Novel Molecular Design for Second-Harmonic Generation: Azlactone Derivatives

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Novel nonlinear optical materials, azlactone derivatives, have been intensively studied for second-harmonic generation (SHG). Some of these derivatives exhibit large powder SHG efficiency and sufficient transparency in the region of the second-harmonic of Nd:YAG laser radiation (0.532 μ m). In particular, the SHG efficiency of 4-(4'-methoxybenzylidene)-2-phenyloxazolin-5-one (MBPO) is found to be about 17 times that of urea. Single crystals of MBPO were prepared by slow evaporation from an acetone solution. These crystals belong to the orthorhombic system with a space group symmetry $P2_12_12_1$. The second-order molecular hyperpolarizability (β) value of MBPO was determined to be 24.5 × 10⁻³⁰ esu by electric field induced SHG (EFISH) and is nearly equal to the reported β value of 2-methyl-4-nitroaniline (MNA). A calculation of β using the CNDO/S-CI method identifies the HOMO-LUMO transition moment as the dominent contribution to β . Furthermore, the oriented gas model description shows that the β component is aligned to yield the near maximum value possible in an MBPO crystal. The estimated d_{14} value is 4.61 pm/V, which is on the same order as in potassium titanyl phosphate (KTP).

Introduction

In recent years, since the large nonlinear optical effects were found in many organic crystals, these materials have been studied intensively for applications such as second-harmonic generation (SHG), electrooptic modulation, sum and difference frequency generation, and optical parametric oscillation.¹ In particular, those organic materials are expected to be useful for frequency up-conversion of conventional lasers. High nonlinearities are found in the molecules with extended conjugated π -electron systems and donor-acceptor groups such as nitroanilines at para positions.² Although these types of molecules possess large second-order molecular hyperpolarizabilities (β), they exhibit no second-order optical nonlinearities in crystals because of centrosymmetric packing. In general, molecules that possess a large β value have a tendency to crystallize in centrosymmetric packing structures due to the cancelation of their large permanent dipole moments and thus exhibit the vanishing SHG coefficient in the crystals.³ Various molecular designs have been applied to prevent centrosymmetric packing in the crystal. For example, the combination of a moderately long π -electron conjugate system and a relatively weak electron donor such as the methoxy, bromo, or iodo group is one of the effective approaches for the design of efficient SHG crystals.⁴⁻⁶ It has also been reported that the bent structures have an advantage in packing in a noncentrosymmetric way, and they easily stack in the same direction.⁷

Following this guiding principle, we investigated the powder SHG efficiencies⁸ of many organic materials that possess the bent conformation and moderately long π -electron conjugate system without a strong polar group. Some azlactone derivatives (2,4-substituted oxazolin-5-one) have been found to show high powder SHG efficiencies. Azlactone derivatives are known as intermediates leading to synthetic dehydro amino acids,⁹ and

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Figure 1. Molecular structures of azlactone derivatives 1-14. the general structural formula is shown in Figure 1. The Z configurations with a bent structure have been established.^{10,11} In addition, since there is no hydrogen bond but van der Waals interactions in the molecules, they are thought to stack easily in the same direction. From these unique molecular structures, the azlactonee derivatives have been expected to crystallize in noncentrosymmetric structures.

This paper presents an investigation of the powder SHG efficiency and transparency of 14 azlactone derivatives. We also describe the crystal structure of 4-(4'-methoxybenzylidene)-2-phenyloxazolin-5-one (1), abbreviated hereafter as MBPO, which showed the highest SHG efficiency in this study. It is also shown that the calculated β value of MBPO agrees with the experimental data. The β values are also used to estimate the nonlinear optical coefficients based on the oriented gas model description.¹²

Synthesis

Compounds 1-14 in Figure 1 were prepared according to the general procedure reported in the literature by reacting the

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corresponding aldehydes with hippuric acid or acetylglycine in acetic anhydride in the presence of sodium acetate.^{9,13} All the melting points were uncorrected. ¹H NMR spectra were recorded with a Varian XL-300 spectrometer, and the chemical shifts (δ) in parts per million (ppm) units were referenced to the TMS internal standard. Mass spectra were determined with a JEOL JMS-DX300 spectrometer. UV-vis spectra were recorded on a Hitachi U-4000 instrument equipped with a quartz cell of 10 mm optical path length. The cutoff wavelength (λ_{cutoff}) was evaluated from a value in a transmittance of 95% of the 1 mM acetonitrile solution.

4-(4'-Methoxybenzylidene)-2-phenyloxazolin-5-one (MBPO) (1). A mixture of *p*-anisaldehyde (24.6 g, 181 mmol), hippuric acid (36.9 g, 206 mmol), and sodium acetate (7.30 g, 89.0 mmol) in acetic anhydride (55 mL) was stirred at 60 °C for 3 h. After cooling the solution to room temperature, water (300 mL) was added, and the crude azlactone was filtered and washed with two portions of water (200 mL). Recrystallization from 1,4dioxane (250 mL) gave MBPO (32.0 g, 63.3%) as yellow needle crystals: mp 159–161 °C; FAB-MS *m*/*z* 280 [(M + H)⁺]; ¹H NMR (CDCl₃) δ = 3.89 (3H, s), 6.99 (2H, d, *J* = 8.7 Hz), 7.20 (1H, s), 7.52 (2H, t, *J* = 7.9 Hz), 7.59 (1H, t, *J* = 7.9 Hz), 8.16 (2H, d, *J* = 7.9 Hz), 8.19 (2H, d, *J* = 8.7 Hz).

Found: C, 73.39; H, 4.79; N, 4.97. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02.

Compounds 2-14 were obtained in a manner similar to that for MBPO.

