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Conformation and Solvent Dependence of the First Molecular Hyperpolarizability of Pyridinium-*N*-Phenoxide Betaine Dyes. Quantum Chemical Calculations

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The static and frequency-dependent first hyperpolarizabilities (β) of Reichardt's betaine dye and two simplest pyridinium-*N*-phenoxide betaines were computed in the gas phase and in aqueous solution. The sum-over-state formalism was used to calculate individual components of the β-tensors. The solvent effect was included via the Langevin dipoles/Monte Carlo approach. The influence of the molecular geometry on the β values of the betaine dyes was investigated as well. The calculations demonstrate that the β values strongly depend on the interplanar angle between the pyridinium and the phenoxide ring. Moreover, we observed dramatically decreased values of β (for all investigated betaines) in aqueous solution as compared to the gas phase.

Introduction

Macroscopic nonlinear optical properties (NLO) of materials ultimately depend on corresponding microscopic hyperpolarizabilities of the constituing molecules. The optimization of materials for nonlinear optical devices requires understanding of NLO processes as a function of electronic and geometrical molecular structures. It is well-known that molecules with electron-donating and -accepting groups at the opposite ends of an extended conjugated π-system have large first-order hyperpolarizabilities (β). The influence of structural parameters such as donor and acceptor strengths as well as the electronic structure and length on β have been extensively studied over recent decades.[1−4] The influence of conformational changes on β is another important problem (especially for two- or multiring systems) to be considered. This effect and solvent dependence on nonlinear optical properties in the case of biphenyl entities has been studied by Puccett et al.[5] and effect of the crystalline environment by Zyss et al.[6] The extent of the planarity influences the size of the π-electron system and the mobility of its electrons. For planar conformations, increasing optical nonlinearities are usually observed as compared to twisted conformers.[7−12] Moreover, experimental and theoretical studies have shown that solute/solvent interactions strongly influence the nonlinear optical properties, too. Especially, these investigations have shown strong solvent contributions to β values for one-dimensional charge-transfer (CT) compounds.[13−26] Recently, we have found[25] dramatic solvent and conformational influences the β values of Reichardt's betaine dye B1[27,28] (see Figure 1). Moreover, we suggested that the optimal (largest) value of β would be reached for a planar structure of this molecule (with an interplanar angle of $\delta = 0°$ between the pyridinium (Py) and phenoxide (Ph) ring). It is not possible to make thorough conformational investigations because there are strong steric constraints which result from the molecular architecture of this betaine molecule.

In this paper, to the best of our knowledge, we present, for the first time, a systematic theoretical study of the influence of solvents and the geometrical structure on the UV−vis absorption spectra and the quadratic hyperpolarizability of Reichardt's betaine dye B1 and its simplest, less substituted representatives, hereafter referred to as B2, B3, and B4 (see Figure 1). The results of our calculations demonstrate that the β values of the molecules B1, B2, and B3 depend strongly on conformational and solvent effects but it should be noted that the β values of B2 and B3 as function of the interplanar angle show opposite trends as compared to B1. The static and frequency-dependent first-order hyperpolarizabilities were calculated using the sum-over-states (SOS) method[29] both in the gas phase and in the aqueous solution. The finite field (FF)[30,31] AM1 method[32] was used to compute the β values in the gas phase, too. The solvent influence was included via the LD/MC (Langevin dipole/Monte Carlo) technique.[33] The ground-state geometry of all betaine molecules was optimized using the AM1 approach of Dewar et al.[32] Other spectroscopic parameters were evaluated by applying our semiempirical all-valence GRINDOL method,[34] including configuration interaction (CI).

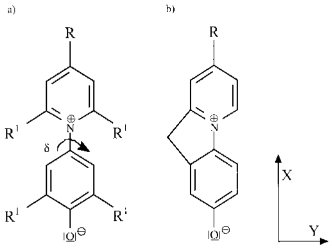

Figure 1. The compounds used in the present study. (a) Reichardt's betaine dye; B1: R = Ph, R^1 = Ph. B2: R = Ph, R^1 = H. B3: R = H, R^1 = H. (b) B4: R = Ph.

