Solvent Effects on Conformationally Induced Enhancement of the Two-Photon Absorption Cross Section of a Pyridinium-*N*-Phenolate Betaine Dye. A Quantum Chemical Study

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A study of the influence of the solvent on the electronic contributions to the two-photon absorption cross section (δ) of the simplest pyridinium-*N*-phenolate betaine dye molecule is presented. The calculations of δ, for the first excited singlet state (connected with the intramolecular charge transfer), were performed as a function of the interplanar angle between the pyridinium and the phenolate ring. It was found that in the gas phase the two-photon absorption cross section is enhanced several times near 80° as compared to the planar structure. The calculations show that in aqueous solution there is no distinct maximum value of δ. The computations of the first- (β) and second-order (γ) hyperpolarizabilities performed for the gas phase have shown that the angle at which δ has its maximum value is exactly the same for β and γ. The behavior of these two parameters in water resembles that of δ. The demeanor of all three nonlinear parameters in the gas phase as well as in aqueous solution has been successfully explained using the two-level model, accounting the lowest-lying charge-transfer state only. The solute/solvent interaction was included within Langevine dipoles/Monte Carlo formalism. All parameters were evaluated by applying the semiempirical GRINDOL method based on the NDO-like Hamiltonian.

1. Introduction

Although a simultaneous absorption of two photons was predicted over seventy years ago,[1] there is still much uncertainty in the field of two-photon absorption properties of molecules. On the basis of several semiempirical[2−15] as well as ab initio[16−21] calculations, various structure−property relationships have been established. Among the few concepts, the observation that a symmetric charge transfer upon excitation, from the ends of the conjugated molecule to the middle and vice versa, is a factor that can significantly enhance the two-photon absorption cross section of a molecule (δ), still remains the most fertile one. Undoubtedly, the influence of environment on the two-photon absorption spectra remains a scarcely investigated area. However, some attempts have been made recently. Kogej et al.[9] have investigated the structure−property relationships of stilbene substituted by the electron-donor and electron-acceptor groups at the ends of the molecule. They employed the IFF (internal finite field) approach to simulate the environment effects (i.e., solvent polarity). The external electric field $\vec{F}$ was applied to facilitate the charge transfer from the electron-donating to electron-accepting group. It was found that the two-photon absorption cross section strongly depends on the BOA (bond-order alternation) parameter.[9] It was also shown that δ follows closely the first-order hyperpolarizability (β) behavior. Similar results were obtained by Luo et al.,[18] who investigated the solvent polarity influence on the nonlinear optical properties of simple push−pull polyene at the ab initio level of theory. However, they reported saturation effects between δ and β different from that given in ref 9. Moreover, these authors suggested that the strengths of the electric field employed by Kogej et al.[9] were too large to be realistic.

Recently, it has been shown that it is possible to tune the nonlinear optical response of molecular π-chromophores by conformational changes in the structure of molecules. In this way, one can obtain remarkable enhancement of first- and second-order hyperpolarizabilities. It was shown by Pati et al,[14] that such an approach can be successfully applied to the two-photon absorption cross sections of conjugated molecules. Moreover, it was also found that the δ values diverge rapidly upon twisting. It seems to be a very promising strategy for searching new materials for several possible applications in the field of nonlinear optics, i.e., optical limiting. Since almost all calculations of δ were performed for isolated molecules (in the gas phase), it is very interesting to obtain theoretical insights into the influence of the solvent on the two-photon absorption cross section. Luo et al.[18] have noticed that the solvent dependence of δ in typical push−pull chromophore with positive solvatochromism was smaller as compared to β. However, it is interesting to check this observation for a representative of another class of compounds exhibiting negative solvatochromic behavior. Bartkowiak and Lipiński have shown that the nonlinear optical response of betaine dye molecules strongly depends on conformational and solvent effects.[29] The values of first-order hyperpolarizability are very sensitive to the interplanar angle between the pyridinium and the phenolate ring. Hence, the simplest pyridinium-*N*-phenolate betaine dye [4-(1-pyridinium-1-yl)phenolate] (see Figure 1) seems to be a perfect candidate for case studies of the influence of the solvent on conformation and the two-photon absorption cross section.