4-(3'-Methoxybenzylidene)-2-phenyloxazolin-5-one (2): mp 106–107 °C; FAB-MS *m*/*z* 280 [(M + H)⁺]; ¹H NMR (CDCl₃) $\delta = 3.91$ (3H, s), 7.01 (1H, d, J = 8.7 Hz), 7.21 (1H, s), 7.38 (1H, t, J = 8.7 Hz), 7.53 (2H, t, J = 7.9 Hz), 7.63 (1H, t, J = 7.9 Hz), 7.67 (1H, d, J = 8.7 Hz), 7.94 (1H, s), 8.17 (2H, d, J = 7.9 Hz).

Found: C, 73.32; H, 4.73; N, 4.98. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02.

4-(2'-Methoxybenzylidene)-2-phenyloxazolin-5-one (3): mp 157–158 °C; FAB-MS m/z 280 [(M + H)⁺]; ¹H NMR (CDCl₃) δ = 3.91 (3H, s), 6.92 (1H, d, J = 8.3 Hz), 7.10 (1H, t, J = 8.3 Hz), 7.41 (1H, t, J = 8.3 Hz), 7.52 (2H, t, J = 7.9 Hz), 7.57 (1H, t, J = 7.9 Hz), 7.86 (1H, s), 8.16 (2H, d, J = 7.9 Hz), 8.96 (1H, d, J = 8.3 Hz).

Found: C, 73.38; H, 4.71; N, 4.93. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02.

4-Benzylidene-2-phenyloxazolin-5-one (4): mp 165–166.5 °C; FAB-MS m/z 250 [(M + H)⁺]; ¹H NMR (CDCl₃) δ = 7.25 (1H, s), 7.47–7.64 (6H, m), 8.14–8.20 (4H, m).

Found: C, 77.45; H, 4.49; N, 5.57. Calcd for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62.

4-(4'-Methylbenzylidene)-2-phenyloxazolin-5-one (5): mp 141.5–143 °C; FAB-MS *m/z* 264 [(M + H)⁺]; ¹H NMR (CDCl₃) $\delta = 2.41$ (3H, s), 7.20 (1H, s), 7.26 (2H, d, J = 8.7 Hz), 7.53 (2H, t, J = 7.9 Hz), 7.60 (1H, t, J = 7.9 Hz), 8.10 (2H, d, J = 8.7 Hz), 8.16 (2H, d, J = 7.9 Hz).

Found: C, 77.91; H, 5.04; N, 5.27. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32.

4-(4'-(Dimethylamino)benzylidene)-2-phenyloxazolin-5one (6): mp 220–221 °C; FAB-MS m/z 292 [M⁺]; ¹H NMR (CDCl₃) δ = 3.09 (6H, s), 6.72 (2H, d, J = 9.2 Hz), 7.20 (1H, s), 7.49 (2H, t, J = 6.9 Hz), 7.52 (1H, t, J = 6.9 Hz), 8.10 (2H, d, J = 9.2 Hz), 8.14 (2H, d, J = 6.9 Hz).

Found: C, 74.19; H, 5.58; N, 9.51. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58.

4-(4'-Cyanobenzylidene)-2-phenyloxazolin-5-one (7): mp 225–226 °C; FAB-MS m/z 275 [(M + H)⁺]; ¹H NMR (CDCl₃) $\delta = 7.17$ (1H, s) 7.55 (2H, t, J = 7.9 Hz) 7.65 (1H, t, J = 7.9 Hz), 7.74 (2H, d, J = 8.7 Hz), 8.20 (2H, d, J = 8.7 Hz), 8.30 (2H, d, J = 7.9 Hz).

Found: C, 74.57; H, 3.67; N, 10.02. Calcd for $C_{17}H_{10}N_2O_2$: C, 74.44; H, 3.68; N, 10.21.

4-(4'-Nitrobenzylidene)-2-phenyloxazolin-5-one (8): mp 246–247 °C; FAB-MS m/z 295 [(M + H)⁺]; ¹H NMR (DMSOd₆) $\delta = 7.47$ (1H, s), 7.66 (2H, t, J = 8.0 Hz), 7.77 (1H, t, J = 8.0 Hz), 8.20 (2H, d, J = 8.0 Hz), 8.35 (2H, d, J = 8.8 Hz), 8.55 (2H, d, J = 8.8 Hz).

Found: C, 65.56; H, 3.36; N, 9.39. Calcd for $C_{16}H_{10}N_2O_4$: C, 65.31; H, 3.43; N, 9.52.

4-(4'-Fluorobenzylidene)-2-phenyloxazolin-5-one (9): mp 188–190 °C; FAB-MS *m*/*z* 268 [(M + H)⁺]; ¹H NMR (CDCl₃) δ = 7.20 (1H, s), 7.26 (2H, d, *J* = 8.7 Hz), 7.53 (2H, t, *J* = 7.9 Hz), 7.60 (1H, t, *J* = 7.9 Hz), 8.10 (2H, d, *J* = 8.7 Hz), 8.16 (2H, d, *J* = 7.9 Hz).

Found: C, 72.15; H, 3.84; N, 5.17; F, 6.87. Calcd for $C_{16}H_{10}NO_2F$: C, 71.91; H, 3.77; N, 5.24; F, 7.11.

4-(4'-Chlorobenzylidene)-2-phenyloxazolin-5-one (10): mp 196.5–197.5 °C; FAB-MS m/z 284 [(M + H)⁺]; ¹H NMR (CDCl₃) δ = 7.19 (1H, s), 7.45 (2H, d, J = 8.7 Hz), 7.53 (2H, t, J = 7.9 Hz), 7.63 (1H, t, J = 7.9 Hz), 8.15 (2H, d, J = 8.7 Hz), 8.18 (2H, d, J = 7.9 Hz).

Found: C, 67.99; H, 3.54; N, 4.89; Cl, 12.67. Calcd for $C_{16}H_{10}NO_2Cl$: C, 67.74; H, 3.55; N, 4.94; Cl, 12.50.