Theoretical Outline

In the present work, the solute/solvent interaction was taken into account using our Langevin dipoles/Monte Carlo (LD/MC) model[33] being a modified Langevin dipoles (LD) model of Warshel and collaborators.[35−37] Solvent molecules are represented in the LD/MC model by a three-dimensional cubic grid of polarizable point dipoles constructed around the solute molecule as described in ref 33, each dipole (an *i*th molecule) being polarized by the local field resulting from a set of charges, dipoles, and quadrupoles located on atoms of the solute molecule

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(E_i), as well as from other solvent dipoles (E_i^{L}), according to eq 1.

$$(E_i)^n = E_i^{\mathrm{o}} + (E_i^{\mathrm{L}})^n \qquad (1)$$

Where E_i^{o} is the field produced by the solute molecule, the E_i^{L} is the field produced by other solvent molecules. The latter parameter is calculated self-consistently; $(E_i^{\mathrm{L}})^{\mathrm{o}} = 0$. In an *n*th iterative step, the polarization (expressed by the *total* dipole moment of an *i*th molecule) is approximated by the Langevin-type function,

$$(\bar{\mu}_i)^{n+1} = (\bar{e}_i)^n |\mu_{\mathrm{s}}| [\coth z_i - z_i^{-1}]^n \qquad (2)$$

where $\bar{e}_i$ is the unit vector in the direction of E_i, μ_{s} is the permanent dipole moment of the solvent molecules, and

$$z_i = \frac{|\mu_{\mathrm{s}}||E_i|}{kT} \qquad (3)$$

The electrostatic potential and electric field around the solute molecule is calculated using so-called cumulative atomic multipole moments (CAMM).[38] In this approach, each atom of the solute molecule is represented by a scalar net atomic charge (q), a vector of atomic dipole (μ), and a tensor of atomic quadrupole ($\mathbf{Q}$).

In the LD model, the solvation free energy depends on the position and orientation of the solute molecule, placed in a cubic grid of polarizable solvent molecules. In the calculations reported in this paper, the optimum position and orientation of the solute molecules were determined using the Monte Carlo (MC) sampling method.[39] The maximum linear displacements (δr) and maximum rotation angle ($\delta\xi$) of the solute molecule (treated at this step as a rigid body) were chosen to bring the acceptance ratio near 0.5, in order to achieve a reasonable convergence. In most simulations, we used $\delta r = 0.005-0.010$ nm, and $\delta\xi = 5-10°$. In each MC step, permanent and induced dipole moments of each solvent molecule were iteratively calculated using eqs 1−3.

In molecular orbital theory, the electrostatic solvent effect may be taken as additional term, V, in the Hamiltonian of the isolated molecule, H^{o}:

$$H = H^{\mathrm{o}} + V \qquad (4)$$

In our approach, the permanent and induced dipole moments of the solvent molecules obtained in the MC run generate the averaged (in the meaning of the MC method) electrostatic potential and electric field vector on each atom of the solute molecule. Thus, the total potential V acting on solute atoms is a sum of the averaged potential due to the permanent (V_{perm}) and induced (V_{ind}) dipole moments of the solvent molecules:

$$V = V_{\mathrm{perm}} + V_{\mathrm{ind}} \qquad (5)$$

These average values of the electrostatic potential and electric field vector are introduced into eq 4. The details of the LD/MC method as well as the results of the calculations solvation energies and solvatochromic shifts are given in refs 33 and 40−42.

