Manipulation of Dipole Moment and Hyperpolarizability Based on Heterocyclic Pyridinium Betaine Structures: *Ab Initio* and INDO/S MO Calculations

Jiro Abe* and Yasuo Shirai

Department of Photo-Optical Engineering, Faculty of Engineering, Tokyo Institute of Polytechnics, Iiyama 1583, Atsugi, Kanagawa 243-02, Japan

Nobukatsu Nemoto and Yu Nagase

Sagami Chemical Research Center, 4-4-1 Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan

Received: July 17, 1996; In Final Form: November 13, 1996[⊗]

This contribution explores the first electronic hyperpolarizabilities β of the heterocyclic pyridinium betaines consisting of a negatively charged aromatic electron-donating group and a positively charged aromatic electron-withdrawing group. On the basis of enhanced charge separation between the pyridinium and benzimidazole rings, the betaines can be represented as a D^-(donor)-A^+ (acceptor) system having a very large ground-state dipole moment in the direction from D^- to A^+. The inversion of the dipole moment direction upon electronic excitation is the most remarkable feature of the heterocyclic pyridinium betaines. This nature of the betaines makes it possible to manipulate the ground-state dipole moment and β. The *ab initio* and INDO/S molecular orbital calculations have shown that the reduction of the ground-state dipole moment, and the enlargement of the excited-state dipole moment and β would be achieved by a D^--A^+-π-A system, in which a traditional A is introduced through a π-conjugation path attached to A^+. On the other hand, the enlargement of the ground-state dipole moment and the reduction of β were achieved by a D^--A^+-π-D system. It is shown that this concept for manipulation of the dipole moments and β can be used to construct more efficient second-order nonlinear optical materials based on the heterocyclic pyridinium betaine structures.

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 stabilities) 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 first electronic 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 missing. The first electronic hyperpolarizability β is 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 traditional push−pull-type (D-π-A) systems, the extension of the conjugation path between the electron-donating and -withdrawing groups gives rise to the significant increase in both $\Delta\mu$ and M_{ge}, which results in a pronounced increase in the β values.[9−14]

In our previous studies, it was shown that the heterocyclic pyridinium betaines which contain both a negatively charged aromatic electron-donating and positively charged aromatic electron-withdrawing groups have large β values by means of the molecular orbital (MO) calculations.[15] Moreover, the β value of one of the simplest heterocyclic pyridinium betaines, 2-(1-pyridinio)benzimidazolate, was measured experimentally with the hyper-Rayleigh scattering technique. The experimen-

2-(1-pyridinio)benzimidazolate
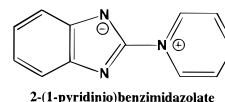
tally obtained $|\beta|$ value, $(115 \pm 25) \times 10^{-30}$ cm^5 esu^{-1}, was in good agreement with the $|\beta|$ values derived from the INDO/S calculations.[16] It has been suggested that the second-order optical nonlinearities arise from a short-range charge transfer. This system is different from the traditional D-π-A systems in that 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. Though it is well established that the heterocyclic pyridinium betaines have a large ground-state dipole moment due to the large charge separation between the pyridinium ring and the heterocyclic ring,[17−23] a strong dipole−dipole interaction in the presence of a large dipole moment favors a centrosymmetric crystalline arrangement, in which a nonlinear electronic bulk susceptibility $\chi^{(2)}$ value will completely vanish even from molecules with a large β value. From this point of view, one would like to design a small μ_g molecule, although a small μ_g does not automatically ensure a noncentrosymmetric crystal. Therefore, it is highly advantageous to have molecular designs where one can independently manipulate the ground-state dipole moment and β.[24] The present study

Manipulation of Dipole Moments

J. Phys. Chem. B, Vol. 101, No. 10, 1997 **1911**

describes the substituent effects for heterocyclic pyridinium betaines in order to manipulate β and the ground-state dipole moment by means of the theoretical investigations.

II. Theoretical Methods

MO calculations were carried out using the *Gaussian* 92 and Fujitsu *MOS-F V3L1* program packages.[25,26] The molecular structures have been fully optimized at the Hartree–Fock (HF) level with a 6-31G basis set. On the basis of these geometries, we have calculated the three crucial two-level properties (the oscillator strength f, the difference between the x-components of the dipole moments in the excited and the ground states $\Delta\mu_x$, and λ_{max}) of the lowest lying optical transition and the frequency dependent β values. The β values for the second-harmonic generation (SHG) were calculated by means of the sum-over-states (SOS) approach[27–29] based on the semiempirical INDO/S Hamiltonian[30–33] with configuration interaction (CI) wave functions. In the SOS expression, all electronic states are included which are generated by singly exciting all electrons in the 20 highest occupied MOs to the 20 lowest unoccupied MOs with respect to the ground state. Moreover, the static (zero frequency) β values are calculated using the coupled–perturbed Hartree–Fock (CPHF) formalism based on the *ab initio* SCF wave functions.[34] In this method, β is determined from the analytical derivatives of the total energy with respect to the applied electric field.