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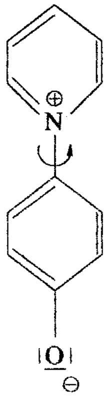

Figure 1. The compound investigated in the present study.

Although the two-photon absorption cross section is associated with the imaginary part of second-order hyperpolarizability, the structure of the relevant formulas describing δ is rather similar to the expressions related to the first-order hyperpolarizability. Hence, the question arises immediately: does the behavior of the δ of the investigated betaine dye molecule upon twisting resemble the demeanor of β or γ? The presented study is to address to this question.

2. Theoretical Methods

In the present study the gas-phase geometries of the pyridinium-*N*-phenolate betaine dye molecule were optimized using the Austin Model 1 approach.[30] The solute/solvent interactions were included within our recently developed quantum-mechanical Langevine dipoles/Monte Carlo (QM/LD/MC) method,[31] originally proposed by Warshel and collaborators.[32−34] All necessary spectroscopic parameters (transition moments, excitation energies, etc.) were evaluated by applying the semiempirical all-valence GRINDOL method[35] including the Tamm-Dancoff approximation. The basic quantity associated with the two-photon absorption process is the two-photon absorption tensor (S_{gf}). In the general case of two different photons (different polarizations $\vec{\mu}_1 \neq \vec{\mu}_2$ and different energies $\hbar\omega_1 \neq \hbar\omega_2$) S_{gf} is given by[36]

$$S_{gf} = \sum_k \left(\frac{\langle g|\vec{\mu}_1\vec{r}\,|\,k\rangle\,\langle k|\vec{\mu}_2\vec{r}\,|\,f\rangle}{\omega_{kg}-\omega_1} + \frac{\langle g|\vec{\mu}_2\vec{r}\,|\,k\rangle\,\langle k|\vec{\mu}_1\vec{r}\,|\,f\rangle}{\omega_{kg}-\omega_2} \right) \qquad (1)$$

where $\hbar\omega_1 + \hbar\omega_2$ should satisfy the resonance condition and $\langle i|\vec{\mu}_1\vec{r}|\ j\rangle$ is the transition moment between states i and j, respectively.

Since in most experiments one source of photons is used, we can substitute the angular frequencies ω_1 and ω_2 for $0.5\cdot\omega_{gf}$. It was shown, that the summation given by eq (1) is well converged for at least 200 terms included.[7] In the present study we performed calculations with the inclusion of 600 intermediate states. However, it is possible to omit eventual truncation by means of analytical description of the S_{gf} matrix elements within the framework of response theory, developed by Olsen and Jørgensen.[37] In their pioneering work, Monson and McClain averaged the two-photon absorption tensor over all orientations of the absorbing molecule (isotropic media case).[38] The averaged two-photon absorption cross section (in atomic units) is given by

$$\langle\delta_{gf}\rangle = \langle|\,S_{gf}(\bar{\mu}_1,\bar{\mu}_2)|^2\rangle = \frac{1}{30}\sum_{ij}\,[S_{ii}S^*_{jj}F + S_{ij}S^*_{ij}G + S_{ij}S^*_{ji}H] \qquad (2)$$

where $F(\bar{\mu}_1, \bar{\mu}_2)$, $G(\bar{\mu}_1, \bar{\mu}_2)$, $H(\bar{\mu}_1, \bar{\mu}_2)$ are polarization variables (for more details see ref 38). Since in the sum (eq 1) we include both ground (g) and final (f) state and the tensor elements are real, the tensor S_{gf} is symmetric. In the case of two linearly polarized photons, all three polarization variables are equal two and the two-photon absorption cross section becomes:

$$\langle\delta_{gf}\rangle = \frac{1}{15}\sum_{ij}\,[S_{ii}\,S^*_{jj} + 2S_{ij}S^*_{ij}] \qquad (3)$$

It should be noted that eq 3, describing the two-photon absorption cross section, can be obtained considering third-order nonlinear optical process (i.e., $\gamma(-\omega;\omega,-\omega,\omega)$; see ref 18).

