

Heterocyclic Pyridinium Betaines, A New Class of Second-Order Nonlinear Optical Materials: Combined Theoretical and Experimental Investigation of First-Order Hyperpolarizability through ab Initio, INDO/S, and Hyper-Rayleigh Scattering

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The first hyperpolarizability, β , of one of the simplest heterocyclic pyridinium betaines, (1-pyridinio)-benzimidazolate, was measured experimentally with the hyper-Rayleigh scattering technique and compared to the calculated values obtained by the semiempirical INDO/S and ab initio molecular orbital methods. Heterocyclic pyridinium betaines are characterized by their zwitterionic character where a negatively charged aromatic electron-donating group and a positively charged aromatic electron-withdrawing group are linked directly. The experimentally obtained $|\beta|$ value, $(115 \pm 25) \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$, was in good agreement with those derived from the INDO/S calculations. The first excited state was found to be characterized by a strong intramolecular charge-transfer state, where the electron transition occurs from a negatively charged aromatic electron-donating group (benzimidazole ring) to a directly linked, positively charged aromatic electron-withdrawing group (pyridinium ring). This nature of the excited state would give rise to a large difference between the dipole moments in the excited and ground states and would contribute to enlargement of β values.

I. Introduction

There is currently a considerable effort to develop new organic materials exhibiting large nonlinear optical response in combination with other desirable physical properties (optical transparency and thermal and mechanical stability) because of their potential applications in optical signal processing and frequency conversion.^{1–6} It is well established that the extension of the conjugation path between the electron-donating and -withdrawing groups strongly increases the molecular hyperpolarizability. The extension of the conjugation path, however, also causes a bathochromic shift of the intramolecular charge-transfer absorption band, and thus, the requirement of high transparency to visible light is not met. Hyperpolarizabilities (β) are often described within the dipolar approximation on the basis of the so-called two-state model.^{7,8} Within the framework of the two-state model, the static β value, $\beta(0)$, is expressed as

$$\beta_{\mu}(0) = \frac{3(M_{ge})^2 \Delta\mu}{2(\hbar\omega_{ge})^2}$$

where $\Delta\mu = \mu_e - \mu_g$ is the difference between the dipole moments in the excited and ground states, $\hbar\omega_{ge}$ is the transition energy, and M_{ge} is the transition dipole moment between the ground and excited states. The two-state model implies that β increases as both $\Delta\mu$ and M_{ge} increase. In the conventional push–pull-type (D– π –A) systems, the extension of the conjugation path between the electron-donating and -withdrawing groups gives rise to significant increases in both $\Delta\mu$ and M_{ge} , which results in a pronounced increase in the β values.^{9–14}

The present study describes a new approach in the molecular design of second-order nonlinear optical (NLO) materials based on the new concept using a short-range charge transfer. We have considered that large β values would be obtained for relatively small molecules via a short-range intramolecular charge transfer from a charged aromatic electron-donating group to a directly linked, charged aromatic electron-withdrawing group. Heterocyclic pyridinium betaines, which contain both a negatively charged aromatic electron-donating and positively charged aromatic electron-withdrawing groups, are found to satisfy this requirement. Heterocyclic pyridinium betaines have received much attention because of their unusually large dipole moments, which are ascribed to their zwitterionic character, and the large hypsochromic shift of the predominant $\pi \rightarrow \pi^*$ transition in polar solvents (negative solvatochromism).^{15–26} From this large negative solvatochromism, it has been proposed that the dipolar character would dramatically decrease in the first excited states,²⁷ i.e., the ground state is characterized by the formula D[–]A⁺, while DA characterizes the excited state. Obviously, this would produce a large negative $\Delta\mu$. This system is different from the conventional D– π –A systems such as polyenes because the optical nonlinearity of the latter system results from a long-range charge transfer from a nonaromatic electron-donating group to a nonaromatic electron-withdrawing group through a long π -electron bridging unit.

Recently, Rutkis et al. reported the second harmonic generation (SHG) efficiency in Langmuir–Blodgett films of indandione-1,3-pyridinium betaine.²³ Moreover, Paley et al. reported the synthesis and characterization of some pyridinium-*N*-phenoxide betaine dyes (including Reichardt's dye) for SHG materials.²¹ They estimated a value of $\beta_{xxx} = 34 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ for Reichardt's dye for SHG at a laser wavelength of 1064 nm using the solvatochromic method. Morley also investigated

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the hyperpolarizability of 4-(benzimidazol-2-ylidene)-1-methyl-1,4-dihydropyridine, which is analogous to (1-pyridinio)benzimidazolate, by means of the CNDOVSB method and suggested the superiority of the cyclopentadienylpyridines over the conventional D- π -A molecules in nonlinear optical devices.²⁸ The present study was motivated by these structural characteristics of the heterocyclic pyridinium betaines, which make these compounds attractive for second-order NLO materials. In our previous paper, we have shown that heterocyclic pyridinium betaines have extremely large molecular hyperpolarizabilities for their molecular sizes by means of the molecular orbital (MO) calculations and have indicated the great potential of heterocyclic pyridinium betaines for applications in the NLO materials.²⁹ The main purpose of the present contributions is to confirm our idea and the validity of our previous theoretical investigations by experimental investigations. Here, we report for the first time the measurement of the β value of one of the simplest heterocyclic pyridinium betaines, 2-(1-pyridinio)benzimidazolate, by the hyper-Rayleigh scattering (HRS) technique and compare the results of the ab initio and INDO/S MO calculations.



