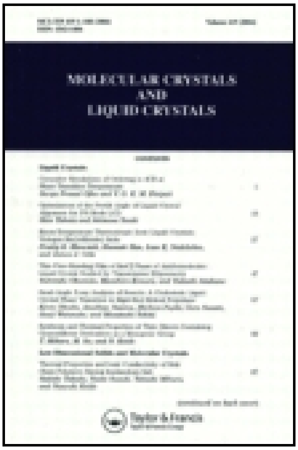

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Organic Species with Short Cutoff Wavelength and Large Second-Order Hyperpolarizability

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ORGANIC SPECIES WITH SHORT CUTOFF WAVELENGTH AND LARGE SECOND-ORDER HYPERPOLARIZABILITY

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Abstract In order to find short cutoff and large β materials for second-order nonlinear optics, a series of substituted aromatic carboxylate anions and esters were investigated by semiempirical molecular orbital calculation. Methyl benzoates with a weak donor or benzoate anions with a weak acceptor at *para*-position were found to satisfy those conditions. Among them, optical properties of methyl 4-methoxybenzoate and its oligomers were studied by both calculation and experiment. The $\mu\beta$ values of oligomers consisting of N monomeric units were found to become N-times larger than the sum of N isolated monomers, though the absorption cutoff of oligomers stays almost the same as that of methyl 4-methoxybenzoate.

INTRODUCTION

Nonlinear optical (NLO) phenomena are expected to play an important role in the technology of photonics,[1] in which photons instead of electrons in the field of electronics are used to acquire, store, transmit, and process information. Since potential of organic materials for NLO devices have been proven, NLO properties of many of organic compounds have been investigated by both experimental and theoretical methods.[1-4] In the molecular design of organic second-order NLO materials applying for frequency doublers or electro-optical modulators, it is well established that π-conjugated systems connected with electron donating and accepting groups at the two ends show large optical nonlinearity. Typical examples are made up of benzene, pyridine, stilbene or azobenzene as π-conjugated systems, amino and dialkylamino groups as donors and nitro or cyano groups as acceptors. *p*-Nitroaniline (*p*NA) is a representative molecule with large second-order hyperpolarizabilities (β) obtained by this approach, though it has absorption in visible region. For UV or blue second-harmonic generation (SHG) devices of laser diodes, the absorption cutoff wavelength of materials is requested to be shorter than 400 nm and large β have to be achieved even under such absorption restriction. In order to obtain those

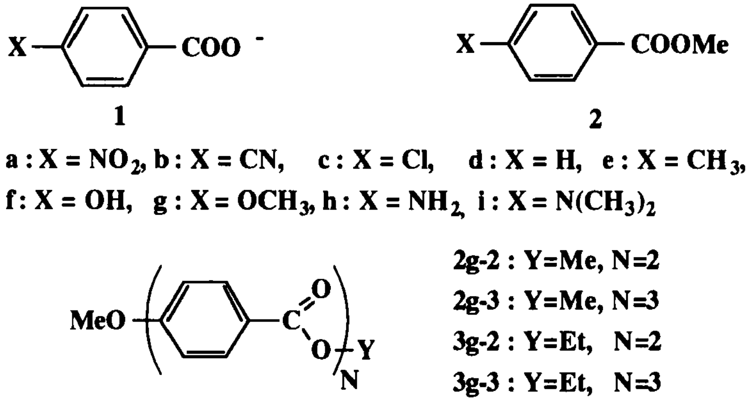


FIGURE 1 Chemical structures of substituted benzoate anions, methyl benzoate esters and methoxybenzoate oligomers.

molecules, we decided to explore new types of donor-acceptor (D-A) molecules excluding the classical strong D-A pair. In our previous studies,[5-8] β values of several organic species were investigated by the hyper Rayleigh scattering (HRS) method and semiempirical molecular orbital (MO) calculation, and an aromatic sulfonate anion was found to have a comparatively large β value in spite of the cutoff wavelength shorter than 280 nm.[5]

In this paper, we extend a series of species to aromatic carboxylate anions and esters. Their β values were studied by semiempirical MO calculation and also by the HRS method for some derivatives. As one of the derivation of a benzoate ester, an oligomeric structure was also investigated and such oligomers were found to have large $\mu\beta$ and the short cutoff of *ca.* 300 nm useful enough for NLO species in poled polymer systems.