4-(4'-Bromobenzylidene)-2-phenyloxazolin-5-one (11): mp 208–210 °C; FAB-MS m/z 328 [(M + H)⁺]; ¹H NMR (CDCl₃) $\delta = 7.16$ (1H, s), 7.55 (2H, t, J = 7.9 Hz), 7.60–7.68 (3H, m), 8.07 (2H, d, J = 8.7 Hz), 8.16 (2H, d, J = 7.9 Hz).

Found: C, 58.68; H, 2.99; N, 4.19; Br, 23.88. Calcd for $C_{16}H_{10}NO_2Cl$: C, 58.56; H, 3.07; N, 4.27; Br, 24.35.

4-(4'-Methoxybenzylidene)-2-methyloxazolin-5-one (12): mp 112-113.5 °C; FAB-MS m/z 218 [(M + H)⁺]; ¹H NMR (CDCl₃) $\delta = 2.37$ (3H, s), 3.86 (3H, s), 6.95 (2H, d, J = 8.7 Hz), 7.09 (1H, s), 8.05 (2H, d, J = 8.7 Hz).

Found: C, 66.56; H, 5.01; N, 6.24. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45.

4-(2'-Furilmethylidene)-2-phenyloxazolin-5-one (13): mp 175.5–177 °C; FAB-MS *m/z* 240 [(M + H)⁺]; ¹H NMR (CDCl₃) $\delta = 6.64$ (1H, t, J = 0.8 Hz), 7.17 (1H, s), 7.52 (2H, t, J = 7.9 Hz), 7.56–7.62 (2H, m), 7.67 (1H, d, J = 0.8 Hz), 8.15 (2H, d, J = 7.9 Hz).

Found: C, 70.44; H, 3.85; N, 5.63. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.86.

4-(2'-Thiophenylmethylidene)-2-phenyloxazolin-5-one (14): mp 178.5–180 °C; FAB-MS *m/z* 256 [(M + H)⁺]; ¹H NMR (CDCl₃) δ = 7.16 (1H, t, *J* = 4.7 Hz), 7.48 (1H, s), 7.52 (2H, t, *J* = 7.9 Hz), 7.57 (1H, t, *J* = 7.9 Hz), 7.62 (1H, d, *J* = 4.7 Hz), 7.70 (1H, d, *J* = 4.7 Hz), 8.16 (2H, d, *J* = 7.9 Hz).

Found: C, 66.17; H, 3.54; N, 5.32; S, 12.65. Calcd for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49; S, 12.56.

SHG Efficiency Measurements

SHG efficiencies were determined by the Kurtz powder method.⁸ For the fundamental light source, we used a Q-switch pulsed Nd:YAG laser operating at 1.064 μ m (10 ns pulse duration and 10 Hz repetition rate). The generated second-harmonic light was detected by a photomultiplier. Samples were ground to a fine powder (50–100 μ m grain size) with a mortar and pestle. The same average size of urea was used as a reference material.

It is suggested that the backbone skeleton of the azlactone has an advantage in crystalline formations lacking inversion symmetry, since the derivatives examined in this study exhibit second-order optical nonlinearities except for compound 2, as

 TABLE 1: Powder SHG Efficiencies Relative to Urea,

 Cutoff Wavelength, and Maxima Absorption Wavelength

compd ^a	λ_{cutoff} (nm)	λ_{\max} (nm)	SHG (× urea)
1	451	437	17.2
2	430	413	0.0
3	453	440	0.1
4	412	401	0.2
5	423	411	1.7
6	552	533	3.5
7	422	408	0.2
8	442	428	0.1
9	413	401	2.1
10	419	408	1.8
11	423	409	3.7
12	453	399	4.6
13	452	438	0.3
14	458	443	0.2

^a See Figure 1.

shown in Table 1. The cutoff wavelength values are also presented in Table 1. The results show sufficient transparency in the region of the second-harmonic light (0.532 μ m) of the Nd:YAG laser radiation, except for compound 6.

The derivatives with an electron-donating substituted benzylidene skeleton (compounds 1, 5, 6, and 9-11) show higher SHG efficiency than that of an unsubstituted derivative (compound 4). In particular, the SHG efficiency of MBPO is found to be about 17 times as large as that of urea. Compound 6 with a strong electron donor group, such as the dimethylamino group, has a large red-shifted cutoff wavelength; however, the value of powder SHG efficiency was smaller than that of either MBPO or 12 with weak electron donor groups, such as a methoxy group. On the other hand, derivatives 7 and 8 with electron-accepting substituted benzylidene skeleton reveal negligibly low SHG activities. Therefore, these results suggest that the electron donor group is more effective for enhancement of the SHG efficiency than the acceptor group at the para-position in the benzylidene skeleton. In general, the extended conjugated π -electron system with the intramolecular charge transfer is responsible for the enhancement of the SHG efficiency. The relationship between the electronic properties and the nonlinearity of the azlactone derivatives is investigated by the theoretical calculations described later.

Although the stabilization of the resonance structure by the electron donor group may be possible at the ortho position, the SHG efficiency of compound 3 was measured to be much smaller than that of MBPO. This may be due to isotropic arrangements of the molecules in the crystal or to a decrease in the resonance effect by thee molecular torsion that arises from steric hindrance between the methoxy group at the ortho position and the oxazolin-5-one skeleton.

The SHG efficiency of MBPO was about 4 times greater than that of compound 12. This is due to contributions from the elongated π -electron system of the phenyl group at the 2-position in the oxazolin-5-one skeleton. However, compound 12 indicates the same degree of SHG efficiency as the other azlactone derivatives with an electron-donating substituted benzylidene skeleton. Moreover, attempts to replace the benzylidene skeleton by the heteroaromatic methylidene skeleton were unsuccessful, where the powder SHG efficiencies of compounds 13 and 14 were smaller than that of MBPO. Therefore, the occurrence of the nonlinearity is mainly dependent on the electronic property of the benzylidene skeleton itself.

