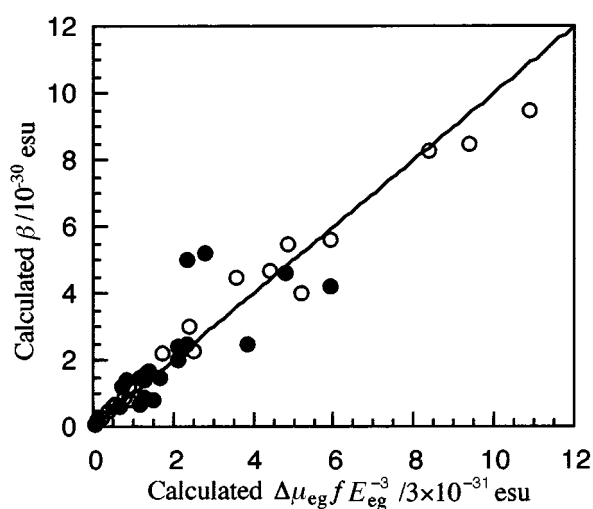


Fig. 4 Plot of calculated β_{gas} and β_{meth} vs. calculated $\Delta\mu_{\text{eg}}f/E_{\text{eg}}^{-3}$ for benzoate anions and esters. Plotted line is for 1 : 1 correlation.

The differences in the dipole moment between the ground state and excited state, $\Delta\mu_{\text{eg}}$, of compounds **1** and **2** are summarized in Table 5 together with their transition energy between the two states (E_{eg}) and oscillator strength of the transition (f). It should be noted that among the calculated results E_{eg} was selected as the lowest excited state energy having maximum f in the dipole moment direction. The $\Delta\mu_{\text{eg}} = |\mu_{\text{e}} - \mu_{\text{g}}|$ is calculated from the square-root of summation $|\mu_{\text{e}} - \mu_{\text{g}}|_i^2$, where i indicates the component of the difference dipole moments on x , y and z directions.

For benzoate anions **1**, $\Delta\mu_{\text{eg}}$ in methanol is much smaller than in the gas phase except for amino and chloro substituted anions which do not differ so much. E_{eg} of donor substituted benzoate anions (**1a–1d**) decreases in methanol, while the opposite relation was found for other compounds. The f values in methanol is generally 2.5 to 3.5 times larger than that in the gas phase except for simple benzoate anion (**1f**). According to the two-level model, β values at zero frequency are proportional to $f\Delta\mu_{\text{eg}}E_{\text{eg}}^{-3}$, which is derived from eqn. (1) where $\omega = 0$. Thus, the considerable increase of β in methanol of **1a**, **1b** was found to originate from the smaller E_{eg} and the larger f values, and the increase of β for the chloro substituted anion (**1g**) originates from the larger f in methanol. The decrease of β in methanol for other compounds is mainly due to the smaller $\Delta\mu_{\text{eg}}$. For benzoate esters **2**, $\Delta\mu_{\text{eg}}$ in methanol is larger than that in the gas

phase for all compounds. There is not such a difference in f values in the gas phase compared with in methanol. Thus, the fact that β_{meth} is larger than β_{gas} for benzoate esters **2** is mainly due to the contribution of increased $\Delta\mu_{\text{eg}}$ and reduced E_{eg} in methanol.

To check the adaptability of the two-level model analysis for the calculated β value, we evaluated the correlation between calculated β values of both compounds **1** and **2** in the gas phase as well as in methanol and their calculated $\Delta\mu_{\text{eg}}fE_{\text{eg}}^{-3}$ as shown in Fig. 4. The plotted line in the figure is for the 1 : 1 correlation. Though several of the data points lie above and below the fitting line, which is not surprising since the β values are calculated on the basis of TDHF method, it is remarkable that the calculation of β in the gas phase as well as in methanol satisfies the two-level model analysis.

In fact, the β_{meth} values of all compounds **1** and **2** are still smaller than their β_{expt} values. This discrepancy is due to the fact that the intermolecular interactions which occur in measurement were not taken into account in the calculation. However, the effect of methanolic solvation on β values of benzoate anions and esters is clearly seen in that the correlation between the β_{meth} values and β_{expt} values shows the same tendency with respect to σ_p . The only exception of the correlation of the β values is found for the β_{gas} of benzoate anions in the negative σ_p .