The first- (β) and the second-order (γ) hyperpolarizabilities were calculated using the finite-field (FF) method developed by Kurtz et al.[39] The calculations were performed at the field strength equal to 0.001 au. The SCF convergence criterion was set to 10^{-12} eV. The T convention (resulting from Taylor expansion) is adopted thoroughly.[40] Because of the fact that most of experiments are performed in isotropic media, the following transformationally invariant quantities have been calculated:

$$\beta_\mu = \frac{\bar{\mu}\cdot\bar{\beta}}{|\mu|} \qquad (4)$$

with

$$\bar{\mu}\cdot\bar{\beta} = \sum_i \mu_i\beta_i;\ \beta_i = \sum_j \beta_{ijj}\ i, j \in (x, y, z) \qquad (5)$$

where μ is the ground-state molecular dipole moment and

$$\langle\gamma\rangle = \frac{1}{15}\sum_{ij}\,(2\gamma_{iijj} + \gamma_{ijji})\ i, j \in (x, y, z) \qquad (6)$$

It should be noted that both quantities (β_μ and $\langle\gamma\rangle$) can be measured experimentally.

It was shown that our method applied to calculations of first- and second-order hyperpolarizabilities of several organic compounds gave reasonable results.[41,42] As in this study we present the enhancement of δ values upon twisting, we hope the possible systematic error (connected with our GRINDOL method) is not important.

3. Results and Discussion

As it was mentioned in the previous section, the geometries of betaine dye **1** were optimized using the AM1 Hamiltonian. Recently, Ishida and Rossky[43] have investigated the structure of the same betaine dye molecule in the gas phase as well as in aqueous solution at the ab initio level of theory. The RISM-SCF method was applied to account for solute/solvent interactions. They found that in the gas phase the optimized torsion angle was 39.91° at the RHF level of theory and 40.72° from CASSCF calculation. Moreover, Ishida and Rossky found the optimized interplanar angle between the pyridinium and the phenolate ring in water solution to be 46.79°.[43] On the basis of the CASSCF results these authors found the RHF results reliable. On the other hand, inclusion of the correlation energy at the MP2 level with the structure optimized at the RHF level leads to change in the potential energy curve (the minimum located at ca. 30°). The above conclusion is supported by the results of our ab initio calculations. It was found that in the gas phase the optimized interplanar angle was 41.5°, 29.9°, and 29.8° at the RHF/6-31G(d), MP2/6-31G(d), and B3LYP/6-31G(d) levels, respectively. These results indicate that the dynamical correlation energy plays an important role in the determination of the geometrical structure of compounds of this type. It should be noted that the equilibrium angle obtained at the AM1 level (25.3°) is closer to the B3LYP and MP2 results. González et al.[44] have found similar behavior in the case of 2-(1-pyridinium-1-yl) phenolate betaine. They have compared the optimized structures of this betaine employing semiempirical (AM1) and ab initio (HF/6-311G and B3LYP/6-311G) methods. Moreover, C=O/C−N bond lengths (1.245/1.388) for the fully optimized AM1 structure of **1** are in good agreement with MP2/6-31G(d) calculations (1.248/1.382). Hence, in our opinion the AM1 method is a reliable technique for predictions of geometrical parameters for the compound **1**. The difference between the torsion angles is the main result of the influence of water on the geometrical parameters of **1**. Hence, we used the same optimized geometry of **1** for calculations in the gas phase and in aqueous solution. During the geometry optimization the interplanar angle was the only parameter kept frozen.

The calculations were performed for the first-excited singlet state ($\pi-\pi^*$ transition). It is well-known that this intramolecular CT band is strongly solvent-dependent and is responsible for the pronounced solvatochromism of this class of compounds.[44−59] The molecule investigated in the present study is a less substituted derivative of Reichardt's dye [2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridinium-1-yl)phenolate], also known as Betaine-30.[45] Reichardt has found that Betaine-30 exhibits the largest hypsochromic band shift of the longest-wavelength absorption band in comparison with other known solvatochromic compounds. In the case of dye **1** investigated in the present work, the calculated transition energy to the lowest-lying singlet state is shifted by $\Delta\bar{\nu}_{\max} = 6517$ cm^{-1}. This result is very close to the recently experimentally measured shift of $\Delta\bar{\nu}_{\max} = 6774$ cm^{-1} in going from dimethyl sulfoxide (less polar solvent) to water (polar solvent).[44] It should be noted that the above computational result was obtained with the equilibrium angle given by the AM1 method (25°).