EXPERIMENTAL

Compounds

Three types of species have been investigated by MO calculation, and their chemical structures are shown in FIGURE 1. Those are substituted benzoate anions **1a** ~ **1i**, esters **2a** ~ **2i** and ester oligomers **2g-2** and **2g-3**. Among them, the compound **2g** was purchased from Kanto Chemical Co., Inc. Oligomers **3g-2** and **3g-3** were synthesized in our laboratory to measure absorption and HRS. These compounds were recrystallized several times from methanol.

Evaluation of β and Absorption

In the semiempirical MO calculation, optimized molecular conformation, energy gap between ground and excited states (E_{eg}), dipole moment in ground state (μ) and β was obtained using the program system MOPAC[9-10] with the MNDO Hamiltonian[11-12] and the PM3 parametrization.[12] Hereafter, the μ value calculated is described as $\mu_{0,\mathrm{calc}}$. The calculated β values ($\beta_{0,\mathrm{calc}}$) are the vector component of β along $\mu_{0,\mathrm{calc}}$ for an isolated species in vacuum at zero frequency. This value was calculated in the program as follows:

$$\beta_{0,\mathrm{calc}}=\frac{3}{5}\sum_{i}\left(\beta_{ixx}+\beta_{iyy}+\beta_{izz}\right)\mu_i/\|\mu\|$$

where i is any of x, y and z. Geometries were fully optimized. The POLAR keyword was used to calculate the β values by a finite field method with both energy and dipole expansions.[13] The PRECISE option in MOPAC was used as a convergence criterion for calculation of both the geometries and the NLO property. The calculations were performed on a SUN SPARC work station.

For experimental evaluation of β values of **2g**, **3g-2** and **3g-3**, the HRS method was used.[14-15] A fundamental beam of Q-switched Nd:YAG laser operated at 1064 nm with 10 ns pulse width and 10 mJ energy per pulse was irradiated to the 10^{-2} ~ 10^{-4} M methanol solution of the compounds in this measurement. Hereafter, β value obtained by HRS is described as β_{expt}. Methanol solutions of the compounds of about 10^{-5} M were also prepared to measure absorption spectra and those of about 10^{-2} M were used to determine cutoff wavelength by 99% transmittance.

RESULTS AND DISCUSSION

Substituted Benzoate Anions and Esters

First, we discuss the substituent effect on the E_{eg}, μ and β values of benzoate anions **1** and methyl benzoates **2**. The Hammet constant[16] for *para*-substituents (σ_{p}), in which positive and negative values correspond to electron withdrawing and donating groups, respectively, was used as an index for electronic properties of substituent **X** attached in **1** and **2**. The correlation between σ_{p} and E_{eg} is shown in FIGURE 2 (a). Although the magnitude of calculated E_{eg} values do not agree with the experimental values obtained from absorption spectra, relative order of E_{eg} is considered to be almost reliable. For substituted benzoate anions **1**, E_{eg} is almost constant for negative σ_{p}, and decreases with increasing σ_{p}. On the contrary, E_{eg} for substituted methyl benzoates **2** increases with increasing σ_{p} for negative σ_{p} and is not so much changed for positive σ_{p}. Since decrease of E_{eg} by changing *para*-substituent **X** is due to π-electron delocalization between **X** and the counter substituent through a benzene ring, anionic carboxylate group in **1** and methoxycarbonyl group in **2** are concluded to be electron donor and acceptor, respectively.

In this connection, charge distribution of benzoate anions **1** and esters **2** was calculated (TABLE I). The minus charge on C part of both anions and esters substituted by