II. Experimental Section

2-(1-Pyridinio)benzimidazolate was prepared as in the literature.²⁰ The HRS measurement was performed by measuring the intensity of the second-order scattered light on focusing an intense laser beam on an isotropic solution. This nonlinear light scattering in isotropic water was first reported by Terhune et al. in 1965.³⁰ Recently, Persoons and co-workers applied this HRS for the determination of the β values of nonlinear optical molecules, and the HRS is established as a new technique as a fast screening tool of newly synthesized second-order NLO materials.^{31,32} Until recently, the electric-field-induced SHG (EFISH) has been the only technique that allows the determination of β values in solution. However, one has to know the dipole moment and the second-order hyperpolarizability γ to determine exact β values. The HRS technique, however, does not need to use these physical parameters, and the dependence of the second-order scattered light intensity on the concentration of the nonlinear optical chromophores allows for an accurate determination of β values. Moreover, since the HRS technique, in contrast to the EFISH technique, does not require a strong orienting electric field, apolar and ionic species can also be evaluated. However, recently, one serious disadvantage of the HRS technique over the EFISH technique was pointed out. Flipse and co-workers reported a comparison of β values determined by the HRS technique and the EFISH technique for a series of electron donor-acceptor-substituted π -conjugated organic compounds and showed that there was a marked discrepancy between their values for NLO chromophores that fluoresce in the frequency-doubled wavelength region.³³ In general, the emission of visible light from the HRS sample being illuminated by an intense laser beam (1064 nm) can be ascribed to either the two-photon fluorescence or the three-photon fluorescence. If this fluorescence is present in the frequency-doubled wavelength region (532 nm), the HRS β value will be enhanced. Persoons et al. proposed that a 3 nm bandwidth interference filter could eliminate the fluorescence caused by the two-photon absorption, since this two-photon fluorescence is always red-shifted with respect to the two-photon excitation

wavelength.³⁴ However, it is difficult to eliminate the fluorescence caused by the three-photon absorption using the same method, since the three-photon fluorescence exhibits a broad emission band. We have considered that there is no simple solution for discriminating between these two processes, since both HRS and fluorescence are incoherent processes and, moreover, the two-photon fluorescence would be detected even in the wavelength region (<532 nm) that is shorter than the frequency-doubled wavelength region (532 nm). However, it is possible to reveal whether such fluorescence is present by substituting the 532 nm interference filter for a 550 nm interference filter or by substituting a 3 nm bandwidth interference filter at 532 nm for a 10 nm bandwidth interference filter at the same wavelength. Anyway, to estimate the accurate β values using the HRS technique, it is very important to ascertain whether or not multiphoton-induced fluorescence is present.

The intensity of the HRS signal ($S_{2\omega}$) is proportional to the number of scattering centers, the square of the β , and the square of the intensity of the fundamental light (I_0).³² The observed HRS signal can be represented as $S_{2\omega} = GB^2I_0^2$ with G being a geometry factor indicating the amount of signal captured by the experimental geometry. For a simple two-component system, $B^2 = N_{\text{solvent}}\beta_{\text{solvent}}^2 + N_{\text{solute}}\beta_{\text{solute}}^2$. N_{solvent} and N_{solute} represent the number density of the solvent molecules and the number density of the solute molecules, respectively. Measurement at different number densities of the solute shows a linear dependence of GB^2 on N_{solute} . From the intercept and the slope, β_{solute} is calculated when β_{solvent} is known.

Our experimental HRS setup is similar to that described by Persoons et al.³¹ A Q-switched Nd³⁺:YAG laser (Spectron SL404G, $\lambda = 1064$ nm, 10 Hz repetition rate, 6 ns pulse duration) was used as the exciting light source after decreasing its pulse energy to less than 1 mJ through neutral density filters. The incident IR intensity can be varied by rotating a half-wave plate between crossed linear polarizers. A small fraction of the incident beam is directed onto a fast photodiode for monitoring the incident fundamental light intensity to which the second harmonic light intensity will be compared. The fundamental laser beam is focused into the sample cell (parallelepipedic spectrophotometric quartz cell, optical path length of 40 mm) using a 70 mm focal length converging lens. Collection of the scattered second harmonic photons is performed using an efficient condenser system consisting of a concave mirror, an aspheric lens, and a planoconvex lens. A 3 nm bandwidth, 532 nm interference filter is placed before the photomultiplier tube. Sample solutions are preliminarily cleaned through 0.2 μm Whatman GD/X syringe filters in order to remove most of the microscopic particles that could induce optical breakdowns in the presence of the focused IR laser beam. The HRS signals were detected by a photomultiplier tube. The signal from the photomultiplier tube was integrated with a boxcar integrator (Stanford Research SR-250). A layout of our experimental setup is shown in Figure 1.