The relationship between the electronic structure of the molecule and the first molecular hyperpolarizability (β) tensor, as derived from time-dependent perturbation theory,[29] is given by eq 6.

$$\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2) = \frac{1}{\hbar^2} P(i,j,k;-\omega_\sigma,\omega_1,\omega_2) \sum_{l\neq 0} \sum_{m\neq 0} \frac{\langle 0|\mu_i|l\rangle\langle l|\bar{\mu}_j|m\rangle\langle m|\mu_k|0\rangle}{(\omega_{0l}-\omega_\sigma)(\omega_{0m}-\omega_2)} \qquad (6)$$

In eq 6, the matrix elements $\langle 0|\mu_i|l\rangle$ and $\langle l|\bar{\mu}_j|m\rangle = \langle l|\mu_j|m\rangle - \langle 0|\mu_j|0\rangle\delta_{lm}$ are the electronic transition moments, ω_{0l} (times $\hbar$) is the energy difference between the electronic ground and excited state l, and $\omega_\sigma = \omega_1 + \omega_2$ is the polarization response frequency. The superscripts i, j, and k refer to the molecular Cartesian coordinates x, y, and z. P is a permutation operator and indicates a summation over six terms obtained by permuting frequencies. In the solution experiments, one observes that the vector component β_{vec} is given by eq 7,

$$\beta_{\mathrm{vec}} = \sum_{i=1}^{3} \frac{\mu_i \beta_i}{|\mu|} \qquad (7)$$

where μ is the ground-state molecular dipole moment and

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{j\neq i}(\beta_{ijj} + \beta_{jij} + \beta_{jji}) \qquad i, j \in (x, y, z) \qquad (8)$$

The SCF CI procedures and CAMM's calculations were realized using our semiempirical GRINDOL program,[34] which is modified version of an NDO-like approach. The calculations were performed as follows: (i) in the first step, the ground-state geometries of the molecules were optimized using the AM1 method of Dewar et al.,[32] (ii) in the second step, the transition energies, dipole moments, and electronic transition moments were calculated using the configuration interaction (CI) technique, with 600 singly excited configurations taken into account; (iii) the individual components β tensors and β_{vec} values were calculated using the SOS method[29] (eqs 6−8). The calculations were carried out for both the isolated molecules in the gas-phase and for molecules in aqueous solution. The so-called B-convention[43] for theoretically determined values of hyperpolarizabilities was used in this work.

Results and Discussion

The influence of the geometry of the betaine dyes B1, B2, and B3 on β was studied in the following cycle of calculations: having fixed a value of δ (see Figure 1), we optimized the values of the remaining geometrical parameters. The calculations were performed for isolated molecules as well as for molecules interacting with a solvent (water), using the procedure described in the previous section. The results of our calculations demonstrate that the minimum of the potential energy is reached for $\delta \approx 60°$ (B1 molecule), $\delta \approx 25°$ (B2 and B3 molecules) in the gas phase, and $\delta \approx 90°$ (for all molecules) in the aqueous solvent. These results of calculations can be compared with an X-ray single-crystal analysis of a bromo-substituted betaine dye (i.e., B1, with a bromine atom on the para phenyl group of the pyridinum ring), showing that in the crystal the interplanar angle between phenolate and pyridinium ring amounts up to 65°.[44] Quantum chemical calculations of solvent effect mainly on the electronic spectra of the B1 dye have been recently carried out also by Rauhut et al.[45] and Zerner et al.[6] These calculated δ values show that the contribution of the solvation energy results in an important modification of the molecule geometry. The value of the ground-state dipole moment (obtained from GRINDOL program) of B2 (B1) increases from 13 (16) D to 20 (19) D for the isolated molecules and from 22