The results of calculations of the two-photon absorption cross section for the isolated dye molecule in the gas phase as well as in water are presented in Figure 2 (upper figure). As one can see, in the gas phase the δ values strongly depend on the interplanar angle between the two rings. The value of δ has its maximum at 80 degrees. This result is very close to that found by Pati et al. for a 4-quinopyran molecule.[14] When the angle reaches zero degrees the value of δ equals 6.22 [au] (which is 4 orders of magnitude lower than at the optimum angle). In aqueous solution the behavior of the two-photon absorption cross section is different. There is no distinct maximum. Moreover, the δ values are clearly lower than in the gas phase. Such behavior can be explained taking into account the lowest CT state. The increase of the energy and the decrease of the oscillator strength associated with transition to this state are key factors responsible for such large lowering of δ values in water as compared to the gas phase. For such case the simplification of eq (1) leads to

$$S_{gCT} = 4\left(\frac{\langle g|\vec{r}\,|\,\mathrm{CT}\rangle\,(\vec{\mu}_{\mathrm{CT}} - \vec{\mu}_g)}{\omega_{g\mathrm{CT}}}\right) \qquad (7)$$

where summation over all intermediate states was reduced to the lowest-lying state only. In this equation $\hbar\omega_{g\mathrm{CT}}$ stands for the transition energy to the CT state and $\vec{\mu}$ denotes the dipole moment. $\langle g|\vec{r}|\mathrm{CT}\rangle$ is transition moment between the ground and the CT state. In the case of strongly polarized transition along the axis along which the charge-transfer occurs (let it be the *x*-axis) the above equation can be further simplified and finally the expression for the two-photon absorption cross section becomes:

$$\langle\delta_{g\mathrm{CT}}\rangle \approx \langle\delta_{g\mathrm{CT}}^{\;xx}\rangle = \frac{16}{5}\,S_{xx}^2 = \frac{16}{5}\,\frac{\langle g|r_x|\mathrm{CT}\rangle^2\,(\Delta\mu)^2}{\omega_{g\mathrm{CT}}^{\;\;2}} \qquad (8)$$

where $\Delta\mu$ is the difference between dipole moments in the ground and the CT state and $\langle g|r_x|\mathrm{CT}\rangle^2$ is proportional to the oscillator strength (*f*). The results of calculations using eq 8 are presented in Figure 2 (lower figure). It is worth noticing that the behavior of δ in the gas phase as well as in water is reproduced very well. The maxima are located at the same angle. However, as it was expected, the absolute values obtained by the use of a two-state model are slightly overestimated.

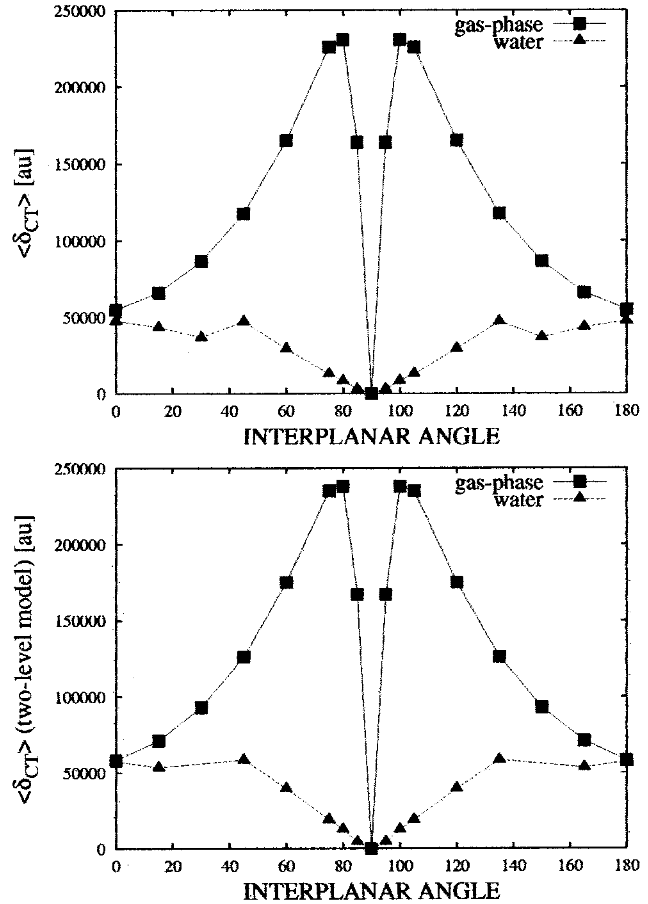

Figure 2. Comparison of the two-photon absorption cross section dependence on the interplanar angle between the piridinium and the phenolate ring for the gas phase and aqueous solution calculated using eq 2 (upper figure) and using a two-level model (eq 8; lower figure).