III. Theoretical Methods

MO calculations were carried out using the *Gaussian 92* and *Fujitsu MOS-F V3L1* program packages.^{35,36} For comparative purposes, the molecular structures have been fully optimized at both the HF level with the 6-31G and 6-31G** basis sets and the MP2 level with the same basis sets. On the basis of these geometries, the frequency-dependent β values were calculated by means of the sum-over-states (SOS) approach in the framework of the time-dependent perturbation theory based on the semiempirical INDO/S (intermediate neglect of differential overlap) Hamiltonian with configuration interaction

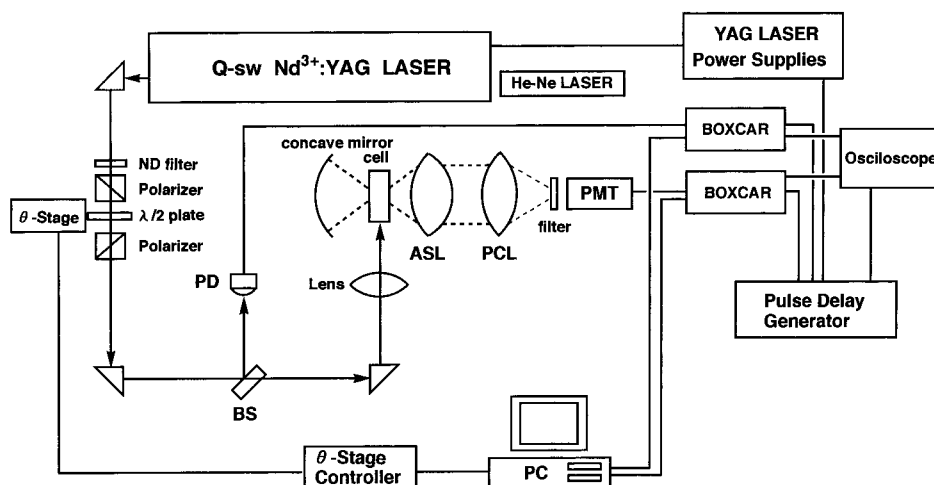


Figure 1. Experimental setup for the hyper-Rayleigh scattering measurement: ASL, aspheric lens condenser; PCL, planoconvex lens; PD, fast photodiode; BS, beamsplitter; PMT, photomultiplier tube.

(CI) wave functions.^{37–40} For the two-center electron repulsion integral, γ_{AB} , the Nishimoto–Mataga–Weiss (NMW) formula was used.³⁷ The NMW formula is expressed as follows.

$$\gamma_{AB} = \frac{f_r}{R_{AB} + \frac{2f_r k}{\gamma_{AA} + \gamma_{BB}}}$$

where R_{AB} is the interatomic distance between the A and B atoms in a molecule and γ_{AA} and γ_{BB} are the one-center electron repulsion integrals of the atoms A and B, respectively. f_r and k are the fitting parameters normally having the values of 1.2 and 1.0, respectively, in the INDO/S method. To reproduce the experimental values for both the dipole moments in the ground state and the transition energies for the heterocyclic pyridinium betaines, in the present paper, we have optimized the values of k and γ_{AA} of the nitrogen atom used in the NMW formula and the ionization potential, I_{N2p} , which corresponds to the 2p orbital of nitrogen atom. We have found that the experimental values could be reproduced well when k , γ_{AA} , and I_{N2p} were set to the values of 0.70, 7.00 (eV), and 10.00 (eV), respectively.

In the SOS expression, all electronic states generated by singly exciting all electrons in the highest 20 occupied molecular orbitals to the lowest 20 unoccupied molecular orbitals with respect to the ground state are included. Moreover, the static (zero frequency) values of β are calculated using the coupled perturbed Hartree–Fock (CPHF) formalism based on ab initio SCF wave functions.⁴¹ In this method, the β is determined from the analytical derivatives of the total energy with respect to the applied electric field.

