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Heterocyclic Betaines Exhibiting Extremely Large First Hyperpolarizability: *Ab Initio* and INDO/S Calculations

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The present study describes a new approach in the molecular design of second-order nonlinear optical (NLO) materials through the use of heterocyclic betaines. The new approach is based on a short-range charge transfer from a charged aromatic electron donor group to a directly linked, charged aromatic electron acceptor group, which gives rise to a large difference between the dipole moments in the excited and the ground states. Heterocyclic betaines which contain both a negatively charged aromatic donor group and a positively charged aromatic acceptor group are found to satisfy this requirement. This system is different from conventional push−pull-type systems such as polyenes in that the optical nonlinearlity of the latter system results from a long-range charge transfer from a nonaromatic donor group to a nonaromatic acceptor group through a π-electron bridging unit. Theoretical investigations have shown that pyridinium betaines have extremely large molecular hyperpolarizabilities for their molecular sizes and have indicated the great potential of pyridinium betaines for applications in nonlinear optics.

Hyperpolarizabilities (β) are often described within the dipolar approximation on the basis of the so-called two-state model.[1,2] Within the framework of the two-state model, the static β value is expressed as

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

where $\Delta\mu = \mu_{\mathrm{e}} - \mu_{\mathrm{g}}$ is the difference between the dipole moments in the excited and the ground states, $\hbar\omega_{\mathrm{ge}}$ is the transition energy, and M_{ge} is the transition dipole moment between the ground and the excited states. The two-state model implies that β increases as both $\Delta\mu$ and M_{ge} increase. In the conventional push−pull polyenes, the extension of the conjugation path between the electron donor group and the electron acceptor group gives rise to significant increases in both $\Delta\mu$ and M_{ge}, which results in a pronounced increase in β.[3−8] 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.

We have considered that large β values could be obtained for relatively small molecules via a short-range intramolecular charge transfer from a charged aromatic donor group to a directly linked, charged aromatic acceptor group. In principle, such a system would possess a large $\Delta\mu$ and a large M_{ge} but at the same time not include a long π-electron bridging unit. Heterocyclic betaines have received much attention because of their unusually high 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).[9−20] From this large negative solvatochromism, it has been proposed that the dipolar character would dramatically decrease in the first excited states;[21] i.e., the ground state is characterized by the formula $\mathrm{D}^-\mathrm{A}^+$, while DA characterizes the excited state. Obviously this would produce a large negative $\Delta\mu$. The present study was motivated by these structural characteristics of heterocyclic betaines which make these compounds attractive for second-order NLO materials. We report for the first time a theoretical investigation of hyperpolarizability of several heterocyclic betaines, **1**−**10** (Figure 1), using *ab initio* SCF/6-31G[22] and semiempirical INDO/S (intermediate neglect of differential overlap) methods.[23−26]

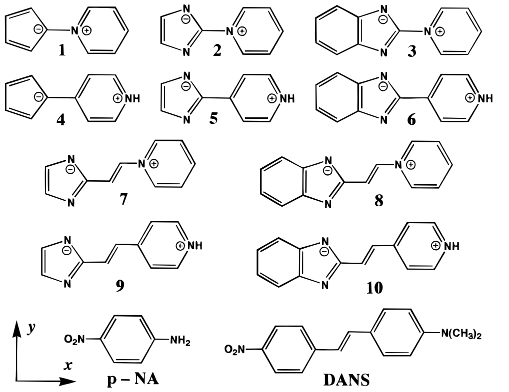

Figure 1. Molecular structures of the compounds studied in this work and coordinate system: **1**, 1-pyridiniocyclopentadienide; **2**, 2-(1-pyridinio)imidazolate; **3**, 2-(1-pyridinio)benzimidazolate; **4**, 1*H*-4-cyclopentadienylidene-1,4-dihydropyridine; **5**, 1*H*-4-(imidazol-2-ylidene)-1,4-dihydropyridine; **6**, 1*H*-4-(benzimidazol-2-ylidene)-1,4-dihydropyridine; **7**, (*E*)-2-[2-(1-pyridinio)vinyl]imidazolate; **8**, (*E*)-2-[2-(1-pyridinio)vinyl]benzimidazolate; **9**, (*E*)-1*H*-4-[2-(imidazol-2-ylidene)ethylidene]-1,4-dihydropyridine; **10**, (*E*)-1*H*-4-[2-(benzimidazol-2-ylidene)ethylidene]-1,4-dihydropyridine; ***p*-NA**, 4-nitroaniline; **DANS**, 4-(dimethylamino)-4′-nitrostilbene.