The results of calculations of the first-order hyperpolarizability (β) are presented in Figure 3. The most important feature is that in the gas phase we can find a maximum of β at the same value of the interplanar angle between rings as in the case of two-photon absorption cross section. Moreover, the demeanor of the β in water is very similar to that of δ. The behavior of β upon twisting in the gas phase as well as in water can be well reproduced by the two-level model proposed by Oudar and Chemla,[60,61] which in atomic units can be expressed as

$$\beta_{\mu}(0;\,0,\,0) \approx \beta_{xxx}(0;\,0,\,0) = 6\,\frac{\langle g|r_x|\mathrm{CT}\rangle^2\,\Delta\mu}{(\omega_{g\mathrm{CT}})^2} \qquad (9)$$

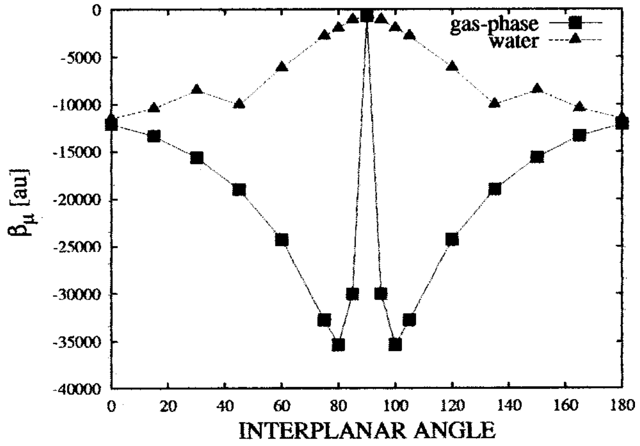

Figure 3. Comparison of the vector component of static second-order polarizability dependence on the interplanar angle between the piridinium and the phenolate ring for the gas phase and aqueous solution.

where $\langle g|r_x|\mathrm{CT}\rangle$ stands for the *x* component of the transition moment to the CT state, $\Delta\mu$ is the difference of dipole moments between the ground and CT state, and $\hbar\omega_{g\mathrm{CT}}$ is the transition energy.

Such simple model explains easily the decrease of the absolute β value of 1 dissolved in water when compared to the gas phase. The detailed analysis of applicability of the two-level model in predictions of the demeanor of β for betaine dyes can be found elsewhere.[31,42] Similarly to the behavior of δ in aqueous environment, one can immediately find that a decrease of the oscillator strength and an increase of the transition energy to the charge-transfer state is a factor that causes lowering of β values. Luo et al.[18] have found that the influence of the solvent on the δ values was smaller than that on β values for typical push−pull molecule. The results of our calculations show different demeanor: $\beta^{\mathrm{gas}}/\beta^{\mathrm{water}} = 18$ and $\delta^{\mathrm{gas}}/\delta^{\mathrm{water}} = 28$ at the optimum angle. This suggests that a generalization is impossible at the moment.

The results of calculations of $\langle\gamma\rangle$ that are presented in Figure 4 show a very similar behavior to that of δ. One can find the maximum in the gas phase at the same angle as in the case of δ and β. The demeanor in water also does not change significantly when compared to that of δ. To check the importance of the above-mentioned CT state for the behavior of $\langle\gamma\rangle$, we used the expression resulting from fourth-order perturbation theory, as originally derived by Orr and Ward:[62]

$$\gamma_{ijkl}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \hbar^{-3} P(i, j, k, l; -\omega_\sigma, \omega_1, \omega_2, \omega_3) \times (S_{ijkl}^{mnq} - V_{ijkl}^{mn}) \quad (10)$$

where

$$S_{ijkl}^{mnq} = \sum_{m\neq0}\sum_{n\neq0}\sum_{q\neq0} \frac{\langle 0|\mu_i|m\rangle\langle m|\bar{\mu}_j|n\rangle\langle n|\bar{\mu}_k|q\rangle\langle q|\mu_l|0\rangle}{(\omega_{m0}-\omega_\sigma)(\omega_{n0}-\omega_2-\omega_3)(\omega_{q0}-\omega_3)}$$