To demonstrate the performance of the COSMO model, we evaluated the correlation between the calculated absorption spectra (λ_{meth}) after the conversion from the COSMO-methanol calculated E_{eg} values (Table 5) and measured absorption maximum (λ_{max}) values of compounds **1** and **2**. It should be noted that the COSMO calculation using PM3 is not very well suited for the calculation of electronic spectra as was reported in the work of Morley *et al.*³¹ for merocyanine. They reported that the calculated absorption is at longer wavelengths compared with the measured absorption even for a solvent with very high relative permittivity. Thus, we may not expect a perfect agreement of calculated and measured λ , but we may clarify whether or not the COSMO-methanol calculation provides a correlation in trend of the solvatochromic shift of benzoate anions and esters. Our results demonstrate that for most of benzoate anions and esters, the experimental λ_{max} values are linearly correlated with calculated λ_{meth} values, as shown in Fig. 5.

In order to explore the trade-off between the second-order hyperpolarizability and transparency, we have evaluated the correlation between the β_{expt} and λ_{max} of the investigated compounds **1** and **2**. For all of the compounds, the chromophores having longer λ_{max} , corresponding to larger molecular charge transfer, were evaluated to have a larger β_{expt} . From the two-

Table 5 The difference ground state and first excited state dipole moments together with the transition energy and oscillator strength for compounds **1** and **2**

Compound	1						2					
	In gas phase			In methanol			In gas phase			In methanol		
	$\Delta\mu_{eg}/D$	E_{eg}/eV	f	$\Delta\mu_{eg}/D$	E_{eg}/eV	f	$\Delta\mu_{eg}/D$	E_{eg}/eV	f	$\Delta\mu_{eg}/D$	E_{eg}/eV	f
a	7.3	4.755	0.22	4.6	4.207	0.77	6.7	4.061	0.84	8.2	4.001	0.88
b	7.1	4.645	0.22	7.1	4.234	0.72	4.1	4.120	0.79	7.4	3.996	0.85
c	7.0	4.688	0.20	1.8	4.614	0.50	2.2	4.508	0.59	7.0	4.413	0.64
d	8.6	4.677	0.20	2.3	4.622	0.50	2.8	4.526	0.57	6.1	4.431	0.63
e	11.5	4.615	0.20	1.8	4.775	0.39	2.0	4.716	0.47	4.0	4.619	0.53
f	10.9	4.631	0.20	0.7	4.930	0.22	1.5	4.872	0.32	3.8	4.799	0.37
g	5.7	4.455	0.20	7.8	4.629	0.49	5.1	4.486	0.60	8.0	4.474	0.61
h	9.4	4.440	0.20	2.0	5.160	0.47	1.2	4.999	0.92	3.3	4.923	0.88
i	12.5	4.414	0.16	1.5	4.767	0.59	1.0	4.747	0.58	1.2	4.733	0.65
j	13.5	4.187	0.15	3.0	4.274	0.54	0.6	4.342	0.32	1.1	4.245	0.38

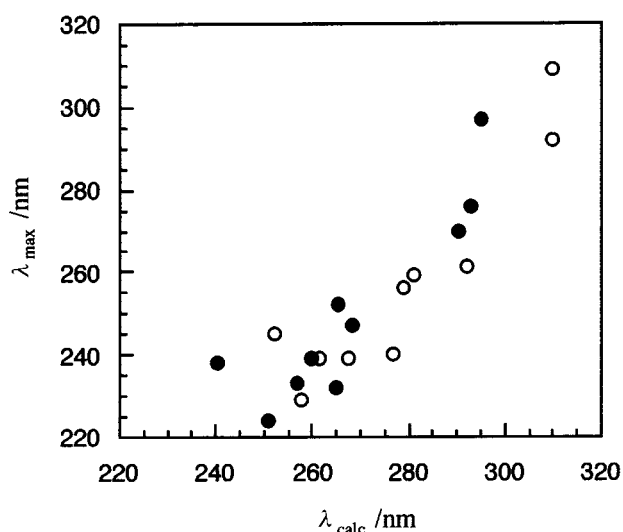


Fig. 5 The plot of experimental absorption (λ_{max}) vs. calculated absorption (λ_{calc}), (●) for benzoate anions and (○) for their esters.