III. Results and Discussion

In our previous papers, the HF/6-31G level of calculation was shown to adequately reproduce both the molecular structure and the dipole moment of the heterocyclic pyridinium betaines.[15,23] Considering the fact that the bond length (1.433 Å by *ab initio* HF/6-31G level) of the optimized central C–N bond linking the pyridinium ring and the benzimidazole ring is close to the normal C–N single bond length, it is suggested that electrons would be weakly delocalized over the whole molecule but heavily localized at each ring, *i.e.*, the degree of the π-electron conjugation between the benzimidazole chromophore and the pyridinium chromophore is considerably weak. The bond length of the conjugated C=N double bond in pyridine is known to be 1.33 Å. Thus, the central C–N bond can be almost regarded as single. That is, 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. Furthermore, we have shown that the benzimidazole ring acts as an electron-donating group (D) and the pyridinium ring acts as an electron-withdrawing group (A), and the first excited state is characterized by a strong intramolecular charge-transfer state, where the electron transition occurs from a negatively charged aromatic D^- to a directly linked, positively charged aromatic A^+. In the traditional D-π-A molecules, D is slightly charged in positive ($D^{\delta+}$) and A is slightly charged in negative ($A^{\delta-}$) by the weak intramolecular charge transfer from D to A, even in the ground state. This situation induces a relatively large dipole vector which is directed from $A^{\delta-}$ to $D^{\delta+}$. The first excited state can be characterized by the intramolecular charge-transfer state, where the electron transition occurs from $D^{\delta+}$ to $A^{\delta-}$. Thus, the excited-state dipole moment is greater than and aligned in the same direction as the ground-state dipole moment as shown in Scheme 1a.

In contrast to the traditional D-π-A molecules, the heterocyclic pyridinium betaines can be represented as a D^--A^+ system having a very large ground-state dipole moment directed

SCHEME 1: The Concept for Manipulating the Dipole Moment using Heterocyclic Pyridinium Betaine Structures
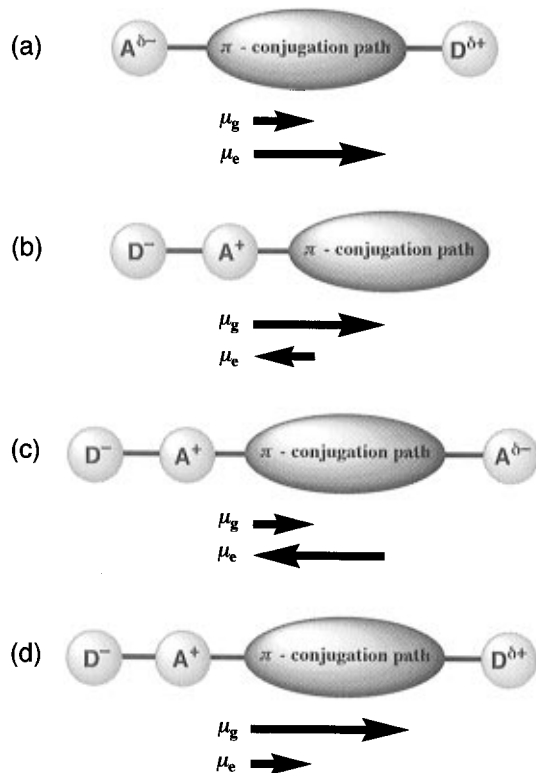
from D^- to A^+. That is, the ground-state dipole vector directs an entirely inverse orientation compared with the traditional D-π-A molecules. However, the dipole vectors of the ground and excited states are antiparallel, since A^+ becomes negatively charged and D^- becomes positively charged upon the electronic transition (Scheme 1b). This mechanism of the inversion in the dipole vector direction is very interesting and is a fundamental feature of the heterocyclic pyridinium betaines. We have considered that the manipulation of the ground-state dipole moment and β can be easily achieved by the heterocyclic pyridinium betaines. As shown in Scheme 1c, if one introduces a traditional A through the π-conjugation path attached at A^+, (this system can be represented as a D^--A^+-π-A system) one can expect the reduction of the ground-state dipole moment in contrast to the enlargement of the excited-state dipole moment. Because the total ground-state dipole moment can be considered as the summation between the component dipole moments originated in the D^--A^+ unit and A^+-π-$A^{\delta-}$ unit, the A^+-π-$A^{\delta-}$ unit could be used to reduce the total ground-state dipole moment. In this D^--A^+-π-A system, the excited-state dipole moment will be enlarged, since both A^+ and A would act as electron-withdrawing groups. Nevertheless, the reduction of the ground-state dipole moment, since the dipole moment difference between the ground and excited states increases, this system will surely give rise to an enhancement of β. On the other hand, the enlargement of the ground-state dipole moment and reduction of β will be achieved by a D^--A^+-π-D system as shown in Scheme 1d.