EFISH Measurements of MBPO

EFISH measurements of the β value for the MBPO molecule were performed by means of the method as described by Garito et al.¹⁴ This method involves an infinite dilution extrapolation method for β that accounts for local fields and minimizes the solute-solute and solvent-solvent interactions. The expression for the β value can be written by using experimentally determined values from studies of the EFISH, dielectric constant, refractive indices, and specific volume as

$$\frac{27M_{1}(n_{0}^{2}+2\epsilon_{0})}{\epsilon_{0}(n_{0}^{2}+2)^{3}(n_{1}^{2}+2)} \left\{ v_{0} \frac{\partial\Gamma_{L}}{\partial w} \Big|_{w=0} + \Gamma_{0} \frac{\partial\nu}{\partial w} \Big|_{w=0} + v_{0}\Gamma_{0} - v_{0}\Gamma_{0} \left[\frac{3}{n_{0}^{2}+2} \frac{\partial n^{2}}{\partial w} \Big|_{w=0} + \left(\frac{1}{\epsilon_{0}} - \frac{2}{2\epsilon_{0}+n_{0}^{2}} \right) \frac{\partial\epsilon}{\partial w} \Big|_{w=0} \right] \right\} = N_{A} \frac{\beta_{1}\mu_{1}}{5kT} (1)$$

Here the subscripts 0 and 1 refer to the solvent and solute, respectively, M_i is the *i*th species molecular weight, n_i are the refractive indices, ϵ_i is the dielectric constant, v_i is the specific volume, μ_i is the molecular dipole moment, Γ_L is the macroscopic solution susceptibility, w is the weight fraction of the solute, Γ_0 is the macroscopic solvent susceptibility, N_A is Avagadro's number, k is Boltzmann's constant, and T is the temperature.

In this measurement, we selected 1,4-dioxane as a solvent. The fundamental light source used was the above-mentioned Nd:YAG laser operating at 1.064 μ m. The sample solutions were injected into a slab-form cell, where a wedged gap between two stainless electrodes was 1.5 mm, and a 5 kV pulse was synchronized with the laser. The refractive indices of the solutions were measured with an Erma Abbe refractometer. The dielectric constants of the solutions were measured with a Yokokawa Hewlett Packard LCR meter. The molecular dipole moments were given by the measured concentration dependence of refrative indices and dielectric constants. A slab-form quartz crystal was used as a reference material for the EFISH measurement.

The observed Maker fringe pattern, specific volume, refractive indices, and dielectric constant in the range w = 0-0.020 gave the following values: $(\partial \Gamma_L/\partial w)_{w=0}, (\partial v/\partial w)_{w=0}, (\partial n^2/\partial w)_{w=0}$, and $(\partial \epsilon/\partial w)_{w=0}$ were 3.58×10^{-12} esu, $-0.20 \text{ cm}^3 \text{ g}^{-1}, 8.76 \times 10^{-1}$, and 7.70, respectively. In the result, the β value of MBPO was determined as 24.5×10^{-30} esu using $\mu = 3.77$ D. The magnitude of β is nearly equal to the reported β value of 2-methyl-4-nitroaniline (MNA) (16.7×10^{-30} esu).¹⁵

X-ray Crystallographic Structure Determination of MBPO

The crystal structure of MBPO was determined by the singlecrystal X-ray diffraction method. Single crystal of MBPO were obtained by slow evaporation of their acetone solution for a period of 2 days. Under these conditions, single crystal were grown to needles with a typical dimension of $5.0 \times 0.5 \times 0.2$ mm³. X-ray data were collected on a four-circle diffractometer (Rigaku AFC-5S) using Cu K α radiation. The structure was determined by the direct method on the TEXSAN program package. Further details of these analyses will be reported separately.¹⁶

The crystallographic data of MBPO are summarized in Table 2. As expected, the crystal belongs to a noncentrosymmetric space group $P2_12_12_1$. The structure of a MBPO molecule is shown in Figure 2. Almost all atoms of the molecule lie on the same plane, allowing a conjugated π -electron system over the whole molecule. The two benzene rings are located in *cis*

TABLE 2: Crystallographic Data of MBPO

formula	C ₁₇ H ₁₃ NO ₃
MW	279.29
crystal system	orthorhombic
space group	P212121
alÅ	16.184(3)
b/Å	21.368(4)
c/Å	3.979(1)
V/Å ³	1375.9(5)
Ζ	4
$D_x/g \text{ cm}^{-3}$	1.348
R	0.039
$R_{\rm w}$	0.037

form with regard to the double bond between C8 and C9, forming the Z configuration as previously established.^{10,11}

The packing of molecules in a crystal is shown in Figure 3. The packing force is dominated by the intermolecular van der Waals interactions and dipole-dipole interactions, but there are no hydrogen bondings. The planar molecules stack at intervals of 3.98 Å along the *c*-axis, which is parallel to the long axis of the needle-like crystal. These stacking interactions stabilize the MBPO crystal structure. The melting point was measured to be 159-161 °C, which is very high compared with other nonlinear organic crystals.

Calculation of Second-Order Molecular Hyperpolarizability

Theoretical calculations of the β values were performed by the all-valence-electron semiempirical CNDO/S-CI method. It has already been proven that the β values calculated by this method agree very well with the measured values of *p*nitroaniline, urea, etc.¹⁷⁻¹⁹ This method involves an initial configuration interaction treatment of ground- (g) and excitedstate (n and n') wave functions. The expression for the individual components of β can be written in terms of transition moments and excitation energies as

$$\beta_{ijk} + \beta_{ikj} = -\frac{e^3}{4\hbar^2} \sum_{n \neq n'} \left\{ (r_{gn'}^j r_{n'n}^i r_{gn}^k + r_{gn'}^k r_{n'n}^i r_{gn}^j) \times \left[\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)} \right] + \frac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} - \omega)} \right] + \frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)} \left[\frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)} \right] + \frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)} \right] + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - 2\omega)} \right] + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - 2\omega)} \right] + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} \right] + \frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} \right\} (2)$$

where e is the charge on an electron, ω is the frequency of the applied radiation field, $r'_{n'n} (=\langle n'|r'|n \rangle)$ is the matrix element of the displacement operator r' along the *i*th molecular axis between the excited-state wave functions $(|n'\rangle)$ and $|n\rangle$, $\Delta r'_n (=r'_{nn} - t'_{nn})$