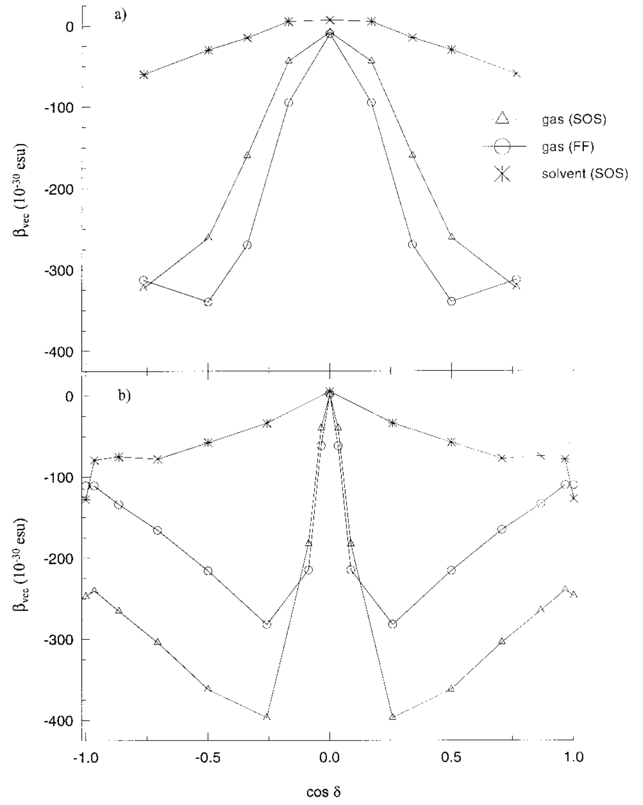

Figure 2. Dependence of the static β_{vec} on the interplanar angle δ between the pyridinium and the phenolate moiety of the betaine dyes. (a) B1 molecule, (b) B2 molecule.

(23) D to 25 (24) D in aqueous solution as the interplanar angle δ changes from 0° (40°) to 90°, that is, the conformer with $\delta \approx 90°$is more stabilized in the solvent as compared to that in the gas phase. The calculated values of the ground-state dipole moment of the remaining betaines are quite similar. Moreover, a similar ground-state geometry for B3 (the simplest of the investigated betaines) was obtained by means of *ab initio* (HF/6-31G*) self-consistent-reaction-field (SCRF) method as implemented in the *Gaussian 94* program.[47] As we can see from Figure 2, the values of static $\beta_{vec}^{SOS}(0)$ for B1 (obtained from SOS calculations) vary from -323×10^{-30} to -8 × 10^{-30} esu (in the gas phase) and from -60×10^{-30} to 7×10^{-30} esu (if we include the solvent effect) as the interplanar angle δ changes from 40° to 90°. The values of $\beta_{vec}^{SOS}(0)$ for B2 vary from -247×10^{-30} to 1×10^{-30} esu and from -128×10^{-30} to 5×10^{-30} esu in the gas phase and in aqueous solution, respectively. The calculated values of $\beta_{vec}^{FF}(0)$, obtained from AM1 finite field (FF) techniques, are shown in Figure 2.

The values of $\beta_{vec}^{FF}(0)$ are comparable with $\beta_{vec}^{SOS}(0)$ for B1 but the values of $\beta_{vec}^{FF}(0)$ are about 2 times smaller as compared to $\beta_{vec}^{SOS}(0)$ for B2 (for δ between 0° and 80°). We have found a similar tendency for the static hyperpolarizabilities of B3, β_{vec}(B3), as function of δ as compared to B2; however, our calculations indicate that static $\beta_{vec}(B2) \approx 2\beta_{vec}(B3)$. Furthermore, the frequency-dependent $\beta_{vec}^{SOS}(2\omega) \approx 2\beta_{vec}^{SOS}(0)$ at $\omega = 0.650$ eV (far from the UV−vis absorption of molecules investigated in this study). The optimal (largest) values of $\beta_{vec}^{SOS}(0)$ are reached for $\delta \approx 40°$ (-323×10^{-30} esu) and 75°−80° (-397×10^{-30} esu) in the gas phase, and for $\delta \approx 40°$ (-60×10^{-30} esu) and 0° (-128×10^{-30} esu) in aqueous solution for B1 and B2, respectively. These results show a dramatic solvent and conformation influence on the values of $\beta_{vec}(0)$ of the betaine dyes investigated here, but it should be noted that the values of $\beta_{vec}(0)$ of B1 show opposite trends as compared to those of B2 and B3. The two-state model[4,48] was employed by us for understanding of behavior of $\beta_{vec}(0)$ for these molecules. In this model eq 9 holds (β's in esu and in the B-convention[43]),