At first, we have investigated three types of the heterocyclic pyridinium betaines **1–3** in order to clarify how the hyperpolarizabilities will be influenced by the substituent groups coupled to the pyridinium ring. The calculated physical properties are summarized in Table 1 along with those of other heterocyclic pyridinium betaines investigated in this study. It should be noted that both $\beta(0)$ values and the dipole moments derived

TABLE 1: *Ab initio* and INDO/S Calculated Electronic Properties[a] of Heterocyclic Pyridinium Betaines

compd	$\beta(0)^b$	$\beta(1907)^c$	$\beta(1064)^d$	$(\mu_x)_g$ (D)	$(\mu_x)_e$ (D)	$\Delta\mu_x$ (D)^e	f	$\hbar\omega_{ge}$ (nm)
1	34^f	48^f	149^f	10.31	−4.68	−14.99	0.44	440
	(33)^g			(10.31)	(−5.90)	(−16.21)	(0.62)	(281)
2	22	31	89	14.17	0.23	−13.94	0.54	416
	(16)			(14.75)	(0.06)	(−14.69)	(0.82)	(252)
3	131	253	855	4.23	−13.07	−17.30	0.48	606
	(132)			(3.54)	(−15.94)	(−19.48)	(0.84)	(358)
4	42	64	291	12.42	−2.69	−15.11	0.77	459
	(46)			(13.44)	(−2.72)	(−16.16)	(1.42)	(302)
5	19	34	223	15.55	3.35	−12.20	1.04	460
	(25)			(17.48)	(9.06)	(−8.42)	(2.05)	(307)
6	70	106	539	4.60	−12.16	−16.76	0.80	474
	(100)			(5.86)	(−13.97)	(−19.83)	(1.31)	(316)
7	42	64	279	12.36	−2.80	−15.16	0.76	456
	(54)			(13.08)	(−3.61)	(−16.69)	(1.33)	(305)
8	22	38	209	15.29	1.99	−13.30	0.92	453
	(9)			(16.86)	(5.28)	(−11.58)	(1.78)	(303)
9	71	107	527	4.58	−11.94	−16.52	0.80	473
	(112)			(5.68)	(−13.92)	(−19.60)	(1.30)	(320)
10	39	62	333	12.96	−1.35	−14.31	0.97	463
	(28)			(14.32)	(0.81)	(−13.51)	(1.95)	(310)
11	33	55	343	13.31	−0.04	−13.35	1.13	466
	(11)			(14.91)	(5.03)	(−9.88)	(2.53)	(316)
12	71	109	595	4.83	−11.15	−15.98	0.98	475
	(102)			(6.40)	(−11.41)	(−17.81)	(1.86)	(319)
13	67	103	562	5.03	−9.91	−14.94	1.13	473
	(89)			(6.74)	(−7.82)	(−14.56)	(2.43)	(321)
14	43	68	374	12.52	−2.10	−14.62	0.85	469
	(53)			(13.15)	(−2.59)	(−15.74)	(1.49)	(312)
15	34	57	402	12.69	0.98	−11.71	1.21	476
	(29)			(13.60)	(4.20)	(−9.40)	(2.17)	(325)