Although all 27 components of the β tensor can be computed with methodologies described above, only the vector component along the dipole moment direction, the so-called β_{vec} , is represented as⁴²

$$\beta_{\text{vec}}(-2\omega; \omega, \omega) = \sum_{i=x,y,z} \beta_i \mu_i / |\mu|$$

where μ is the ground-state molecular dipole moment and β_i is

$$\beta_i(-2\omega; \omega, \omega) = \frac{1}{3} \sum_k (\beta_{ikk} + \beta_{kik} + \beta_{kki})$$

where i and k run over the molecular Cartesian directions x , y , and z . The individual tensor components of the β based on the

SOS approach are given as^{42–46}

$$\beta_{ijk}(-2\omega; \omega, \omega) = \frac{1}{4_{e,e' \neq g}} \sum \left[\frac{\langle 0 | \bar{\mu}_i | e \rangle \langle e | \bar{\mu}_j | e' \rangle \langle e' | \bar{\mu}_k | 0 \rangle}{(\Delta E_e - 2\hbar\omega)(\Delta E_{e'} - \hbar\omega)} + \frac{\langle 0 | \bar{\mu}_i | e \rangle \langle e | \bar{\mu}_k | e' \rangle \langle e' | \bar{\mu}_j | 0 \rangle}{(\Delta E_e - 2\hbar\omega)(\Delta E_{e'} - \hbar\omega)} + \frac{\langle 0 | \bar{\mu}_j | e \rangle \langle e | \bar{\mu}_i | e' \rangle \langle e' | \bar{\mu}_k | 0 \rangle}{(\Delta E_e + \hbar\omega)(\Delta E_{e'} - \hbar\omega)} + \frac{\langle 0 | \bar{\mu}_j | e \rangle \langle e | \bar{\mu}_k | e' \rangle \langle e' | \bar{\mu}_i | 0 \rangle}{(\Delta E_e + \hbar\omega)(\Delta E_{e'} + 2\hbar\omega)} + \frac{\langle 0 | \bar{\mu}_k | e \rangle \langle e | \bar{\mu}_i | e' \rangle \langle e' | \bar{\mu}_j | 0 \rangle}{(\Delta E_e + \hbar\omega)(\Delta E_{e'} - \hbar\omega)} + \frac{\langle 0 | \bar{\mu}_k | e \rangle \langle e | \bar{\mu}_j | e' \rangle \langle e' | \bar{\mu}_i | 0 \rangle}{(\Delta E_e + \hbar\omega)(\Delta E_{e'} + 2\hbar\omega)} \right]$$

where ijk are molecular Cartesian coordinates and ω is the incident laser frequency. $|0\rangle$ denotes the wave function of the molecular ground state; $|e\rangle$ and $|e'\rangle$ are the wave functions of the excited states of the system having transition energies given by ΔE_e and $\Delta E_{e'}$, respectively.

The dipole difference operator $\bar{\mu}_i$ is defined as

$$\bar{\mu}_i = \hat{\mu}_i - \langle 0 | \hat{\mu}_i | 0 \rangle$$

where $\hat{\mu}_i$ is the dipole moment operator defined as

$$\hat{\mu}_i = -e \sum_{s=1}^N i_s$$

where N represents the number of electrons.

The total intrinsic hyperpolarizability, β_{tot} is represented as

$$\beta_{\text{tot}}(-2\omega; \omega, \omega) = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

The β_{vec} will be identical with the β_{tot} when the charge transfer is collinear to the molecular dipole moment. Therefore, in chromophores where the charge transfer direction is obviously parallel with the ground-state dipole moment direction (for example, the x direction), the β_x will be identical with both the β_{vec} and the β_{tot} .⁴¹

One of the important properties of pyridinium betaines is their response to solvent effects. As described before, heterocyclic pyridinium betaines show a large negative solvatochromism.^{15–26} To take into account the solvent effect, we adopted Onsager's self-consistent reaction field (SCRF) approach as implemented in the *Gaussian 92* program. In this approach, the solute dipole