and

$$V_{ijkl}^{mn} = \sum_{m\neq0}\sum_{n\neq0} \frac{\langle 0|\mu_i|m\rangle\langle m|\mu_j|0\rangle\langle 0|\mu_k|n\rangle\langle n|\mu_l|0\rangle}{(\omega_{m0}-\omega_\sigma)(\omega_{n0}-\omega_2)(\omega_{n0}-\omega_3)}$$

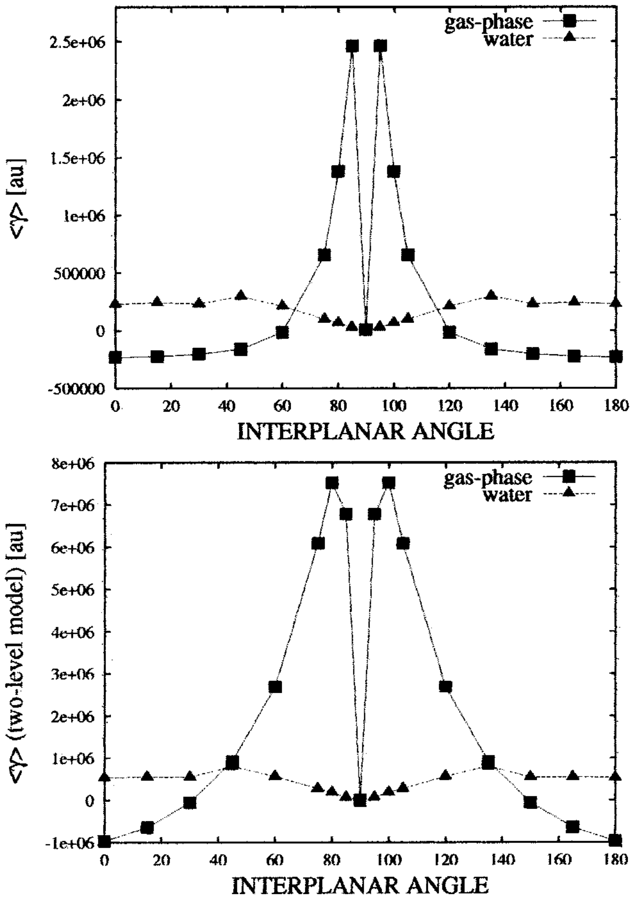

Figure 4. Comparison of the average static third-order polarizability dependence on the interplanar angle between the piridinium and the phenolate ring for the gas phase and aqueous solution calculated using FF method (upper figure) and using eq (11) (lower figure).

In the above expressions $\langle l|\bar{\mu}_j|m\rangle = \langle l|\mu_j|m\rangle - \langle 0|\mu_j|0\rangle\,\delta_{lm}$ and *P* stands for the permutation operator which indicate summation over 24 terms. In the above expression we have included only the charge-transfer state ($|m\rangle = |n\rangle = |q\rangle = |\mathrm{CT}\rangle$):

$$\gamma_{xxxx}(0; 0, 0, 0) = 24\,\frac{\langle g|r_x|\mathrm{CT}\rangle^2\,(\Delta\mu)^2 - \langle g|r_x|\mathrm{CT}\rangle^4}{(\omega_{g\mathrm{CT}})^3} \quad (11)$$

The meaning of the symbols is as previously explained. The results of calculations using above equation are presented in Figure 4 (lower figure). Similarly to δ, the obtained values of both in the gas phase as well as in water are overestimated (what is obviously related to the truncation of all other intermediate states), but the general behavior remains unchanged in comparison with FF calculations. To the best of our knowledge, there scarcely exist any relevant examples of compounds for which it was possible to employ successfully a two-level model to predict the demeanor of $\langle\gamma\rangle$.