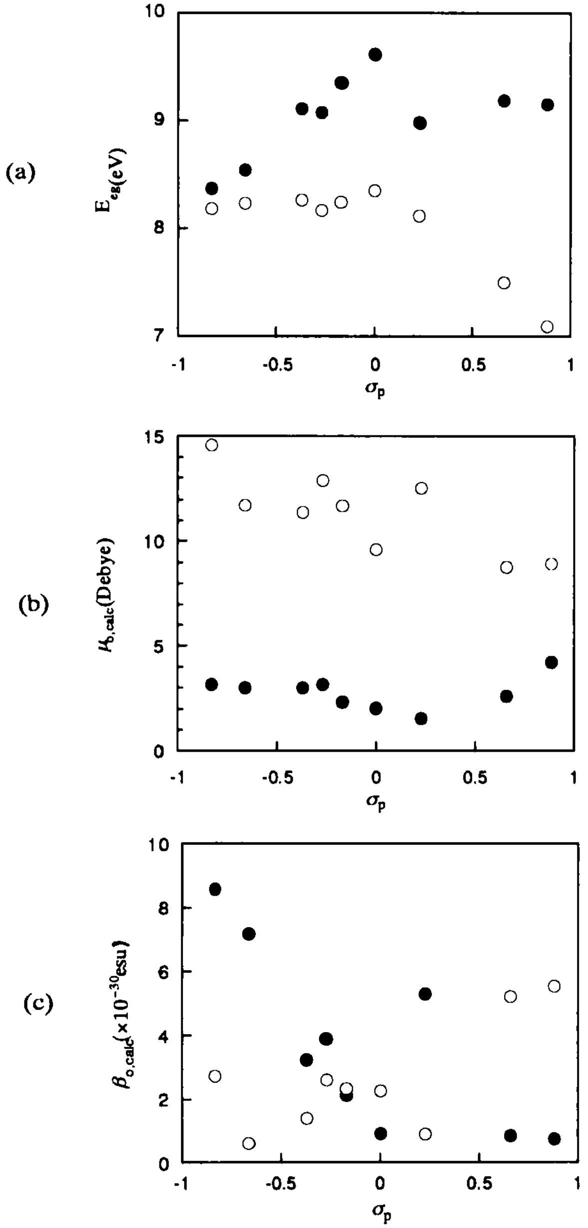
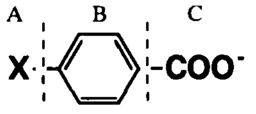
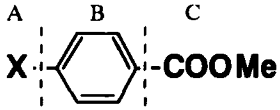


FIGURE 2 Plots of the Hammet constant for *para*-substituents (σ_p) *vs*. energy gap between ground and excited states (E_{eg}) (a), dipole moment in ground state ($\mu_{0,calc}$) (b), and second-order hyperpolarizability ($\beta_{0,calc}$) (c). Open and closed circles indicate benzoate anions **1** and esters **2**, respectively. The order of substituents from ***a*** to ***i*** in FIGURE 1 just correspond to the order of the σ_p magnitude from positive to negative.

TABLE I Calculated charge distribution of subsitituented benzoate anions and esters. The unit of charge is in elementary electric charge (*e*).

Compounds	A part	B part	C part
			
NO_2	0.05	-0.30	-0.75
CN	-0.20	-0.04	-0.76
Cl	-0.02	-0.21	-0.77
H	0.08	-0.30	-0.78
CH_3	0.04	-0.26	-0.78
OH	-0.07	-0.15	-0.78
OCH_3	-0.10	-0.12	-0.78
NH_2	0.07	-0.29	-0.78
$N(CH_3)_2$	0.00	-0.22	-0.78
			
NO_2	0.12	-0.10	-0.02
CN	-0.15	0.18	-0.03
Cl	0.08	-0.05	-0.03
H	0.11	-0.07	-0.04
CH_3	0.08	-0.04	-0.04
OH	-0.02	0.06	-0.04
OCH_3	-0.02	0.06	-0.04
NH_2	0.15	-0.11	-0.04
$N(CH_3)_2$	0.11	-0.07	-0.04

donor show almost the same values with the corresponding non-substituted ones. Those substituted by acceptor decrease a little with increasing electron withdrawing abilities of the substituents. Since the minus charge on C part of benzoate anions is decreased from 1 *e*, electrons are considered to be transferred to other parts in the π-conjugated system, indicating that anionic carboxylate group behaves as a donor as was mentioned above. In the case of esters, the C part has a little minus charge, and weak electron accepting property of methoxycarbonyl group is confirmed.