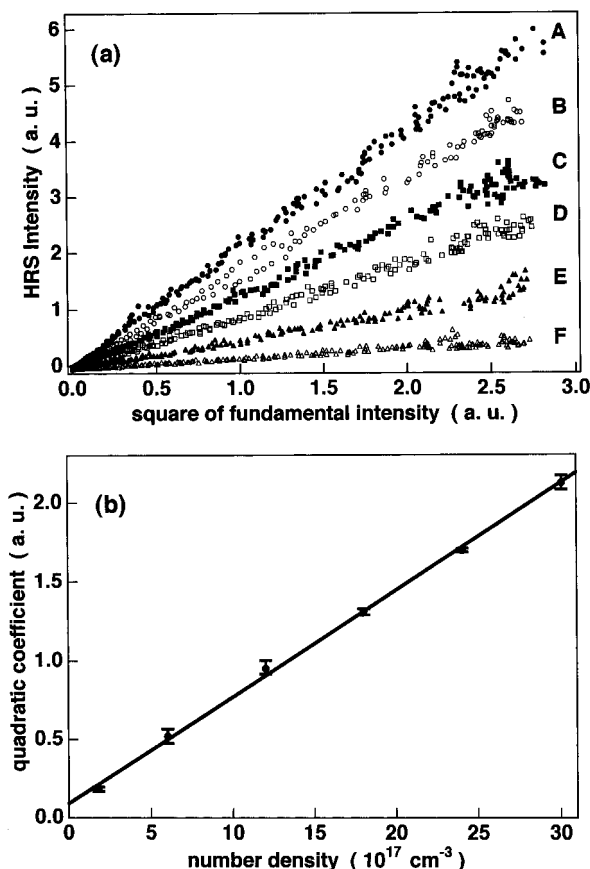


Figure 2. (a) Hyper-Rayleigh scattering signal for 2-(1-pyridinio)benzimidazolate in chloroform at different number densities in units of 10^{17} cm^{-3} : (A) 30.1; (B) 24.1; (C) 18.1; (D) 12.0; (E) 6.0; (F) 1.8. (b) Quadratic coefficient $G(N_{\text{solvent}}\beta_{\text{solvent}}^2 + N_{\text{solute}}\beta_{\text{solute}}^2)$ versus N_{solute} , the number density of 2-(1-pyridinio)benzimidazolate.

is considered to occupy a spherical cavity in a continuum of solvent molecules (medium of dielectric constant ϵ). We have carried out geometry optimization in the presence of the appropriate dielectric. Moreover, the β values were calculated by means of the CPHF formalism. All the SCRF calculations were carried out at the SCF/6-31G level.

IV. Results and Discussion

A. Determination of Hyperpolarizability by HRS. In measurements of HRS, the theoretically expected quadratic dependence of the HRS signal on the incident laser intensity was always observed according to $S_{2\omega} = GB^2I_0^2$. By substituting a 532 nm interference filter in front of the photomultiplier tube for a 520 or a 550 nm interference filter, we confirmed that no multiphoton-absorption-induced fluorescence was present in the frequency-doubled wavelength region (532 nm) in the chloroform solution. Experimental dependence of the HRS signal intensity $S_{2\omega}$ as a function of the square of the fundamental laser intensity I_0^2 for chloroform solutions of 2-(1-pyridinio)benzimidazolate at various concentrations are shown in Figure 2a. Figure 2b shows the linear dependence of the retrieved value for the quadratic coefficient GB^2 on the number density N_{solute} . With the known value of $\beta_{\text{solvent}} = -0.49 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ for chloroform⁴⁷ and the intercept and the slope obtained from Figure 2b, we have calculated the absolute value of $|\beta| = (115 \pm 25) \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ for 2-(1-pyridinio)benzimidazolate. 4-Nitroaniline (*p*-NA) is a typical D- π -A system containing a nitro group as an electron acceptor and an amino group as an electron donor, and the reported β value of *p*-NA is $23 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ in chloroform at a fundamental wavelength of 1064

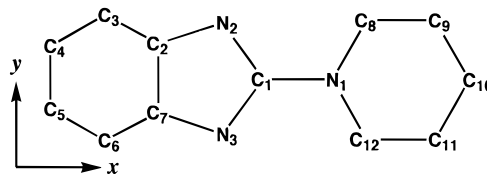


Figure 3. Coordinate system and atomic labeling of 2-(1-pyridinio)benzimidazolate.

nm.³² By comparison of the β of (1-pyridinio)benzimidazolate with that of *p*-NA, it can be found that the pyridinium betaine has a relatively large value of β even though it has no well-defined π -bridging unit.

We have tried to investigate the solvent dependence of β values in the HRS experiment. In the case of the typical D- π -A systems, it is widely known that β increases as the polarity of solvent increases.^{32,48-51} For example, the reported β of *p*-NA increases up to $34.5 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ (at 1064 nm) in methanol.³² Moreover, the β of all-*trans*-retinal is $730 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ (at 1064 nm) in methanol. However, it comes down to a value of $270 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ (at 1064 nm) in chloroform.⁴⁹ This solvent dependence of the β of polyenes has been explained in terms of a positive solvatochromic behavior where the predominant $\pi \rightarrow \pi^*$ transition is red-shifted in polar solvents because of the large dipole moment in the excited state.^{48,52,53} Therefore, it is of great interest to investigate the solvent dependence of the β values for the pyridinium betaines, since the ground state of the pyridinium betaine is characterized by the formula D⁺A⁺ while the excited state will be characterized by the formula DA, which is the opposite situation in comparison with the conventional D- π -A systems.

We have carried out the HRS measurement for the methanol solution of (1-pyridinio)benzimidazolate. By comparison to the chloroform solution, a significant decrease in the HRS signal was observed in methanol solution. Though the quadratic dependence of the HRS signal on the incident laser intensity was also observed in the methanol solution, multiphoton-absorption-induced fluorescence was present in the frequency-doubled wavelength region (532 nm). We have concluded that the signal detected could partly arise from the two-photon fluorescence, since we could observe a cubic dependence of the fluorescence signal detected using a 550 nm interference filter on the fundamental laser intensity. Therefore, it is highly regrettable that we could not determine an accurate value of β in methanol. However, we have confirmed from the intensity of the HRS signal that the β value in methanol would decrease compared to that in chloroform. This trend is opposite to that found in the conventional D- π -A systems. A detailed interpretation of this result will be discussed in the next section.