The calculated values of the transition energy (ΔE_{CT}), the oscillator strength (*f*) and the dipole moment for the ground and the CT excited state as well as ($\Delta\mu$) for molecule **1** as a function of the interplanar angle for the gas phase and for aqueous solution are shown in Figures 5 and 6, respectively. These parameters are used in two-state models presented in this work. As we can see, the values of E_{CT} and *f* in the gas phase decrease monotonically as the interplanar angle changes from 0° to 90° while $\Delta\mu$ increases. The same behavior of E_{CT} and *f* have been found by Fabien et al.,[63] at the ab initio level (CIS 6-31+G(d,p)). The similar tendency is observed for $\Delta\mu$ and *f* in water. The oscillator strength of the CT transition is negligibly small for 90°, resulting in a very large decrease of δ, β, γ.

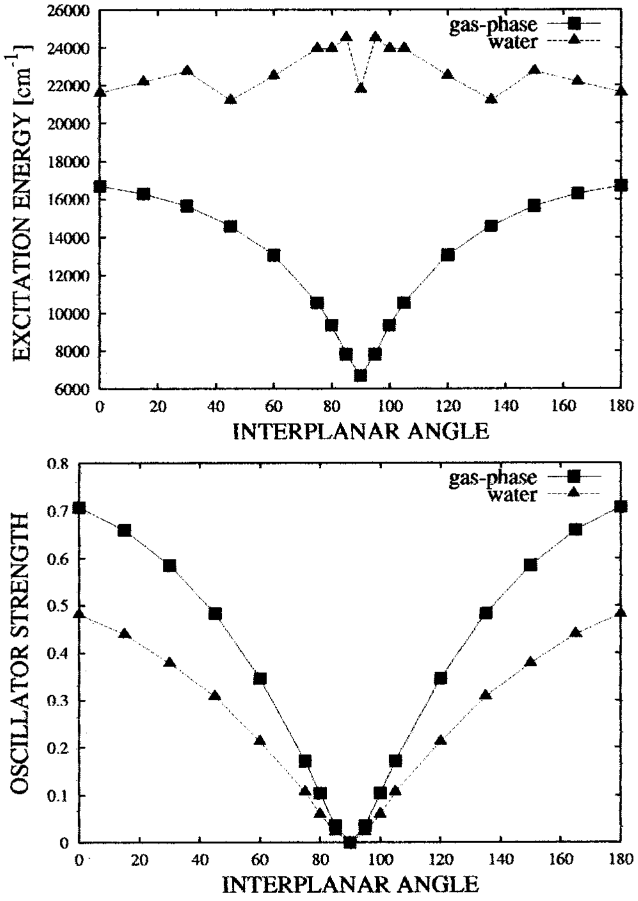

Figure 5. Calculated excitation energies (upper figure) and oscillator strengths (lower figure) for the transition to CT state in the gas phase and water.

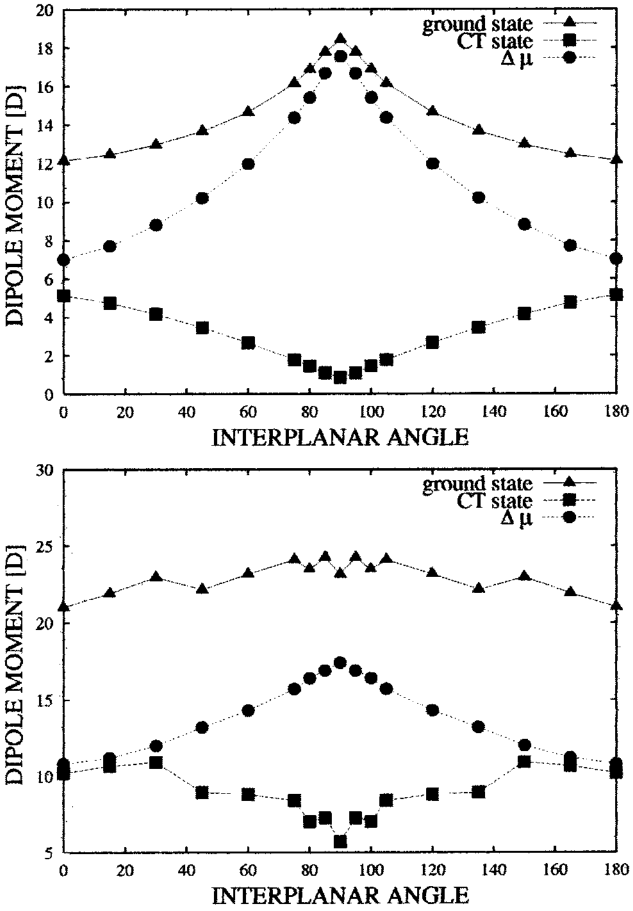

Figure 6. Calculated dipole moments for the ground and CT state, and difference between them for the gas phase (upper figure) and water (lower figure).