The geometries of all of the molecules were fully optimized at the *ab initio* SCF level of theory using a 6-31G double ζ quality basis set. On the basis of these geometries, the β^{SCF}-(static) values, in the limit of a static field, were calculated using the coupled-perturbed Hartree−Fock (CPHF) formalism based on *ab initio* SCF wave functions.[27,28] In this method, β^{SCF}-

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[1] Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.

[2] Brédas, J. L.; Meyers, F.; Pierce, B. M.; Zyss, J. *J. Am. Chem. Soc.* **1992**, *114*, 4928.

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

[4] Tsunekawa, T.; Yamaguchi, K. *J. Phys. Chem.* **1992**, *96*, 10268.

[5] Jain, M.; Chandrasekhar, J. *J. Phys. Chem.* **1993**, *97*, 4044.

[6] Morley, J. O. *J. Phys. Chem.* **1995**, *99*, 10166.

[7] Dekhtyar, M. L.; Rozenbaum, V. M. *J. Phys. Chem.* **1995**, *99*, 11656.

[8] Blanchard-Desce, M.; Wortmann, R.; Lebus, S.; Lehn, J.-M.; Krämer, P. *Chem. Phys. Lett.* **1995**, *243*, 526.

[9] Alcalde, E.; Roca, T.; Redondo, J.; Ros, B.; Serrano, J. L.; Rozas, I. *J. Org. Chem.* **1994**, *59*, 644.

[10] Alcalde, E.; Dinarés, I.; Pons, J.-M.; Roca, T. *J. Org. Chem.* **1994**, *59*, 639.

[11] Alcalde, E. *Adv. Heterocycl. Chem.* **1994**, *60*, 197.

[12] Alcalde, E.; Perez-Garcia, L.; Frigola, J. *Chem. Pharm. Bull.* **1993**, *41*, 614.

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

[14] Alcalde, E.; Dinarés, I.; Elguero, J.; Fayet, J.-P.; Vertut, M.-C.; Miravitlles, C.; Molins, E. *J. Org. Chem.* **1987**, *52*, 5009.

[15] Paley, M. S.; Harris, J. M. *J. Org. Chem.* **1991**, *56*, 568.

[16] Apen, P. G.; Rasmussen, P. G. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1992**, *30*, 203.

[17] Rutkis, M. A.; Gerca, L. E.; Silinsh, E. A.; Neilands, O. Y.; Roze, M. P.; Berzinsh, E. L.; Klimkans, A. B.; Larsson, S. *Adv. Mater. Opt. Electron.* **1993**, *6*, 319.

[18] Bacquet, G.; Bassoul, P.; Combellas, C.; Simon, J.; Thiébault, A.; Tournilhac, F. *Adv. Mater.* **1990**, *2*, 311.

[19] Barzoukas, M.; Fort, A.; Boy, P.; Combellas, C.; Thiébault, A. *Nonlinear Opt.* **1994**, *7*, 41.

[20] Runser, C.; Fort, A.; Barzoukas, M.; Combellas, C.; Suba, C.; Thiébault, A.; Graff, R.; Kintzinger, J. P. *Chem. Phys.* **1995**, *193*, 309.

[21] Boyd, G. V. *Tetrahedron Lett.* **1966**, *29*, 3369.

[22] 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.

[23] Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026.

[24] Ridley, J.; Zerner, M. C. *Theor. Chim. Acta (Berlin)* **1973**, *32*, 111.

[25] Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta (Berlin)* **1979**, *53*, 21.

[26] *MOS-F V3L1*; Fujitsu, Ltd.: Tokyo, Japan, 1995.