B. Theoretical Computations. The pyridinium betaines do not belong to ordinary organic compounds because of their very large charge separation in the ground state. To confirm the reliability of the Hartree-Fock single-reference wave function, we have studied the effects of an electron correlation with the second-order Møller-Plesset perturbation (MP2) theory using double ζ basis sets (6-31G) and a double ζ basis set with diffuse polarization functions (6-31G**). Optimized bond lengths and bond angles, and dipole moments computed at four different levels of theory (HF/6-31G, HF/6-31G**, MP2/6-31G, and MP2/6-31G**) are shown in Table 1 along with the experimental values determined by X-ray diffraction analysis.²⁰ The angle between the mean plane of the imidazole ring (root-mean-square distance of 0.03 Å) and the mean plane of the pyridinium ring (root-mean-square distance of 0.01 Å) is reported to be 1.9°. The X-ray diffraction analysis indicates that neither the pyridinium ring nor the benzimidazole ring is symmetrical.

TABLE 1: Geometric Structures^a Optimized at Different Levels of Theory

	expt ^b	HF/6-31G <i>C</i> _{2v}	HF/6-31G** <i>C</i> _{2v}	MP2/6-31G <i>C</i> _{2v}	MP2/6-31G** <i>C</i> _{2v}
C1–N1	1.45	1.433	1.446	1.429	1.436
C1–N2	1.33	1.321	1.306	1.332	1.317
C2–N2	1.38	1.380	1.370	1.376	1.362
C2–C7	1.42	1.414	1.409	1.421	1.417
C2–C3	1.40	1.399	1.400	1.402	1.403
C3–C4	1.37	1.374	1.372	1.378	1.375
C4–C5	1.39	1.414	1.411	1.417	1.414
N1–C8	1.36	1.344	1.337	1.351	1.344
C8–C9	1.38	1.375	1.373	1.382	1.381
C9–C10	1.37	1.389	1.386	1.392	1.390
N1–C1–N2		120.2	119.0	120.5	119.5
N2–C1–N3		119.5	121.8	119.0	121.0
C1–N2–C2		101.9	100.5	101.9	100.7
N2–C2–C7		108.3	108.6	108.5	108.8
C7–C2–C3		120.8	120.8	120.6	120.6
C2–C3–C4		117.8	117.8	118.0	118.0
C3–C4–C5		121.4	121.4	121.4	121.4
C1–N1–C8		119.0	119.3	119.2	119.4
C8–N1–C12		121.9	121.5	121.7	121.3
N1–C8–C9		120.0	120.5	119.9	120.4
C8–C9–C10		119.3	119.0	119.9	119.7
C9–C10–C11		119.4	119.4	118.6	118.6
μ^c	10.33	10.31	10.50	10.37	10.41

^a The distances are in angstroms and angles in degrees. ^b Reference 20. ^c Total dipole moment in debye.

TABLE 2: Ab Initio and INDO/S Calculated Electronic Properties

optimization level	INDO/S				ab initio CIS		expt
	HF/6-31G	HF/6-31G**	MP2/6-31G	MP2/6-31G**	HF/6-31G	HF/6-31G**	
$(\mu_x)_g$	10.31	10.27	10.23	10.14	10.31	10.50	10.33 ^e
$(\mu_x)_e$	−4.68	−5.01	−4.31	−4.50	−5.90	−6.24	
$\Delta\mu_x^a$	−14.99	−15.28	−14.54	−14.64	−16.21	−16.74	
oscillator strength	0.441	0.408	0.471	0.450	0.624	0.603	
transition energy (nm)	440	432	450	445	281	288	425 ^f (385) ^g
transition energy (ev)	2.82	2.87	2.75	2.78	4.41	4.30	
$\beta_{\text{vec}}(0)^b$	−34.4	−30.1	−39.1	−36.0	−33.3 ^d	−35.4 ^d	
$\beta_{\text{vec}}(1064)^c$	−149.0	−120.5	−191.3	−165.5			115 ± 25 ^h

^a $\Delta\mu_x = (\mu_x)_e - (\mu_x)_g$. ^b All β are in units of 10^{-30} cm² esu^{−1}. ^c Calculated values at 1064 nm ($\hbar\omega = 1.16$ eV). ^d Calculated by the ab initio CPHF method. ^e Reference 20. ^f Measured in chloroform solution. ^g Measured in methanol solution. ^h Determined by means of the hyper-Rayleigh scattering in chloroform solution in this work, and this value corresponds to $|\beta_{\text{vec}}(1064)|$ value.