Figure 2. ORTEP drawing for MBPO with atom numbering.

 r_{gg}^i is related to the difference between the excited- and groundstate dipole moments ($\Delta \mu_n^i = -e\Delta r_n^i$), and $\hbar \omega_{ng}$ is the magnitude of the transition energy between the excited and ground states.¹⁹ Now, the vector components (β_i : i = x, y, z) of β are expressed by the following formula:²⁰

$$\beta_{i} = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}), \, i, j = x, \, y, \, z \quad (3)$$

and the magnitude of β is given by

$$|\beta| = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$
(4)

Geometrical parameters of MBPO were taken from the crystallographic data as described previously. For the study of compounds 2 and 3, the hydrogen atom in the 3' or 2' position of MBPO was replaced by the methoxy group in the 4' position. Similarly, for compounds 4-8, the methoxy group in the 4' position of MBPO was replaced by the corresponding substitution group; and for compound 12, the phenyl group in the 2 position of MBPO was replaced by the methyl group. Then the substituted groups and the aromatic ring were made coplanar in each molecule, as in MBPO. The molecular coordinate system (x',y',z') attached to the molecule is set up as shown in Figure 4, where the MBPO molecule lies almost in the x'y'plane, with the x'-axis being along the carbonyl bond (C10-O2) and the y'-axis being close to the C8–C9 double bond. Similarly, for compounds 2-8 and 12, the same coordinate system was selected. The molecular coordinate system attached to an MNA molecule, which is considered as a reference in this calculation, is set up where the molecule lies in the x'y'plane, with the y'-axis being along the permanent dipole moment. For the summation of β in eq 2, 120 configurations were involved for the configuration interaction calculation, since the $|\beta|$ value converged to an optimum with about 80 excited states.

When the *i*-axis is along the molecular dipolar direction in eq 3, the projection of the vector β onto the permanent dipole moment, β_M , corresponds to the measured β value obtained by the EFISH method, as described previously. The calculated β_i value along the permanent dipole moment (β_M) for MBPO is 10.80×10^{-30} esu, and this value is in satisfactory agreement with the experimental result. Therefore, the β value calculated by this method can be used for the analysis of the relationship between electronic properties and the second-order nonlinearity in the azlactone derivative molecule and also for the estimation of the crystalline nonlinear optical coefficients.

A. Relationship between Electronic Properties and Hyperpolarizability. The sum-over-states expression (eq 2) can be separated into two contributions, the two-level term (the fourth term in eq 2 and the three-level terms (the first, second, and third terms in eq 2). In general, the dominant contribution



Figure 3. Crystal structure of MBPO along the a-axis, the b-axis, and the c-axis.



Figure 4. Molecular coordinate system for MBPO.

to β comes from the two-level terms.²¹ In the numerator of the two-level terms, the primary contributor to the summation is the state that has the largest transition moment ($M_{gn} = -er_{gn}$) and also the largest difference between the ground- and excited-state dipole moments. Similarly, in the denominator when the magnitude of the transition energy between the ground and excited states ($\hbar\omega_{ng}$) is close to $\hbar\omega$ or $\hbar(2\omega)$ or the magnitude of $\hbar\omega_{ng}$ is small, the contribution to β increases. These conditions for the enhancement of β tend to be fulfilled in single-electron excitation from the highest occupied molecular orbital (LUMO) among nonlinear organic molecules.

Table 3 shows the calculated results of electronic properties and β values in the azlactone derivatives. The value of $|\beta_{y'y'y'}|$, which is the product of $\Delta \mu$ in the direction of the y'-axis ($\Delta \mu^{y'}$) and M_{gn} in the same direction $(M^{y'}_{gn})$, is almost equal to the magnitude $|\beta|$ calculated from excitations throughout all of the azlactone derivatives, where the correlation coefficient value is 0.98 in Figure 5. Moreover, a strong correlation is also obtained between $|\beta|$ and $|\beta_{HOMO \rightarrow LUMO}|$, which is calculated only for the two-level term from the excited state including the HOMO-LUMO π -electron transition dominantly (correlation coefficient value of 0.97 in Figure 6), although the magnitude of the latter is almost twice as large as that of the former. These results suggest that the HOMO-LUMO transition predominantly contributes to the value of $|\beta|$. The values of $|\beta|$ for the azlactone derivatives except for compounds 3 and 7 are larger than that of MNA.

We analyzed in detail the relationships between electronic properties, such as $\hbar\omega_{ng}$, $\Delta\mu$, and M_{gn} for the HOMO-LUMO transition of the azlactone derivatives in the context of the two-level term, and the magnitude of $|\beta|$. In Figure 7, we present

a plot of $|\beta|$ as a function of the inverse of the squared HOMO– LUMO transition energy value corresponding to the chargetransfer transition $(1/(\hbar\omega_{ng})^2)$. The correlation coefficient between the $|\beta|$ and $1/(\hbar\omega_{ng})^2$ is found to be 0.50. Therefore, the HOMO–LUMO transition energy is somewhat responsible for the value of $|\beta|$. The calculated values for the HOMO– LUMO transition energy are consistently larger than the experimental values that are estimated from the absorption maxima (λ_{max}) in Figure 8. This may be partly explained by the solvatochromism of the acetonitrile solutions, while the CNDO/S-CI results are related to isolated molecules (gas phase).