The relation between σ_p and $\mu_{0,calc}$ of substituted benzoate anions **1** and esters **2** is shown in FIGURE 2 (b). The $\mu_{0,calc}$ values of benzoate anions are larger than those of esters. Those of ions irrespective of anionic or cationic obtained by the MNDO calculation using MOPAC program always become larger than those of the corresponding neutral species.[8] This is because the existence of positive or negative charge on organic conjugated systems make charge distribution larger than the corresponding neutral ones. The $\mu_{0,calc}$ values of benzoate anions generally decrease with increasing σ_p and those of methyl benzoates show a similar tendency except for large positive σ_p.

The correlation of σ_p and $\beta_{0,calc}$ of substituted benzoate anions **1** and esters **2** is shown in FIGURE 2 (c). For benzoate anions, the $\beta_{0,calc}$ values increase with increasing σ_p. On the other hand, the $\beta_{0,calc}$ values of methyl benzoates decrease with increasing σ_p. For the chlorinated derivatives corresponding to plots at σ_p=0.23, exceptionally large $\beta_{0,calc}$ for esters and small $\beta_{0,calc}$ for anions even in positive σ_p were obtained. In the case of stilbazolium derivatives studied previously, halogenated ones were found to have large β values compared with non-substituted one having similar cutoff.[17] These effects may be caused by π-electron donation as well as σ-electron induction of substituted halogens.

Because the $\beta_{0,calc}$ increase with decreasing E_{eg} as clarified by FIGURE 2 (a) and (c), better selection for the molecules with short cutoff (λ_{co}) and large β seemed to be methyl benzoates with a weak donor or benzoate anions with weak acceptor at *para*-position. Among them, we chose methyl 4-methoxybenzoate **2g** and evaluated its β_{expt} and λ_{co} experimentally to be 22x10^{-30} esu and 299 nm, respectively. Since comparatively large β value about 0.6 times of that of *p*NA and short cutoff wavelength of **2g** was confirmed, we decided to use this species as an NLO monomer unit for non-conjugated rigid-linear oligomers. And a new concept for designing NLO species, especially favorable to be utilized in poled polymer systems, has been created as is discussed in the next section.

Oligomers of Methyl 4-Methoxybenzoate

Let us consider about β and $\mu\beta$ values for various arrangement of two pieces of an NLO moiety having dipole μ and major β component in that direction as shown in FIGURE 3. FIGURE 3 (a) shows random orientation of molecules with an NLO moiety resulting that μ and polarization related to β are totally canceled in macroscopic scale. The models in FIGURE 3 (b) ~ (d) are polar structures. Table II summarizes number of molecule in the system (***n***), μ and β of a molecule and β and $\mu\beta$ of a system, i.e. $[\beta]_s$ and $[\mu\beta]_s$, respectivrly, for the models in FIGURE 3 (b) ~ (d). In FIGURE 3 (b), molecules composed of single NLO moiety are aligned in parallel not to cancel their dipoles, and the $[\beta]_s$ and $[\mu\beta]_s$ values become 2β and $2\mu\beta$, respectively. When two moieties are connected perpendicularly in head-to-head manner by a non-conjugated rigid linkage like Λ-type molecules[18] as shown in FIGURE 3 (c), the $[\beta]_s$ and $[\mu\beta]_s$ values of this molecular system become $\sqrt{2}\beta$ and $2\mu\beta$,

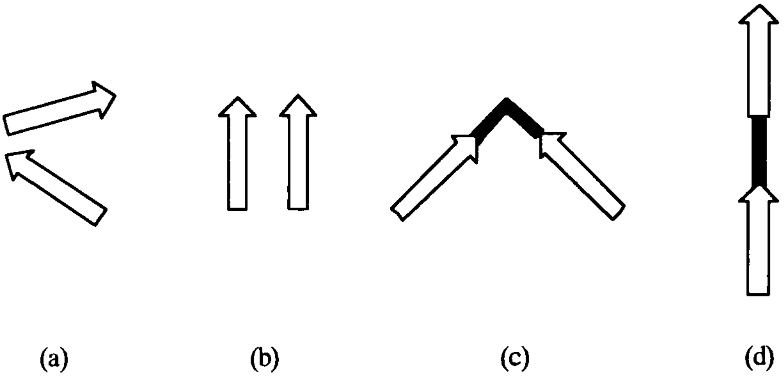


FIGURE 3 Schematic drawing of various arrangement of two pieces of an NLO moiety; (a): random orientation, (b): parallel orientation, (c): two moieties connected perpendicularly in head-to-head manner (Λ-type), (d): two moieties connected linearly in head-to-tail manner.