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Table 1. *Ab Initio* and INDO/S Calculated Electronic Properties of Heterocyclic Betaines

property	***p*-NA**	**DANS**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
						Ab Initio/SCF 6-31G CPHF Method						
β^{SCF}(static)[a]	9.0	68.0	54.8	27.2	33.3	5.0	19.4	67.5	161.5	244.7	9.3	78.5
						INDO/S-SCI Sum-Over-States Method						
$\hbar\omega_{\mathrm{ge}}$ (eV)	3.60	3.25	2.13	2.18	2.22	3.29	2.92	2.54	1.94	1.71	2.72	2.32
f	0.50	1.16	0.51	0.40	0.37	1.09	1.11	1.25	1.13	0.90	1.55	1.91
$(\mu_x)_{\mathrm{g}}$ (D)	8.49	9.88	8.38	8.48	11.39	6.64	6.49	10.44	10.40	16.82	6.46	10.81
$(\mu_x)_{\mathrm{e}}$ (D)	18.86	27.60	−1.46	−4.42	−6.31	7.71	5.25	3.91	−0.46	−2.46	11.02	10.41
$\Delta\mu_x$ (D)[b]	10.37	17.72	−9.84	−12.90	−17.70	1.07	−1.24	−6.53	−10.86	−19.28	4.56	−0.40
$\beta^{\mathrm{INDO/S}}$(static)	12.0	43.4	74.6	69.2	76.1	0.7	13.1	71.1	217.3	454.1	20.5	40.0
$\beta^{\mathrm{INDO/S}}$(1.91 μm)[c]	14.6	56.9	133.2	120.1	132.4	0.3	16.7	104.9	462.1	1347.4	33.2	55.7

[a] All β are in units of 10^{-30} cm^5 esu^{-1} and calculated by the use of the following equation: $\beta = (\beta_x{}^2 + \beta_y{}^2 + \beta_z{}^2)^{1/2}$, $\beta_i = (1/3)\sum_k(\beta_{ikk} + \beta_{kik} + \beta_{kki})$, $k = x, y, z$. [b] $\Delta\mu_x = (\mu_x)_{\mathrm{e}} - (\mu_x)_{\mathrm{g}}$. [c] Calculated values at 1910 nm ($\hbar\omega = 0.65$ eV).

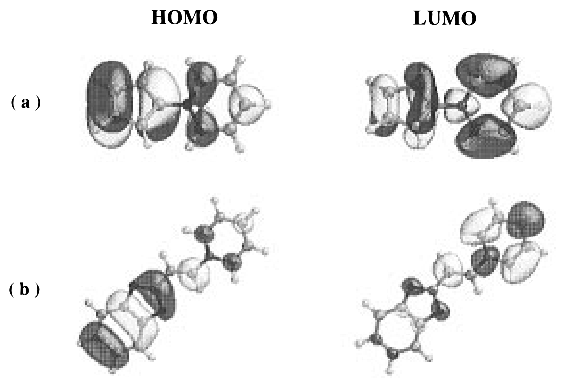

Figure 2. Frontier molecular orbitals of (a) **1** and (b) **8** calculated using the *ab initio* SCF/6-31G method.

(static) is determined from the analytical derivatives of the total energy with respect to the applied electric field. Furthermore, the frequency-dependent $\beta^{\mathrm{INDO/S}}$ at 1.91 μm (far from the absorption of molecules investigated in this study) was calculated by means of the sum-over-states (SOS) approach,[29−31] in the framework of time-dependent perturbation theory, on the basis of the semiempirical INDO/S 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 molecular orbitals to the 20 lowest unoccupied molecular orbitals with respect to the ground state. The calculated values of $(\mu_x)_{\mathrm{g}}$, $(\mu_x)_{\mathrm{e}}$, $\Delta\mu_x$, $\hbar\omega_{\mathrm{ge}}$, the oscillation strength f, and hyperpolarizability β for the heterocyclic betaines are shown in Table 1, along with those for the widely adopted standard compounds 4-nitroaniline (***p*-NA**) and 4-(dimethylamino)-4′-nitrostilbene (**DANS**).