Next, the dependence of $|\beta|$ on $\Delta\mu^{y'}$ was investigated. In Figure 9, there is a strong correlation between $\Delta\mu^{y'}$ and $|\beta|$, and the correlation coefficient is found to be 0.96. All the values of $\Delta\mu^{y'}$ of the azlactone derivatives are smaller than that of MNA, while the values of $|\beta|$ of the azlactone derivatives are larger than that of MNA. Therefore, the effect of $\Delta\mu^{y'}$ on $|\beta|$ seems to be strong. However, the derivatives 7 and 8, which include the strong electron-accepting substitution, show negligibly low SHG activities, as previously mentioned. The larger ground-state dipole moment along the y'-axis ($\mu^{y'}g$) of 7 and 8 leads to a stronger dipole—dipole interaction between the molecules to form isotropic arrangements of the molecules in the crystal and eventually to cancel partly the hyperpolarizabilities to each other.

The difference of the calculated values M'_{gn} are within 1.5 D among the azlactone derivatives, while there is a wide difference in the $|\beta|$ values, as shown in Figure 10. These results indicate that the transition moment between HOMO and LUMO does not play a major role in the change of the $|\beta|$ values. However, the large magnitudes of $|\beta|$ are generally due to the large magnitudes of M'_{gn} , since the M'_{gn} value of the azlactone derivatives are more than twice as large as that of MNA.

Therefore, from these considerations, it is clear that the magnitude of $|\beta|$ is almost the same as that of $\Delta\mu^{y'}$, and the large $|\beta|$ values of the azlactone derivatives are due to their large M'_{gn} values. In addition, since most azlactone derivatives have large $|\beta|$ values in contrast to small $\mu^{y'}_{g}$ values as compared with that of MNA molecule, they have an advantage for crystallizing in a noncentrosymmetric form and are expected to be useful nonlinear optical molecules.

B. Origin of Hyperpolarizability of the MBPO Crystal. From the calculated values of β components, the nonlinear coefficients d_{IJK} in crystal can be estimated by the oriented gas

TABLE 3: Results of Electronic Properties and the Magnitudes of Hyperpolarizability from the HOMO-LUMO Transition $(|\beta_{\text{HOMO}-\text{LUMO}}|)$ and from the Entire Transition $(|\beta|)$ in Azlactone Derivatives

compd ^a	ħω _{HOMO→LUMO} (eV)	μ ^{у′} номо-lumo (D)	$ \begin{array}{c} \mu^{y' g} \\ (D) \end{array} $	M ^{y'} HOMO→LUMO (D)	$ \beta_{\text{HOMO} \rightarrow \text{LUMO}} $ (10 ⁻³⁰ esu)	$ \beta_{y'y'y'} $ (10 ⁻³⁰ esu)	$\frac{ \beta }{(10^{-30}\mathrm{esu})}$
1	3.66	-5.73	-0.72	9.61	37.99	17.44	19.09
2	3.75	-4.59	-1.10	9.51	23.71	11.10	11.69
3	3.69	-3.68	-1.15	9.14	16.79	8.38	9.46
4	3.76	-3.05	-0.60	9.43	16.32	10.11	10.97
5	3.70	-4.71	-0.10	9.50	33.02	14.36	15.82
6	3.64	-4.66	0.64	9.59	40.71	18.77	20.84
7	3.68	4.49	5.59	10.13	9.05	4.71	4.97
8	3.56	12.69	7.79	10.12	45.38	17.80	22.30
12	3.93	-4.62	-1.12	8.77	16.14	9.64	12.64
MNA	4.22	14.74	8.22	4.32	15.88	12.23	10.40

^a See Figure 1.



Figure 5. Relationships between $|\beta|$ and $|\beta_{y'y'y'}|$: (O) MBPO; (\bullet) compounds 2-8 and 12; (\Box) MNA.



Figure 6. Relationships between $|\beta|$ and $|\beta_{HOMO-LUMO}|$: (O) MBPO; (\bigcirc) compounds 2-8 and 12; (\Box) MNA.

model description:12

$$d_{IJK} = \frac{f^{2\omega} f^{\omega} f^{\omega} f \omega_{K}}{V} \sum_{i,j,k} \sum_{s} (\cos^{(s)} \theta_{Ii}) (\cos^{(s)} \theta_{Jj}) (\cos^{(s)} \theta_{Kk}) \beta_{ijk}^{(s)}$$
(5)

where V is the unit cell volume, $f'_I = \{(n^{\nu}_i)^2 + 2\}/3$ is a Lorentz local field factor for the principal dielectric axis I, the frequency ν , and the refractive index n^{ν}_I , θ_{Ii} is the angle between the principal dielectric axis I and the crystallographic axis i, and the summation is performed over all the molecules (indexed by s) in the unit cell. For the $2_12_12_1$ point group, such as the MBPO crystal, there are only three nonvanishing nonlinear



Figure 7. Relationships between $|\beta|$ and the HOMO-LUMO excitation energy ($\hbar\omega$): (\bigcirc) MBPO; (\bigcirc) compounds 2–8 and 12; (\Box) MNA.



Figure 8. Relationships between transition energy $(\hbar\omega)$ of experimental data estimated from maximum absorption wavelength and calculated value: (\bigcirc) MBPO; (\bigcirc) compounds 2–8 and 12; (\Box) MNA.

coefficients: d_{14} , d_{25} , and d_{36} .²² When the Kleinman's symmetry relation²³ are applied, the following equality holds:

$$d_{14} = d_{25} = d_{36} \tag{6}$$

Therefore, only d_{14} , that is, d_{XYZ} in the principal dielectric coordinate system, is an independent nonvanishing tensor component. Moreover, for the $2_12_12_1$ point group, where the principal dielectric axes X, Y, and Z are found to be parallel to the crystallographic axes a, b, and c, respectively, d_{XYZ} is reduced from eq 5 to the simpler form

$$d_{XYZ} = \frac{\int_{-\infty}^{\infty} \sqrt{f^{(0)}} \sqrt{f^{(0)}} Z}{V} \sum_{s} \beta^{(s)}_{xyz}$$
(7)



Figure 9. Relationships between $|\beta|$ and the difference of dipole moment ($\Delta \mu$): (\bigcirc) MBPO; (\oplus) compounds 2–8 and 12; (\Box) MNA.