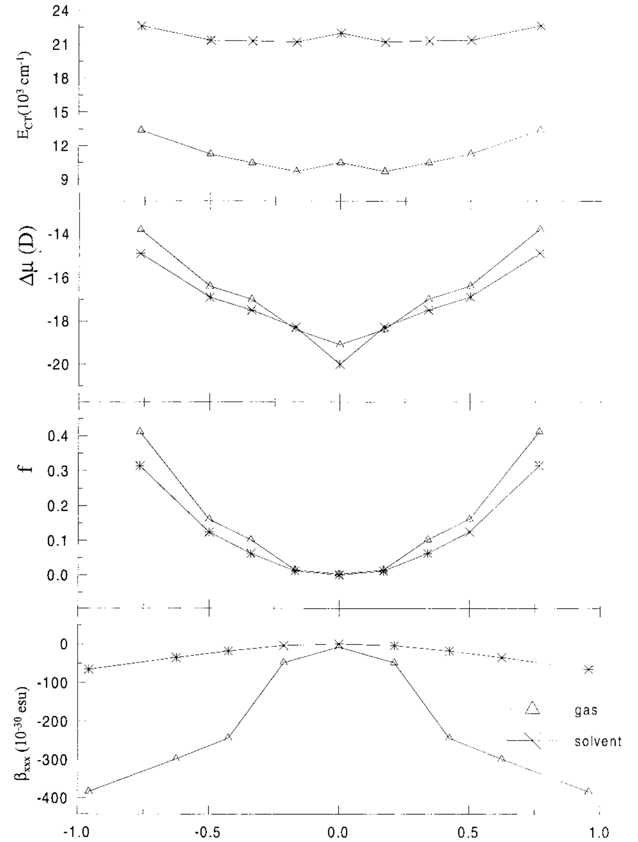

Figure 3. Dependence of the transition energy (E_{CT}), the difference in dipole moment between the ground state and the CT excited state ($\Delta\mu$), the oscillator strength (f), and the β_{xxx} calculated from the two-state model of B1 molecule on the interplanar angle δ.

$$\beta_{vec}(0) \approx \beta_{xxx}(0) = 1.618 \times 10^{-16} \frac{f\Delta\mu}{(E_{CT})^3} \qquad (9)$$

where f is the oscillator strength, $\Delta\mu$ (in D) is the difference of dipole moment between the electronic ground state and the charge transfer (CT) excited state, and E_{CT} (in cm^{-1}) is the transition energy. In this model, we considered only one strongly allowed $\pi \rightarrow \pi^*$ excited state (CT), polarized along the x-axis of the molecule (see Figure 1). In the betaine dyes investigated in this work, the CT direction is parallel with the ground-state dipole moment direction; therefore, the $\beta_{vec}(0)$ is practically identical with the $\beta_{xxx}(0)$. The two-state model correctly predicts a dependence of the $\beta_{vec}(0)$ values on the dihedral angle δ. The values of $\beta_{vec}(0)$ for B1, B2, and B3, calculated from this model, are 5−20% more negative than those obtained from full CI calculations. The calculated values of E_{CT}, $\Delta\mu$, and f and β_{xxx} (eq 9) for B1 and B2 as a function of interplanar angle δ in the gas phase and in aqueous solution are shown in Figures 3 and 4, respectively. The results of E_{CT} and $\Delta\mu$ for B3 are similar to those obtained for B2, but we found that the f values of B3 are about 30% smaller than that of B2. It is well-known that the intramolecular charge-transfer (CT) absorption band of Reichardt's betaine dye (B1) is strongly solvent-dependent. The maximum absorption wavelength of