^{a} All β are in units of 10^{-30} cm^5 esu^{-1} and calculated using the following equation: $\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$, $\beta_i = (^1/_3)\Sigma_k (\beta_{ikk} + \beta_{kik} + \beta_{kki})$, $k = x, y,$ and z. ^{b} Static β values. ^{c} Frequency dependent β values at 1907 nm. ^{d} Frequency dependent β values at 1064 nm. ^{e} $\Delta\mu_x = (\mu_x)_e - (\mu_x)_g$. ^{f} Calculated through the INDO/S-SCI sum-over-states method. ^{g} Calculated through the *ab initio* CPHF formalism at the RHF/6-31G level of theory. The values in parentheses were derived from the *ab initio* MO calculations.
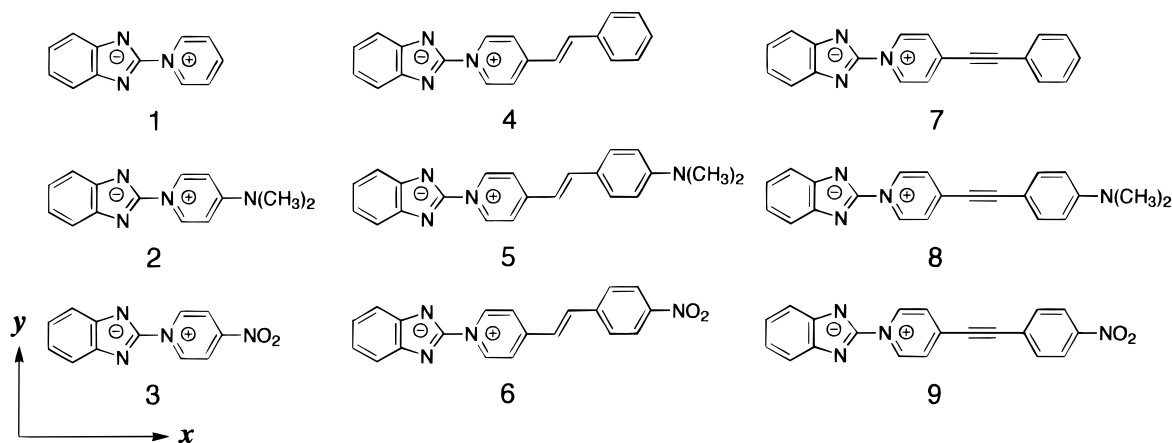

Figure 1. Molecular structures of pyridinium betaines **1**−**9** and the coordinate system.

from the INDO/S MO method are in good agreement with the values derived from the *ab initio* MO method. Though a large discrepancy is found in the transition energies obtained by the two different MO methods, a fairly strong correlation can be found between them. This large discrepancy 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. These similarities in physical properties obtained by the two different theoretical methods are found in other pyridinium betaines. After the dipole moments obtained by the INDO/S MO method were compared, the NO$_2$ group is found to reduce the ground-state dipole moment from 10.31 D in **1** to 4.23 D in **3** but enlarge the excited-state dipole moment from −4.68 to −13.07 D. (See

Figure 1). In addition to the changes in the dipole moments, the NO$_2$ group also induces the red shift in the λ_{max}. As a result, these changes in the dipole moments and the transition energy cause the enhancement of the β values. On the contrary, the N(CH$_3$)$_2$ group is found to induce an entirely opposite contribution to these molecular properties as can be seen in **2**. That is, the ground-state dipole moment is enlarged to 14.17 D and the excited-state dipole moment is reduced to 0.23 D, moreover, the β values are decreased. As we would expect, it has been apparent that we can manipulate the ground-state dipole moment, the excited-state dipole moment, and the hyperpolarizability using the heterocyclic pyridinium betaine structures. The *ab initio* MO calculations also predict the same tendency. These findings are significant in developing more efficient second-order NLO materials, and to manipulate the ground-state dipole moment.
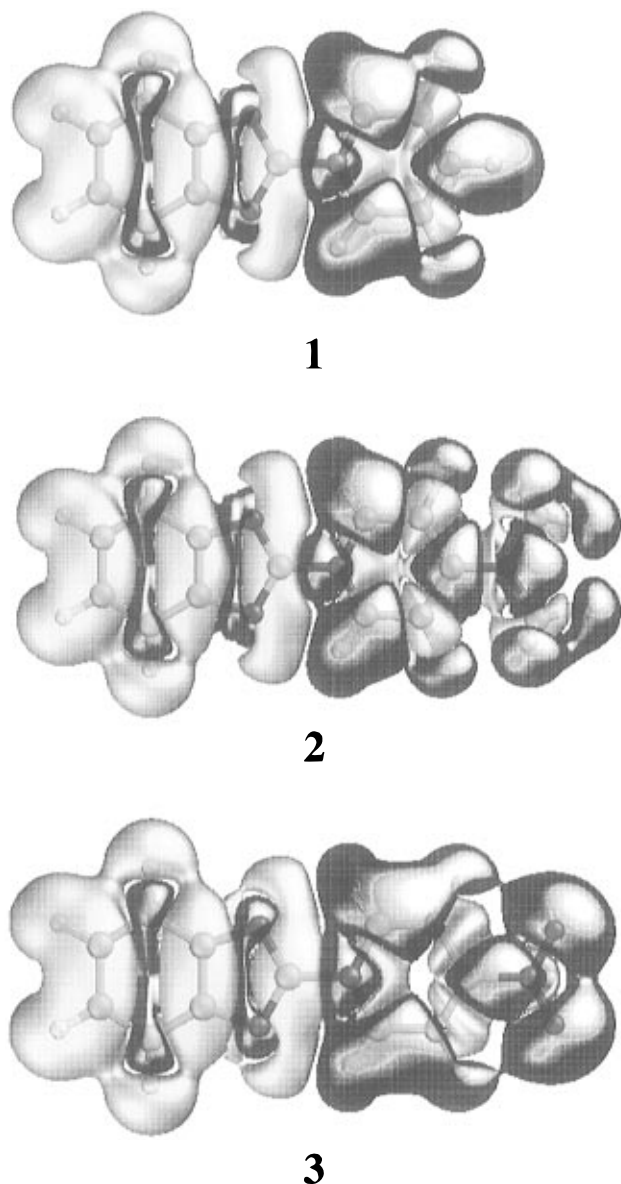
Manipulation of Dipole Moments