TABLE II Molecular number (n), dipole moment (μ) and second-order hyperpolarizability (β) of per molecule, $[\beta]_s$ and $[\mu\beta]_s$ of the models in FIGURE 3 (b) ~ (d).

	(b)	(c)	(d)
n	2	1	1
μ of per molecule	μ	$\sqrt{2}\ \mu$	2μ
β of per molecule	β	$\sqrt{2}\ \beta$	2β
$[\beta]_s$	2β	$\sqrt{2}\ \beta$	2β
$[\mu\beta]_s$	$2\mu\beta$	$2\mu\beta$	$4\mu\beta$

respectively. In this case, apparent β value per moiety becomes smaller than that for FIGURE 3 (b), expected second-order NLO efficiency in poled polymers proportional to $[\mu\beta]_s$ values are the same between (b) and (c) systems. When the two moieties are combined linearly in head-to-tail manner by a non-conjugated rigid linkage as shown in FIGURE 3 (d), the $[\beta]_s$ and $[\mu\beta]_s$ values of this molecular system are obtained to be 2β and $4\mu\beta$, respectively. Since apparent β value per moiety is almost the same as that for FIGURE 3 (b), $[\mu\beta]_s$ value becomes maximum among those systems. Since the two NLO moieties are combined by a non-conjugated linkage, the absorption cutoff should not be changed in spite of increase of β and $[\mu\beta]_s$ of a system. Extending the system in FIGURE 3 (d) to the oligomeric molecule with N species of an NLO moiety linearly bonded by a non-conjugated rigid linkage, the $[\beta]_s$ and $[\mu\beta]_s$ values of this system are calculated to be $N\beta$ and $N^2\mu\beta$, respectively, without any absorption shift to longer wavelength and any change on β value per moiety. Namely, N-times of linear combination of an NLO moiety provides N-

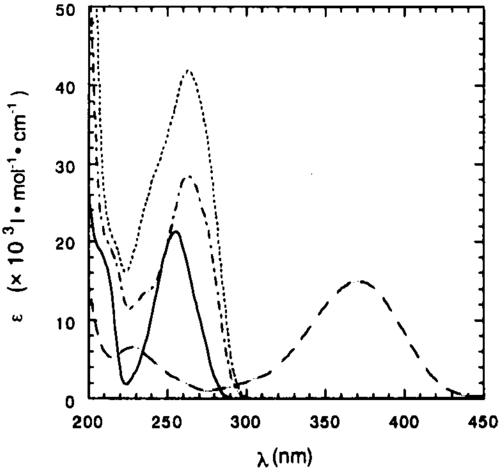


FIGURE 4 UV-visible absorption spectra of methyl 4-methoxybenzoate **2g** (—), its dimer **3g-2**(- - -), its trimer **3g-2**(······), and *p*-nitroaniline (– –).

TABLE III Calculated dipole moment ($\mu_{0,calc}$), calculated and experimental second-order hyperpolarizabilities ($\beta_{0,calc}$ and β_{expt}), and absorption data of methyl methoxybenzoate and its oligomers together with *p*-nitroaniline (*p*NA).

Compound	$\mu_{0,calc}$ (Debye)	$\beta_{0,calc}$ ($\times 10^{-30}$ esu)	β_{expt} ($\times 10^{-30}$ esu)	λ_{max} (nm)	λ_{co} (nm)	ε_{max} ($l \cdot mol^{-1} \cdot cm^{-1}$)
2g	1.9	3.9	22	255	299	21300
2g-2/3g-2*	4.0	8.8	49	263	301	28400
2g-3/3g-3*	5.6	11.5	71	263	302	41900
*p*NA	6.6	6.6	39	371	473	15000

* $\mu_{0,calc}$ and $\beta_{0,calc}$ values are for **2g** and the β_{expt}, λ_{max}, λ_{co} and ε_{max} values are of **3g**.

times of enhancement for second-order NLO efficiency in poled polymer systems, compared with the case of *N* species of isolated moieties. This consideration was experimentally confirmed by a series of oligomers **2g-2** and **2g-3** whose corresponding monomer is methyl 4-methoxybenzoate **2g**.