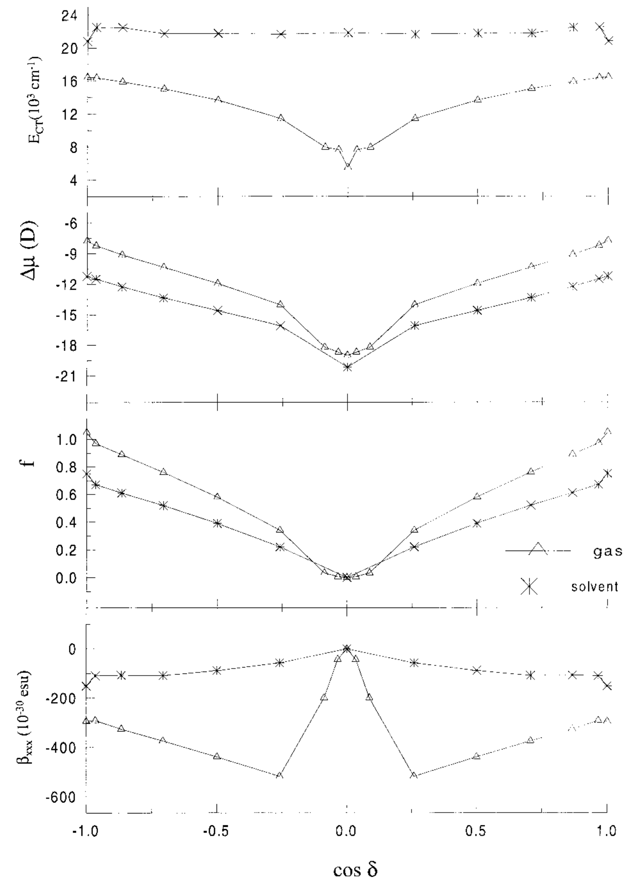

Figure 4. Dependence of the transition energy (E_{CT}), the difference in dipole moment between the ground state and the CT excited state ($\Delta\mu$), the oscillator strength (*f*), and the β_{xxx} calculated from the two-state model of B2 molecule on the interplanar angle δ.

B1 shifts from $\lambda = 810$ nm in diphenyl ether to $\lambda = 453$ nm in water.[27,28] On going to polar solvents, the CT absorption band is strongly blue shifted with diminished intensity (*f*). From this large negative solvatochromism, it has been proposed that the dipolar character dramatically decreases in the first excited state,[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 $\Delta\mu$. Our previous calculations (including higher excited states) are in reasonable agreement with the above experimental results.[33] We observe dramatically reduced values of $\beta_{vec}(0)$ (for all investigated betaines) in aqueous solution as compared to the gas phase, because the transition energy between the ground and CT excited state increases strongly with increasing solvent polarity. In the FF calculations of urea[49] small negative value of $\Delta\mu$ (and β) has been obtained, but, contrary to our results of calculations for betaines, inclusion of the polar crystalline environment distinctly enhances (i.e., the β is more negative) the intramolecular nonlinear processes. It is rather due to a effect of a strong hydrogen bonding in the crystalline state which much more decreases negative $\Delta\mu$ value than increases transition energy between the ground and excited state of the urea.

Differences between the $\beta_{vec}(0)$ values (for the isolated molecules and molecules interacting with the solvent) are larger with increasing δ values. The calculated values of $\beta_{vec}^{SOS}(0)$ at δ between 40° and 80° (for B1) and between 0° and 80° (for B2) in the gas phase are larger by a factor of 5−9 and 2−12 than the corresponding values calculated for the aqueous solution. On the other hand, our calculations demonstrate that the values of $\beta_{vec}^{SOS}(0)$ are largest (-128×10^{-30} esu for B2) for planar conformations in the aqueous solution. Moreover, we observed that the oscillator strength of the CT transition is negligibly small for $\delta \approx 90°$ for all investigated betaines. Thus, the higher excited states significantly contribute to the $\beta_{vec}^{SOS}(0)$ values for this twisted conformation, resulting in very large decreased of $\beta_{vec}^{SOS}(0)$ values with change of sign. Hence, an example of optimal structure for nonlinear optical activity in polar environments is the planar bridged betaine dye B4 shown in Figure 1. The calculated β_{vec} values for the fully optimized AM1 structure of the B4 molecule are equal to -204×10^{-30} esu and -105×10^{-30} esu in the gas phase and in aqueous solution, respectively. These values can be compared with respective data for the planar (i.e., unstabled) B2 dye -247×10^{-30} esu (gas phase) and -128×10^{-30} esu (aqueous solution, see also Figure 2). It is worth noting that our calculations[26] (utilizing these same methods) recently performed for the 4-nitro-aniline (PNA) give much lower absolute β_{vec} values: $+10.6 \times 10^{-30}$ esu (gas phase) and 26×10^{-30} esu (aqueous solution).