J. Phys. Chem. B, Vol. 101, No. 10, 1997 **1913**

1

2

3

Figure 2. Difference electron densities between the ground and first excited states for **1**−**3** calculated by the *ab initio* CIS/6-31G method. The black-colored region indicates the region in which the electron density increases upon transition to the excited state, and the yellow colored region indicates the region in which the electron density decreases upon the transition.

On the basis of the above considerations, we have investigated the pyridinium betaines **4**−**9**, which have extended π-conjugation unit connected to the pyridinium ring. Both **5** and **8** can be classified into the D$^-$-A$^+$-π-D molecule, while **6** and **9** were designed as the D$^-$-A$^+$-π-A molecule. Upon comparing the ground- and excited-state dipole moments between **1** and **4**, we have been shown that the extended π-conjugation unit can be regarded as a weak electron-donating group, since the ground-state dipole moment enlarged to 12.42 D and the excited-state dipole moment reduced to −2.69 D in **4**. However, the β values were enhanced mainly due to the bathochromic shift. This tendency is also found in **7**, and the physical properties of **4** and **7** are very similar with each other. In these molecules, the enlargement of f and the bathochromic shift are considered to result in the large enhancement of the frequency dependent β-(1064) values. Though it is well-known that the extension of the conjugation path between D and A gives rise to a significant increase in β in the traditional D-π-A system, the obtained enhancement effect of β values found in **4** and **7** is a unique
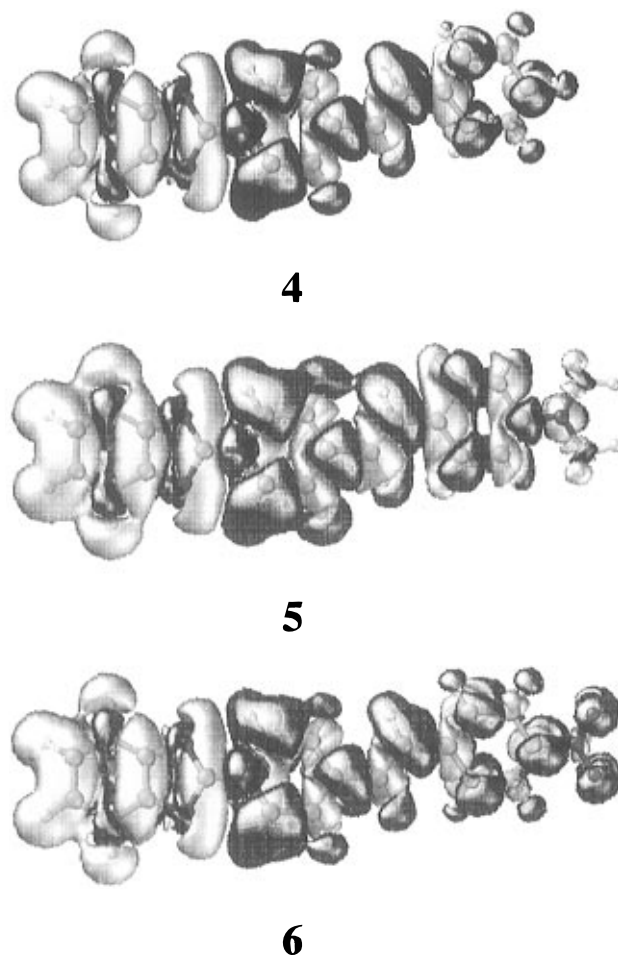