As expected, the betaines have large negative $\Delta\mu_x$ values and large f values compared with ***p*-NA**. A comparison of β^{SCF}(static) for the betaines with that for ***p*-NA** shows that, except for **4**, the betaines have relatively large β values. This tendency is also seen in the results for $\beta^{\mathrm{INDO/S}}$(static) and $\beta^{\mathrm{INDO/S}}$(1.91 μm). The x-components of the dipole moments of the excited and ground states of 1-pyridinio compounds (**1**−**3**, **7**, and **8**) are antiparallel, whereas those of 1,4-dihydropyridine compounds (**4**−**6**, **9**, and **10**) are in the same direction. It is found that $\beta^{\mathrm{INDO/S}}$(static) and $\beta^{\mathrm{INDO/S}}$(1.91 μm) values of 1-pyridinio compounds are enlarged compared with those for the corresponding 1,4-dihydropyridine compounds. This tendency also applies to the results of *ab initio* calculations except for the cases for **3** and **6**. Therefore, it may be considered whether the change in the sign of the x-components of the dipole moments of the excited and ground states has any fundamental significance in the enlargement of β values.

Surprisingly, the static β value for **1**, which is the simplest of the pyridinium betaines, is about six times larger than that of ***p*-NA**. Thus, it is clear that **1** has a large β value compared to its molecular size. Moreover, in contrast to the conventional push−pull polyenes, **1** is not planar but is twisted 28.9° around the central C−N bond. Some noticeable differences between the β^{SCF}(static) and $\beta^{\mathrm{INDO/S}}$(static) values for the betaines may be due to the parametrization introduced in the semiempirical INDO/S method. INDO/S is parametrized to reproduce optical data for selected ordinary organic compounds. However, the betaines do not fit this description due to their very large charge separation in the ground state. Therefore, it may be difficult to reproduce the optical properties of the betaines using the INDO/S method.

DANS is widely known to have a large β value and is often used as the active constituent of organic NLO materials. While **7** and **8** have never been synthesized, in spite of the attempts of Alcalde et al.,[9] it is significant that the β^{SCF}(static) values for **7**, **8**, and **10** are larger than that of **DANS**. To the best of our knowledge, the β^{SCF}(static) value of 245 × 10^{-30} esu for **8** is the largest value ever reported for β^{SCF}(static) calculated by the *ab initio* CPHF method. It should be kept in mind, however, that some enhancement in the dynamic β values are expected due to resonance effects in the cases of **7** and **8**. The dynamic β values for **7** and **8** are about two and three times greater than the static values. In the case of **8**, the theoretical value shows a remarkable increase because the $\hbar\omega_{\mathrm{ge}}/2$ calculated value (0.86 eV) is relatively close to the theoretical incident light frequency (1.91 μm, 0.65 eV). However, it can be seen that the β^{SCF}(static) values for **7**, **8**, and **10** are enlarged compared with those for the corresponding betaines **2**, **3**, and **6**. This means that the vinylene group surely contributes to the enhancement of the β value even in betaines.

From the CI coefficient of the lowest excited state of the betaines, it has been found that the major electronic transition is HOMO → LUMO, and the lowest excited state is characterized by this transition. The frontier orbitals of **1** and **8** are shown in Figure 2.[32] It is evident that the HOMOs exhibit enhanced charge density around the five-membered ring and the benzimidazole ring, respectively. On the other hand, the charge density around the pyridinium ring is enhanced in the LUMOs. These characteristics of the HOMOs and LUMOs indicate that the five-membered ring and the benzimidazole ring will act as electron-donating groups and the pyridinium ring will act as an electron-withdrawing group.[21] From these considerations, the lowest excited states are characterized by a strong intramolecular charge transfer state. As expected, the nature of the lowest excited state of the betaines leads to large values of $\Delta\mu$ and thus contributes to the extremely large calculated β values.

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[27] Hurst, J. B.; Dupuis, M.; Clementi, E. *J. Chem. Phys.* **1988**, *89*, 385.

[28] DeMelo, C. P.; Silbey, R. *J. Chem. Phys.* **1988**, *88*, 2558.

[29] Li, D.; Marks, T. J.; Ratner, M. A. *Chem. Phys. Lett.* **1986**, *131*, 370.

[30] Li, D.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 1707.

[31] Kanis, D. R.; Ratner, M. A.; Marks, T. J.; Zerner, M. C. *Chem. Mater.* **1991**, *3*, 19.

[32] *ANCHOR II V1L5*; Fujitsu, Ltd., and Kureha Chemical Industry, Co. Ltd.: Tokyo, Japan, 1995.