As can be seen from Figures 3 and 4, the parameters (E_{CT}, $\Delta\mu$, *f*, and β_{xxx} of two-state model show the same tendency (for B1 and B2) with increasing values of the interplanar angle δ, but the calculated oscillator strength (*f*) is quite different for the two molecules; *f* for B1 in the gas phase is about 3 ($\delta \approx 60°$) and 15 ($\delta \approx 80°$) times smaller as compared that for B2. Hence, replacing the peripheral phenyl groups at the phenoxide and pyridinium rings by hydrogen atoms causes a small change of the solvatochromism of these betaine dyes, but causes also a significant decrease in their *f* values and a change of the second-order polarizabilities tendency as a function of the interplanar angle δ.

Qualitatively, solvent effect can be understood by a simpler models based, for example, on the Onsager reaction field theory.[3,27] The stabilization of the perpendicular conformation ($\delta = 90°$) can be explained as due to a larger ground-state dipole moiment (μ_g) of this conformation (as compared with twisted conformations) and thus larger solvation energy (note that solvation energy is proportional to $\mu_g{}^2$) (e.g., calculated dipole moment of B2 is equal to 13.3 D and 20.0 D for the planar and the perpendicular conformation, respectively). Similarly, calculations for B1 predict 16.8 D (at $\delta = 60°$) and 19.2 D (at $\delta = 90°$). The solvent effect on the β values can be discussed based on the two-state model and solvent dependence of the shift of absorption (in isotropic dielectric medium characterized by its static relative electric permittivity (ϵ) and refractive index (n)) CT band given, for example, by Amos and Burrows[50]

$$\Delta E_{sol} = 5036\frac{1}{a^3}[2\mu_g(\mu_g - \mu_e)(\varphi(\epsilon) - \varphi(n)) + (\mu_g^2 - \mu_e^2)\varphi(n)] \quad (10)$$

where ΔE_{sol} is expressed in cm^{-1}, parameter *a* denotes the radius of a spherical cavity (in Å) occupied by the solute molecule, $\varphi(\epsilon) = (\epsilon - 1)/(\epsilon + 2)$, $\varphi(n) = (n^2 - 1)/(n^2 + 2)$, and μ_g and μ_e denote the ground-state and the excited-state dipole moment (its direction being assumed collinear with μ_g), respectively. Thus, large blue shift of the CT absorption band calculated for the betaines is due to $\mu_e < \mu_g$. It must be stressed, however, that the absolute values of the solvent effect strongly depend mainly on radius of cavity and thus reaction field models should be used with caution, although it may be useful in case of molecules with one strongly allowed transition and large $\Delta\mu$ value.

Conclusions

We have investigated the influence of changes in the environment and molecular geometry on the first hyperpolarizabilities of Reichardt's betaine dye (B1) and two simpler pyridinium-*N*-phenoxide (B2, B3) betaines. The solvent effect was included via the Langevin dipoles/Monte Carlo approach. As it was shown above, the influence of changes of the solvent, the conformation, and the substitution of the molecules on the first molecular hyperpolarizability are very important aspects to be considered when searching for compounds with optimized structures with highly efficient nonlinear optical effects.

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