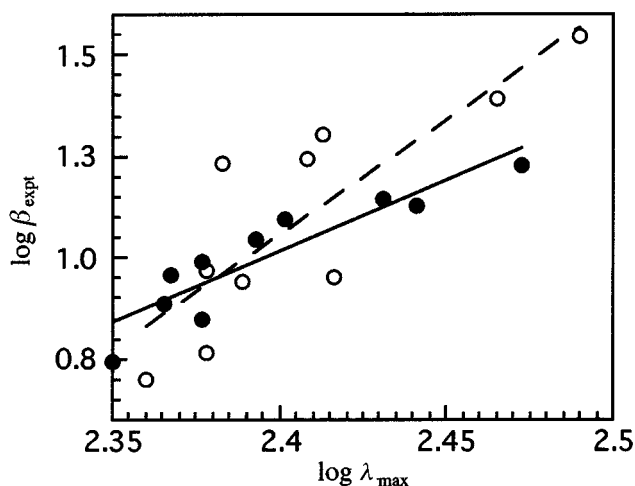


Fig. 6 Plot of the $\log \beta_{expt}$ vs. $\log \lambda_{max}$, (●) for benzoate anions and (○) for their esters.

level model [eqn. (1)] and the resonance correction [eqn. (2)], the β_{expt} can be deduced to be proportional to $(\lambda_{max})^3 f \Delta\mu_{eg}$, *i.e.* the product of cubed wavelength with oscillator strength and difference of dipole moments. Since there is no known systematic dependence of f and $\Delta\mu_{eg}$ on λ_{max} , the $f \Delta\mu_{eg}$ value is approximated to $f \Delta\mu_{eg} \propto (\lambda_{max})^m$ where m is an unidentified positive constant to allow the contribution of donor–acceptor strength. Thus, the two-level model predicts that β is proportional to $(\lambda_{max})^n$, $n = 3 + m$. In order to clarify this predic-

tion, the logarithmic β_{expt} values of all compounds **1** and **2** were plotted as a function of logarithmic λ_{max} values, as shown in Fig. 6. The best fitted plot for all the data of benzoate anions and esters, with some deviation especially for esters, gives slopes of 3.5 and 5.6, respectively. This indicates that in experiment the substituted benzoate anions, similar to neutral molecules, and esters also satisfy the two-level model prediction, and also λ_{max} evidently correlates positively with $f \Delta\mu_{eg}$ or $\Delta\mu_g$. From the logarithmic plot, it is also remarkable that for λ_{max} values shorter than 250 nm, corresponding to $\log \lambda_{max} = 2.4$, benzoate anions give a better trade-off between hyperpolarizability and transparency than benzoate esters, and for longer λ_{max} the opposite tendency was observed.

Conclusion

The first hyperpolarizability of substituted benzoate anions, and their esters as a comparison, has been systematically evaluated by experimental and semiempirical calculation methods. Through this study, the substituent and the methanol solvation effects on β values of the substituted benzoate anions and esters were discussed. The COSMO-methanol calculation results show good correlation with experimental results for both β values and absorption maximum. Since some of the benzoate anions studied have larger β than colored *p*NA, they should be good candidates for SHG materials for laser diodes. In order to obtain the noncentrosymmetric crystals, research on complexation of benzoate anions with appropriate cations is in progress. Also they may be used as a counter anion to control molecular alignment of large β cations such as stilbazoliums. Actually sodium salts of **1c** and **1g** were found to be SHG active materials.

For benzoate esters, donor substituted ones show larger β values in general: they are about twice as large as those of the corresponding anions. Since benzoate ester oligomers of **1d** have been found to have advantages as NLO chromophores, especially for poled polymer systems,^{22,32} synthetic expansion of benzoic acid derivatives into oligomers, *i.e.* chained chromophores, is an interesting subject.

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