Pati et al.[14] found divergent behavior of δ for 4-quinopyran at similar angle to the value reported in the present study. They observed that at that angle the transition energy to one of the intermediate states (one-photon allowed state) that are included in summation given by the eq (1) approached the value that was half of the two-photon gap. In the case of betaine 1 it was sufficient to account for one state only, i.e., lowest-lying charge-transfer state. In this case, one can recognize the different mechanism of the enhancement of the nonlinear optical response. The datailed analysis of eqs (8), (9), and (11) as well as Figures 5 and 6 leads to the conclusion that the general behavior of δ, β, and γ is predictable. Since, the angle at which the maximum is located depends on the relative behavior of f, $\Delta\mu$, and ΔE_{CT}, its prediction based on qualitative analysis is in our opinion very difficult. However, the oscillator strength (f) seems to be key factor responsible for rapid decrease of nonlinear optical response for angles greater than 85° (its small value cannot be compensated by large difference between dipole moments and small value of excitation energy). Moreover, we observed dramatically reduced values of δ, β, and γ in aqueous solution as compared to the gas phase. It is mainly due to the fact that the transition energy between the ground and CT excited state increases significantly with increasing solvent polarity. On going to polar solvent, the CT absorption band for this class of compounds is strongly blue-shifted with diminished intensity (f).[31,45] Our results based on the QM/LD/MC method confirm this observation.

To check the validity of our approach based on Tamm-Dancoff approximation we performed calculations of all necessary spectroscopic parameters at the CISD (configuration interaction with single and double excitations) level of theory. Prior to the fact that the double excitations do mix with the RHF ground state one expects the increase of the excitation energy to the CT state. The results of our calculations at the CISD level show that the excitation energies are ca. 0.8 eV higher that their counterparts at the CIS level. The values of oscillator strength decreased slightly. The difference between dipole moments for the CT state and the ground state also decreased. However, it should be pointed out that relative behavior does not change. The small decrease of oscillator strength does not influence the values of the two-photon absorption cross section significantly. The higher the excitation energy is, the lower value of δ is obtained. However, it should be mentioned that CT band shift and absolute values of excitation energies obtained for compound **1** at the CIS level are reproduced very well.[44] Kanis et al.[61] have indicated that calculation of second-order polarizability (β) at the semiempirical level would be more consistent where performed using the CIS method. This is due to the fact that the semiempirical Hamiltonians are based on parametrization consistent with calculation of optical properties in which the ground state is taken as a single determinant, and the excited states at monoexcited configuration interaction level.[61] On the basis of above considerations we concluded that the analysis of nonlinear optical response of compound **1** can be performed at the CIS level. Additionally, we performed the calculations of δ within the Tamm-Dancoff approximation for compound studied by Pati et al.[14] We observed analogous behavior of δ as a function of the interplanar angle, although our results were slightly underestimated to that reported in ref 14.

4. Conclusions

The semiempirical GRINDOL method was applied in order to calculate first- and second-order hyperpolarizability as well as two-photon absorption cross section of the simplest pyridinium-*N*-phenolate betaine dye molecule. The solvent influence on these properties was taken into account within the Langevine dipoles/Monte Carlo formalism. The calculations of β, γ, and δ were performed as a function of the interplanar angle between the pyridinium and the phenolate ring.

It was found that in the gas phase all three nonlinear optical parameters have their maxima at 80 degrees. In all three cases it was possible to explain the behavior of β, γ, and δ taking into considerations the ground and the lowest-lying charge-transfer state, only. We believe that it was possible to describe the behavior of all presented nonlinear optical parameters (δ, β, γ) in water in terms of two states because of the unique solvatochromic deportment of the betaine molecule **1**. It would be interesting to check whether a similar behavior can be observed for other negatively solvatochromic species and relevant work is now in progress. The calculations indicated that δ values are large. The conformational tunability of the δ values seems to be a very promising feature for possible applications in the field of nonlinear optics.

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