4

5

6

Figure 3. Difference electron densities between the ground and first excited states for **4**−**6** calculated by the *ab initio* CIS/6-31G method.

feature of the pyridinium betaine compounds, since these betaines cannot be classified into the traditional D-π-A system but are classified as the D$^-$-A$^+$-π system. The investigation about the effect of conjugation length on β will be described in the last part of this paper. The behavior of the physical properties of the D$^-$-A$^+$-π-A molecules (**6** and **9**) and the D$^-$-A$^+$-π-D molecules (**5** and **8**) also shows the same tendency as was found in **2** and **3**. That is, the β values of the D$^-$-A$^+$-π-A molecules are enlarged by introducing the NO$_2$ group, though those of the D$^-$-A$^+$-π-D molecules are reduced by introducing the N(CH$_3$)$_2$ group. Interestingly, **3**, **6**, and **9** have almost the same value of the ground-state dipole moment. In order to investigate the effects of the NO$_2$ and N(CH$_3$)$_2$ groups on the nature of the first excited states of **1**−**9**, the difference electron densities between the ground and first excited states calculated by the *ab initio* CIS/6-31G method are shown in Figures 2−4.[34,35,36] The black-colored region indicates the region in which the electron density increases upon transition to the excited state, and the yellow-colored region indicates the region in which the electron density decreases upon the transition. The difference electron densities of **5** and **8** indicate that the C$_6$H$_4$−N(CH$_3$)$_2$ group acts as an electron-donating group, resulting in the reduction of the excited-state dipole moment. On the other hand, the electron-withdrawing ability of the C$_6$H$_4$−NO$_2$ group has become apparent from the difference electron densities of **6** and **9**.

Next, we have investigated the effects of π-conjugation length on β. The investigated model compounds (**10**−**15**) are shown in Figure 5. Upon comparing the ground- and excited-state dipole moments among **1**, **4**, **10**, and **11**, one can find that the
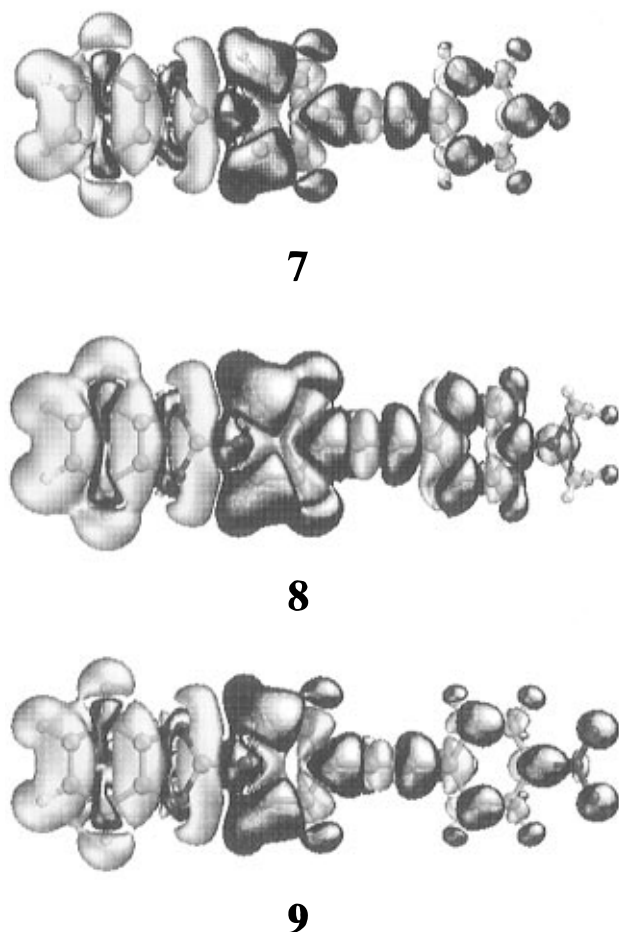
7

8

9

Figure 4. Difference electron densities between the ground and first excited states for **7**−**9** calculated by the *ab initio* CIS/6-31G method.