However, the small difference between related bonds is tentatively ascribed to the packing effect, and mean values for bond lengths are listed in Table 1. All the optimized structures by ab initio calculations are found to be planar and belong to the *C*_{2v} symmetry group. These results are consistent with the result of the X-ray diffraction analysis. Though one can find a small difference in the bond lengths between calculated values at different levels of theory, it is reasonable to consider that the contribution from the effects of an electron correlation is negligibly small, at least from the standpoint of the reproducibility of the molecular structure. Moreover, even the HF/6-31G level of calculation seems to adequately reproduce both the molecular structure and the dipole moment. Considering the fact that the central C1–N1 bond is not so different from the normal C–N single bond (1.45 Å), electrons would be weakly delocalized over the whole molecule but heavily localized at each ring; i.e., the π -electron conjugation between the benzimidazole chromophore and the pyridinium chromophore is not so strong. The bond length of the conjugated C=N double bond in pyridine is known to be 1.33 Å. Thus, the central C1–N1 bond can be almost regarded as a single bond; namely, the charge separation completely takes place in the pyridinium betaines and the large dipole moment is brought about despite the short distance between the positively charged pyridinium ring and the negatively charged benzimidazole ring. From these considerations, one can easily distinguish the fundamental feature of the pyridinium betaines from that of the

widely investigated D– π –A systems in which electron-donating and -withdrawing groups are linked with a long π -conjugation path. On the basis of these geometries, the β values were calculated with the INDO/S SOS method and the ab initio CPHF method. The calculated values of $(\mu_x)_g$, $(\mu_x)_e$, $\Delta\mu_x$, the oscillator strength, transition energy, and β are shown in Table 2. The results of INDO/S calculations for the ab initio optimized geometries reproduced the value of $(\mu_x)_g$ compared to the results of ab initio calculations and the experimental value. However, a large discrepancy for the transition energies is found between the results of INDO/S and ab initio calculations. This is due to the fact that the INDO/S Hamiltonian was parametrized to reproduce the optical data for selected ordinary organic compounds, though the ab initio MO method does not compensate for insufficiency of approximations through an introduction of fitting parameters as was done in a semiempirical MO method. The small differences found in the INDO/S transition energies are attributable to the slight differences in the molecular geometries obtained with different optimization levels.

The dipole moment has only an *x*-component in both the ground state and in the excited state. This means that the charge-transfer direction is obviously parallel with the ground-state dipole moment direction (the *x*-direction). Therefore, β_x will be identical with β_{vec} as described before. It should be noted that the dipole vectors of the ground state and excited state are antiparallel, resulting in negative solvatochromic behavior and negative β_{vec} values. Figure 4 shows the difference

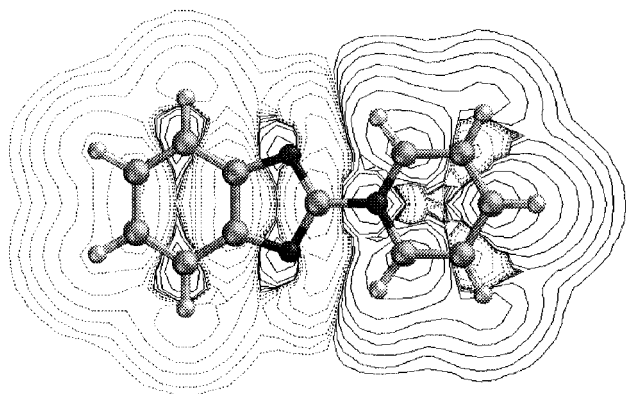


Figure 4. Difference electron density map between the ground and the first excited states calculated by the ab initio CIS/6-31G** method.

electron density between the ground and the first excited states obtained by the ab initio CIS/6-31G** calculation.^{54,55} The solid line indicates the region in which electron density increases on transition to the excited state, and the broken line indicates the region in which electron density decreases on transition. This result clearly indicates that the benzimidazole ring acts as an electron-donating group and that the pyridinium ring acts as an electron-withdrawing group, and it has become apparent that the first excited state is characterized by a strong intramolecular charge-transfer state. This nature of the first excited state of the pyridinium betaine leads to large values of $\Delta\mu$ and thus contributes to the large hyperpolarizability.