Figure 10. Relationships between $|\beta|$ and the transition moment (M_{gn}) : (O) MBPO; (\bullet) compounds 2-8 and 12; (\Box) MNA.

It is shown that the value of d_{XYZ} for MBPO is dependent only on the β_{xyz} value.

To investigate which portions in the structure of MBPO contribute to the β_{xyz} value, we calculated in detail the molecular hyperpolarizability tensor components. The relationship between the foregoing molecular coordinate system (x',y',z') and the crystallographic coordinates (x,y,z) system is presented as follows:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} a_{xx'} & a_{xy'} & a_{xz'} \\ a_{yx'} & a_{yy'} & a_{yz'} \\ a_{zx'} & a_{zy'} & a_{zz'} \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -0.1539 & 0.9870 & 0.0457 \\ -0.8286 & -0.1039 & -0.5501 \\ -0.5382 & -0.1226 & 0.8338 \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} (8)$$

where $a_{ii}' = \cos \theta_{ii'}$ and $\theta_{ii'}$ is the angle between the crystallographic *i*-axis and the molecular coordinate *i'*-axis. Then the relationship between β_{ijk} and $\beta_{i'j'k'}$, which are the β tensor components in the corresponding coordinate systems, is presented as follows:

$$\beta_{ijk} = \sum_{i',j',k'} a_{ii'} a_{jj'} a_{kk'} \beta_{i'j'k'}$$
(9)

From eqs 8 and 9 the tensor component β_{xyz} is predominantly represented by the $\beta_{y'x'y'} = \beta_{y'y'x'}$, $\beta_{y'x'x'}$, and $\beta_{y'y'y'}$ values, and



Figure 11. Relationships between molecular orbitals and excited states $|1\rangle$, $|5\rangle$, and $|7\rangle$ of MBPO.

TABLE 4: Results of Transition Energy ($\hbar \omega_{ng}$), Dipole Moment Change ($\Delta \mu$) and Transition Moment (M_{ng}) for Excited States |1 \rangle to 18 \rangle of MBPO

excited state	$\hbar\omega_{ng} ({ m eV})$	$\Delta \mu^{x'}(\mathbf{D})$	$\Delta \mu^{y'}(D)$	$M^{x'}_{ng}(\mathbf{D})$	$M^{y'}_{ng}(D)$
$ 1\rangle$	3.66	-0.02	-5.01	-0.08	-9.61
$ 2\rangle$	4.21	1.12	1.70	0.06	0.01
3	4.36	0.39	1.56	0.82	-0.61
$ 4\rangle$	4.61	0.31	-0.89	-0.34	-0.34
$ 5\rangle$	4.67	2.25	-7.69	3.11	1.00
$ 6\rangle$	5.21	1.75	-5.21	0.76	-0.55
17)	5.25	-3.76	-0.42	-2.89	1.42
8>	5.55	-1.49	-0.61	1.32	-1.52

the relationship is given as follows:

$$\beta_{xyz} \approx 0.100\beta_{y'x'y'} + 0.055\beta_{y'y'x'} + 0.440\beta_{y'x'x'} + 0.013\beta_{y'y'y'}$$
$$= 0.155\beta_{y'x'y'} + 0.440\beta_{y'x'x'} + 0.013\beta_{y'y'y'} = -1.42 \times 10^{-30} \text{ esu} (10)$$

where the values of $\beta_{y'x'y'}$, $\beta_{y'x'x'}$, and $\beta_{y'y'y'}$ are -4.76, -1.04, and -17.44 (×10⁻³⁰ esu), respectively. This result exhibits an appreciable agreement with the directly calculated value $\beta_{xyz} =$ -1.29 × 10⁻³⁰ esu in the crystallographic coordinate system. As expected from the mathematical requirement of $P2_12_12_1$ space symmetry, $\beta_{y'y'y'}$, the largest component of β , has a much smaller contribution than $\beta_{y'x'y'}$ and $\beta_{y'x'x'}$, as shown in eq 10.

As can be seen from Table 4, the excited states $|1\rangle$, $|5\rangle$, and $|7\rangle$ have large $\Delta \mu^{y'}$ and $M^{y'}_{gn}$ components for the two-level term calculation in the molecular coordinate system. The excited states $|1\rangle$, $|5\rangle$, and $|7\rangle$ are characterized, respectively, by single excitation from HOMO to LUMO, from HOMO to the second lowest unoccupied molecular orbital (SUMO), and from the second highest occupied molecular orbital (SOMO) to LUMO, as shown in Figure 11. The SOMO, HOMO, LUMO, and SUMO of MBPO are shown in Figure 12 with their orbital coefficients, and the localizations of π electrons along the y'axis in each orbital can be seen. Moreever, it is found that the transition moments $(M_{nn'})$ among these excited states, contributing to the three-level terms in eq 2, also have large magnitudes (Table 5). From Table 6, $\beta_{y'x'y'}$, $\beta_{y'x'y'}$, and $\beta_{y'y'y'}$ are well represented by the contributions from the three-level terms $\{|1\rangle$, $|7\rangle$ and $\{|1\rangle, |5\rangle\}$ and the two-level term $\{|1\rangle\}$, respectively. The main portion of $\beta_{y'x'y'}$, which has about 60% contribution to β_{xyz} , comes from the three-level term: $M^{y'_{1g}}$, $M^{y'_{17}}$, and $M^{x'_{7g}}$, in which the y' component of the HOMO-LUMO transition moment $M^{y'}_{1g}$, almost parallel to the π -conjugated chain through C5-C8-C9-N1-C11-C12 of MBPO, has the dominant contribution. Similarly, the HOMO-LUMO transition moment $M^{y'_{1g}}$ has large contributions to both $\beta_{y'x'x'}$, and $\beta_{y'y'y'}$, which have 35% and 15% contributions to β_{xyz} , respectively. The HOMO-LUMO excitation along this extended π -conjugated chain induces a large charge transfer and enhances the transition moment along the direction of this chain $(r^{y'}_{ng})$. However, $\beta_{y'y'y'}$, the largest component of β , which consists of the product of $\Delta \mu_{y'}$ and $M^{y'}_{1g}$, is not well reflected in the occurrence of the