Figure 5. Molecular structures of pyridinium betaines **10**−**15** and the coordinate system.

dipole moments in the ground state increase, while those in the excited-state decrease in that order. As described above, the weak electron-donating ability of the extended π-conjugation unit was clearly proved. As the π-conjugation length increases in the order of **4**, **10**, and **11**, the β(1064) values increase in this order from 291×10^{-30} to 343×10^{-30} cm^5 esu^{-1}, while β(0) values decrease in this order from 42×10^{-30} to 33×10^{-30} cm^{5}esu^{-1}. The reduction of β(0) values can be attributable to the decrease in the $\Delta\mu_x$ values. Upon considering the decrease in β(0) values, we can ascribe the enlargement of the β(1064) values to the resonance effects. Thus, it has been found that the elongation of the π-conjugation path of the D$^-$-A$^+$-π system is not effective in enlarging the β values. Moreover, as can be found in **14** and **15**, the thiophene and bithiophene rings are also regarded as a weak electron-donating group. The similarity in the ground- and excited-state dipole moments between **4** and **14** suggests the similarity of the electron-donating ability between the phenyl and thiophene rings. In addition, the thiophene and bithiophene rings are found to induce the bathochromic shift, resulting in the enlargement of the frequency dependent β values. The comparison of the electronic properties of **15** with those of **4** revealed that the bathochromic shift of 18 nm brings about the enhancement of the frequency dependent β(1064) value from 291×10^{-30} to 402×10^{-30} cm^5 esu^{-1}, while the static β(0) value decreases from 42×10^{-30} to 34×10^{-30} cm^5 esu^{-1}. Furthermore, the results for the D$^-$-A$^+$-π-A systems have shown that the β values do indeed become saturated at very short π-conjugation length as can be found in **12**. This early saturation of the β was also observed in the push−pull polyynes, and Jain and Chandrasekhar concluded that
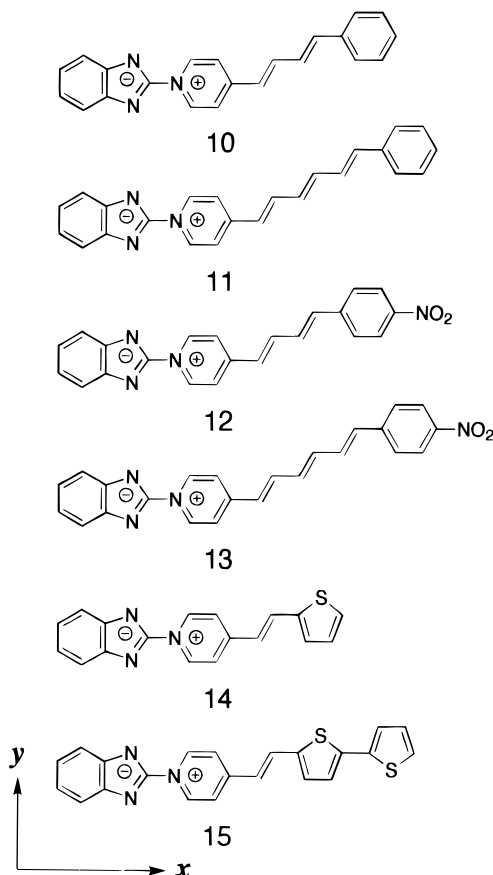
this phenomenon was ascribable to configuration mixing of $\pi \rightarrow \pi^*$ transitions.[37] We have considered that this early saturation of β originates in the reduction of the excited-state dipole moment and is a characteristic feature of the D$^-$-A$^+$-π-A system. It should be noted that the long conjugation path between the terminal electron-withdrawing and pyridinium groups weakens the electron-withdrawing ability of the latter moiety.

IV. Conclusion

We have shown that it is possible to manipulate the ground- and excited-state dipole moments β by the use of the heterocyclic pyridinium betaine structures. Our manipulation method is not applicable to the traditional D-π-A system but only effective to the pyridinium betaine compounds consisting of a negatively charged D$^-$ and a positively charged A$^+$. The pyridinium betaine compounds have a very large dipole moment directed from D$^-$ to A$^+$, whereas the dipole vector of the traditional D-π-A molecules directs from A to D, which is an entirely inverse orientation with the pyridinium betaine compounds. An electron-withdrawing group introduced in the pyridinium ring was found to be effective for the enlargement of β. On the contrary, an electron-donating group was found to induce an entirely opposite effect as can be seen in the D$^-$-A$^+$-π-D systems. It should be noted that this concept for manipulation of the dipole moments and β values can be used to construct more efficient second-order NLO materials based on the heterocyclic pyridinium betaine structures.

Manipulation of Dipole Moments

J. Phys. Chem. B, Vol. 101, No. 10, 1997 **1915**

Azuma Matsuura and Tomoaki Hayano of Fujitsu Laboratories, Ltd., for the helpful discussions of the semiempirical MO method and the β calculation.

References and Notes

(1) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Boston, 1987.

(2) *Molecular Nonlinear Optics*; Zyss, J., Eds.; Academic Press: Boston, 1994.