Both the INDO/S and ab initio calculations predicted the static $|\beta|$ values to be around $(30\text{--}40) \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$. Thus, the static $|\beta|$ value of (1-pyridinio)benzimidazolate is about 4 times that of *p*-NA ($9.0 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ by the ab initio HF/6-31G). On the other hand, the frequency-dependent $|\beta(1064)|$ values were ranging from 120.5×10^{-30} to $191.3 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$. These variations are due to the difference in the values of transition energy, since the frequency-dependent β is sensitive to the transition energy. Therefore, one should consider the transition energy in evaluating the reliability of the frequency-dependent β values. The result of the INDO/S calculation with the geometry optimized at HF/6-31G** predicted the absorption wavelength to be 432 nm and $|\beta(1064)|$ to be $120.5 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$. These values are in good agreement with the experimental values of 425 nm and $115 \pm 25 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$. As described before, we have confirmed that the β value in methanol would decrease compared to that in chloroform; namely, the β of the pyridinium betaine decreases as the dielectric constant increases. This trend is opposite that found in the D- π -A systems. To investigate this anomalous behavior, we have carried out geometry optimization in the presence of the appropriate dielectric in the range $\epsilon = 1.0\text{--}90.0$ and calculated the static β through the CPHF formalism with the ab initio HF/6-31G level of theory. Figure 5a shows the dependence of the $|\beta_{\text{vec}}|$ on the dielectric constant. As we would expect, contrary to the case for *p*-NA, the β of the pyridinium betaine decreases as the dielectric constant increases. We have considered that this would be ascribable to the negative solvatochromic behavior of the pyridinium betaine. Figure 5b shows the dependence of the HOMO and the LUMO energies on the dielectric constant. This dependence can be easily understood by assuming that a HOMO reflects the nature of the ground state and a LUMO reflects that of the excited state. In general, it is widely accepted that the highly polar electronic state is stabilized in a polar solvent, while a more neutral electronic state is stabilized less. Thus, with increasing dielectric constant, the ground state (HOMO level) of the pyridinium

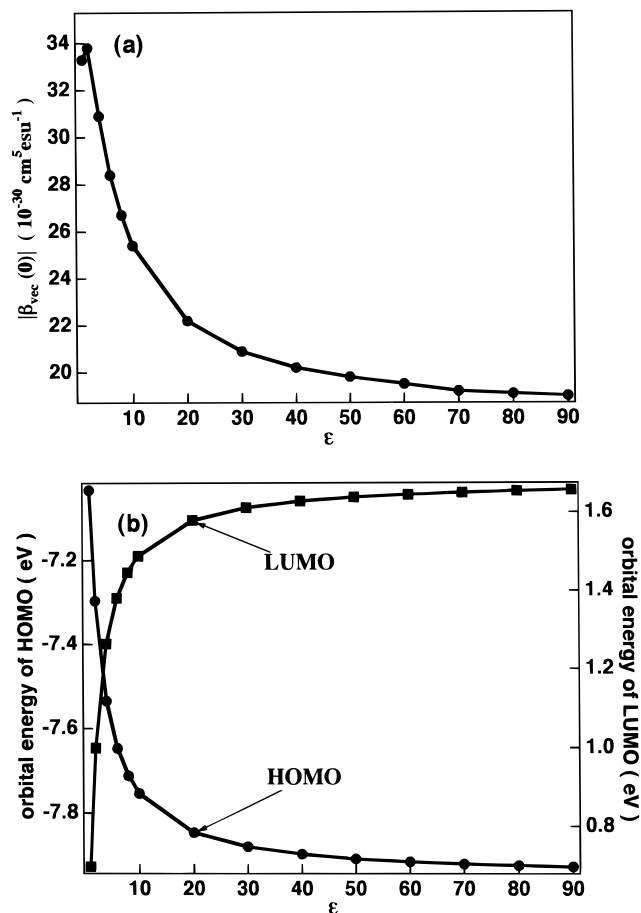


Figure 5. (a) Dependence of $|\beta_{\text{vec}}(0)|$ of 2-(1-pyridinio)benzimidazolate on ϵ calculated by the ab initio SCRF/6-31G method. (b) Dependence of the orbital energies of the HOMO and the LUMO on ϵ .

betaine is found to be stabilized while the excited state (LUMO level) will be destabilized. It may be considered that a HOMO–LUMO energy gap corresponds to the transition energy. Therefore, the transition energy increases with the increase of the dielectric constant, and the contribution from a resonance enhancement of the β , which is related to the dispersion term of the expression of β , will be reduced, and finally, it leads to the decrease of the β .

V. Conclusion

We have investigated for the first time, experimentally and theoretically, the first hyperpolarizability of one of the simplest heterocyclic pyridinium betaines, (1-pyridinio)benzimidazolate. The first hyperpolarizability has been estimated to be $(115 \pm 25) \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ with the HRS technique, and this value is in good agreement with the value derived from the semiempirical INDO/S calculations. From the ab initio CIS calculation, it was found that the benzimidazole ring acts as a strong electron-donating group and the pyridinium ring acts as a strong electron-withdrawing group, and it has become apparent that the first excited state is characterized by a strong intramolecular charge-transfer state. Our new approach to the molecular design, based on a short-range charge transfer from a negatively charged aromatic electron-donating group to a directly linked, positively charged aromatic electron-withdrawing group, for the second-order NLO materials by the use of heterocyclic pyridinium betaines has been shown to have a bright prospect in the development of efficient NLO materials.

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