FIGURE 4 shows UV-visible absorption spectra of **2g**, **3g-2** and **3g-3** together with those of a typical D-A compound of *p*NA, and the μ and β values and absorption data of those four compounds are tabulated in TABLE III. Though **2g-2** and **2g-3** were used for MO calculation and **3g-2** and **3g-3** were used for experiment, no marked difference in optical properties are expected between **2g-2** and **3g-2** and between **2g-3** and **3g-3**, respectively, because of the same π-conjugated structures. The monomeric and oligomeric esters

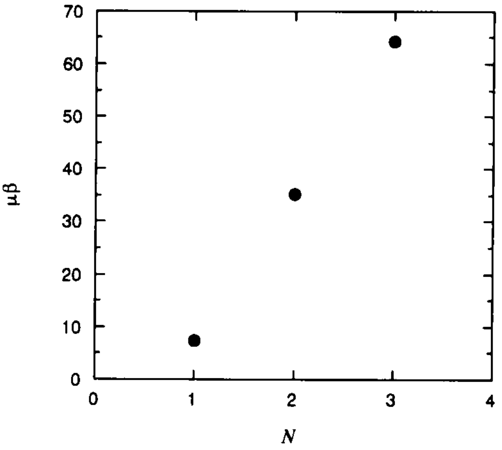


FIGURE 5 Relationship between number of repeating unit *N* in FIGURE 1 and $\mu_{o,calc}\beta_{o,calc}$ of methyl 4-metroxybenzoate and its oligomers.

show far shorter cutoff than *p*NA, and have no absorption in visible region. Among the ester compounds, there is few shift of 8 nm for λ_{max} from **2g** to **3g-2** and **3g-3**, and λ_{co} is almost maintained around 300 nm up to the trimer **3g-3**. The optimized calculated structures of oligomers showed that benzene rings are twisted in **2g-2** and **2g-3** and dihedral angles between two benzene ring planes are from 67° to 78°, suggesting no efficient π-conjugation between two benzene rings. This result well explains very few shift to longer wavelength in λ_{max} and λ_{co} and monotonical increase in ε_{max}.The μ and β values also monotonically increase with increasing the number of repeating unit (*N* indicated in FIGURE 1) for esters up to the trimer. The difference between experimental and calculated β values is considered to be due to difference in conditions, i.e. the calculated values are for at zero frequency and *in vacuo*, and the experimental values were obtained at 1064 nm in methanol solution. Though β of **2g** is less than that of *p*NA, the dimer and trimer showed about 1.3 and 1.7 times larger β than that of *p*NA in spite of about 170 nm shorter cutoff than *p*NA. The relationship of *N* and $\mu\beta$ is shown in FIGURE 5. The $\mu\beta$ ratios of **2g-2** and **2g-3** to **2g** are 4.8 and 9.0. They are confirmed to be almost agreed with theoretical ratios of 4 and 9 obtained by N^2 described above.This result clearly indicates new guideline to design large $\mu\beta$ molecules advantageous for poled polymers with host-guest or side-chain modified systems. The research on such poled polymers using these oligomers is in progress.

CONCLUSION

For short cutoff materials with large β useful for UV and blue SHG devices of laser diodes, a series of aromatic carboxylate anions and esters were investigated. Substituent effect at *para*-position of those derivatives were discussed in the relation between σ_p and calculated values such as E_{eg}, μ and β. Methyl benzoates with a weak donor or benzoate anions with a weak acceptor at *para*-position were found to be promising for such purpose. As one of the derivative satisfying above conditions, methyl 4-methoxybenzoate **2g** was selected to check its absorption and β experimentally, and was confirmed cutoff around 300 nm and comparatively large β of 22×10^{-30} esu. Its oligomers were also investigated to ascertain the possibility to attain large $\mu\beta$ molecules useful for NLO species in poled polymer systems without absorption shift to **2g** by using non-conjugated rigid-linear combination of 4-methoxybenzoate moiety. Both calculated and experimental results supported that the oligomeric system is actually useful to enhance $\mu\beta$ value.

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