Figure 12. Comparisons of SOMO, HOMO, LUMO, and SUMO in the MBPO molecule. The $2p_{z'}$ orbital coefficients are summed up for each atomic center.

nonlinearity in the MBPO crystal because of the space group symmetry, $P2_12_12_1$.

C. Theoretical Estimation of Nonlinear Coefficient d_{14} in the MBPO Crystal. d_{14} of the MBPO crystal, the only independent nonvanishing coefficient, can be estimated from eq 7 using the calculated value $\beta_{xyz} = -1.29 \times 10^{-30}$ esu. The refractive indices along the *c*-axis of the MBPO crystal were measured by means of the Becke line method²⁴ in the visible range (500-650 nm), as shown in Table 7, and fitted with the Sellmeir's dispersion formula as follows:

$$n^2 = 2.2253 + 0.0372/(\lambda^2 - 0.0163)$$
(11)

where λ is the wavelength in micrometers. The Sellmeir formula gives the refractive indices at 1064 and 532 nm as 1.503 and 1.538, respectively. In the result, d_{14} is estimated to be 4.61 pm/V. This is the same order as KTP ($d_{eff} = 7.37$ pm/V)²⁵ and 2-methyl-4-nitroaniline (POM) ($d_{14} = 9.4$ pm/V)²⁶ crystals.

Conclusion

The nonlinear optical properties of some azlactone derivatives have been investigated. It has been clarified that the backbone skeleton of the derivatives has an advantage in noncentrosymmetric packing in the crystals, since the derivatives examined in this study exhibit SHG efficiencies in powder form except for compound **2**. Moreover, the azlactone derivatives show sufficient transparency in the region of the second-

TABLE 5: Transition Moments ($M_{nn'}$) among the Excited States $|1\rangle$, $|5\rangle$, and $|7\rangle$ of MBPO

excited states	$M^{x'}{}_{nn'}(D)$	$M^{y'}_{nn'}(D)$		
1>, 5>	3.77	-7.24		
$ 1\rangle, 7\rangle$	0.09	-9.44		
5), 17)	1.40	1.31		

TABLE 6: Calculated Hyperpolarizability (β) of MBPO

excited state(s)	contribution term in eq 2	$\frac{\beta_{y'x'y'}}{(10^{-30}\mathrm{esu})}$	$\beta_{y'x'x'} $ (10 ⁻³⁰ esu)	$\frac{\beta_{y'y'y'}}{(10^{-30}\mathrm{esu})}$
1>	two-level	-0.26	-0.00	-37.99
5	two-level	-0.54	-0.51	-0.29
17>	two-level	-0.05	0.29	-0.02
1), 5)	three-level	3.15	-2.67	3.88
1), 17	three-level	-4.16	0.03	6.14
5>, 7>	three-level	0.04	-0.08	0.06
total		-4.76	-1.04	-17.44

TABLE 7:	Measurement	of	Refractive	Indices	for	MBPO
Crystal						

wavelength (µm)	refractive index
0.450	1.557
0.500	1.545
0.550	1.535
0.600	1.527
0.650	1.521
0.700	1.519

harmonic wave (0.532 μ m) of the Nd:YAG laser radiation except for compound **6**. Therefore, these derivatives are good candidates as frequency conversion to the region of the green and blue light. The relationship between their structure and SHG efficiencies suggested that the dominant role played was expansion of the delocalized range of π -electrons of the azlactone derivative by the electron donor group rather than acceptor at the para position in the benzylidene skeleton. In particular, the SHG efficiency of MBPO is found to be about 17 times as large as that of urea. The β value of the MBPO molecule was measured by means of the EFISH and determined as 24.5×10^{-30} esu. This magnitude is nearly equal to the reported β value of MNA (16.7×10^{-30} esu).

We have performed the theoretical calculation of β by using the CNDO/S-CI method to understand the occurrence of the nonlinearity in MBPO molecules. It has been found that the large β is dominated by the large M_{gn} values in the HOMO-LUMO transition, while the β value of MNA is due to the $\Delta \mu$ values. In addition, since most azlactone derivatives including MBPO have the large β but small μ_g values as compared with those of the MNA molecule, they have an advantage for crystallizing in a noncentrosymmetric form. Furthermore, the occurrence of the nonlinearity of the MBPO crystal and the estimation of d_{14} , the only independent nonvanishing tensor component in the $2_12_12_1$ space group, have been performed on the basis of the oriented gas model description. In that result, the second-order nonlinearity for the MBPO crystal mainly originates from the HOMO-LUMO transition moment along the direction that is almost parallel to the extended π -conjugated chain of MBPO. However, it has been found that the large $\Delta \mu$ as well as M_{gn} or $M_{nn'}$ in the direction of the chain is not effectively reflected in the occurrence of the nonlinearity in the MBPO crystal because of the space group symmetry, P212121. The estimated d_{14} value (4.61 pm/V) is on the same order of the KTP crystal ($d_{eff} = 7.37 \text{ pm/V}$) and POM ($d_1 = 9.4 \text{ pm/V}$) crystals. We also have confirmed the phase-matching ability of MBPO crystals from the powder SHG as a function of particle size. From the present study, MBPO is expected to be

promising as a new nonlinear optical material for SHG in the green to blue region with low-power laser sources such as laser diodes.

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