(3) *Materials for Nonlinear Optics*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991.

(4) *Organic Molecules for Nonlinear Optics and Photonics*; Messier, J., Kajzar, F., Prasad, P., Eds.; NATO ASI Series E; Kluwer Academic Publishers: Dordrecht, 1991; Vol. 194.

(5) Zerbi, G., Eds. *Organic Materials for Photonics*; North−Holland: Amsterdam, 1993.

(6) *Polymers for Second-Order Nonlinear Optics*; Lindsay, G. A., Singer, K. D., Eds.; ACS Symposium Series 601; American Chemical Society: Washington, DC, 1995.

(7) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.

(8) Brédas, J. L.; Meyers, F.; Pierce, B. M.; Zyss, J. *J. Am. Chem. Soc.* **1992**, *114*, 4928.

(9) Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643.

(10) Tsunekawa, T.; Yamaguchi, K. *J. Phys. Chem.* **1992**, *96*, 10268.

(11) Jain, M.; Chandrasekhar, J. *J. Phys. Chem.* **1993**, *97*, 4044.

(12) Morley, J. O. *J. Phys. Chem.* **1995**, *99*, 10166.

(13) Dekhtyar, M. L.; Rozenbaum, V. M. *J. Phys. Chem.* **1995**, *99*, 11656.

(14) Blanchard-Desce, M.; Wortmann, R.; Lebus, S.; Lehn, J.-M.; Krämer, P. *Chem. Phys. Lett.* **1995**, *243*, 526.

(15) Abe, J.; Shirai, Y. *J. Am. Chem. Soc.* **1996**, *118*, 4705.

(16) Abe, J.; Shirai, Y.; Nemoto, N.; Miyata, F.; Nagase, Y. *J. Phys. Chem. B* **1997**, *101*, 576.

(17) Alcalde, E.; Roca, T.; Redondo, J.; Ros, B.; Serrano, J. L.; Rozas, I. *J. Org. Chem.* **1994**, *59*, 644.

(18) Alcalde, E.; Dinarés, I.; Pons, J.-M.; Roca, T. *J. Org. Chem.* **1994**, *59*, 639.

(19) Alcalde, E. *Adv. Heterocycl. Chem.* **1994**, *60*, 197.

(20) Alcalde, E.; Perez-Garcia, L.; Frigola, J. *Chem. Pharm. Bull.* **1993**, *41*, 614.

(21) Alcalde, E.; Dinarés, I.; Frigola, J.; Jaime, C.; Fayet, J.-P.; Vertut, M.-C.; Miravitlles, C.; Rius, J. *J. Org. Chem.* **1991**, *56*, 4223.

(22) Alcalde, E.; Dinarés, I.; Elguero, J.; Fayet, J.-P.; Vertut, M.-C.; Miravitlles, C.; Molins, E. *J. Org. Chem.* **1987**, *52*, 5009.

(23) Abe, J.; Nemoto, N.; Nagase, Y.; Shirai, Y. *Chem. Phys. Lett.* **1996**, *261*, 18.

(24) Pan, H.; Gao, X.; Zhang, Y.; Prasad, P. N.; Reinhardt, B.; Kannan, R. *Chem. Mater.* **1995**, 7, 816.

(25) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision F.4: Gaussian, Inc.: Pittsburgh, PA, 1992.

(26) *MOS-F V3L1*; Fujitsu, Ltd.: Tokyo, Japan, 1995.

(27) Li, D.; Marks, T. J.; Ratner, M. A. *Chem. Phys. Lett.* **1986**, *131*, 370.

(28) Li, D.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1707.

(29) Kanis, D. R.; Ratner, M. A.; Marks, T. J.; Zerner, M. C. *Chem. Mater.* **1991**, *3*, 19.

(30) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026.

(31) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta.* **1973**, *32*, 111.

(32) Bacon, A. D.; Zerner, M. C. *Theoret. Chim. Acta.* **1979**, *53*, 21.

(33) Kotzian, M.; Rösch, N.; Scröder, H.; Zerner, M. C. *J. Am. Chem. Soc.* **1989**, *111*, 7687.

(34) Hurst, J.; Dupuis, M.; Clementi, E. *J. Chem. Phys.* **1988**, *89*, 385.

(35) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frish, M. J. *J. Phys. Chem.* **1992**, *96*, 135.

(36) *ANCHOR II V1L5*; Fujitsu, Ltd., and Kureha Chemical Industry, Co. Ltd.: Tokyo, Japan, 1995.

(37) Jain, M.; Chandrasekhar, J. *J. Phys. Chem.* **1993**, *97*, 4044.