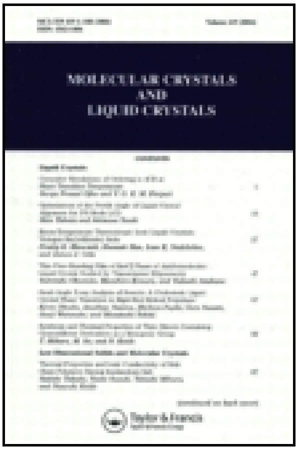

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DIPOLE MOMENTS AND SECOND-ORDER HYPERPOLARIZABILITIES OF IMIDAZOLE-BASED BETAINES DETERMINED FROM THE SOLVATOCHROMIC EFFECT

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Abstract We report on results of measurements of the solvatochromic effect in two benzimidazole-based betaines (hereafter referred to as IB1 and IB2). The solvatochromic shifts exceed 2000 cm^{-1} in both molecules; however, the directions of the shift were found opposite in spite of similar chemical structures of the molecules under study. The ground-state dipole moments in both betaines exceed 13 Debye units, whereas the excited-state moments, calculated from the solvatochromic shift, differ markedly amounting to ca. 3 D in IB1 and 18 D in IB2. Quantum-chemical calculations indicate that betaines enjoy some freedom of orientation of their fragments which may influence the energies and intensities of the electronic transitions. The second-order hyperpolarizabilities, estimated from the measurements amount to ca. 20×10^{-40} m^4/V (4.8×10^{-30} esu) for IB1 and 55×10^{-40} m^4/V (13.8×10^{-30} esu) for IB2.

INTRODUCTION

Electronic properties of electronically "soft" molecules have been extensively studied over two recent decades, one of the reasons for the growing interest in such systems being their possible application in non-linear optics (e.g. Refs. 1,2 and references therein). In this paper, we report on the determination of the ground- and excited state dipole moments, as well as the second-order hyperpolarizability in two benzimidazole-based betaines hereafter referred to as IB1 and IB2, (cf. Fig.1). The results described here supplement those given in our previous paper[3]. The molecules under study belong to the family of zwitterionic molecules, its best known representative being the Reichardt's betaine[4-6]. The method used in our experiments is the measurement of the solvatochromic shift - the simplest one among the methods allowing one to obtain information about the parameters of excited states[5,7].

The solvatochromic effect manifests itself as a shift of the position of the low-energy band(s) in electronic absorption and/or emission spectra of solute molecules resulting from interactions with solvents of various polarities. For polar molecules, the shift is

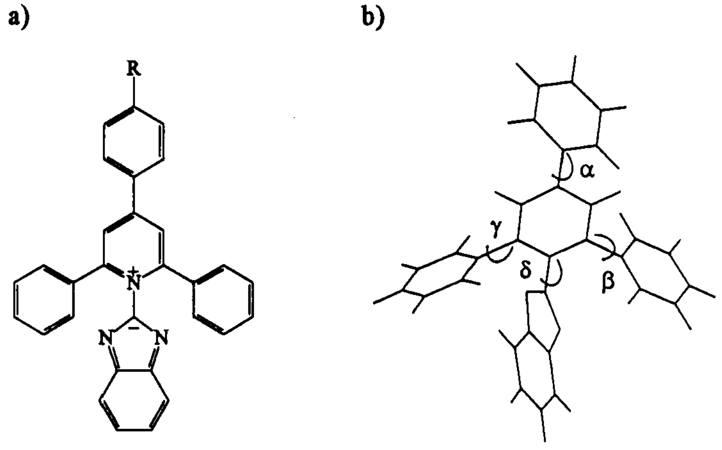

FIGURE 1 The betaines used in the present study
a) chemical formulae: IB1 - R=H, IB2 - R=N(CH_3)$_2$
b) optimized conformation of an isolated molecule of IB1

related to changes of the dipole moments upon excitation[5,7]. In the analysis of the results reported in this paper, we employed the equation derived in Ref. 7, resulting from the model of Abe[8]

$$hc(\bar{\nu}_A^s - \bar{\nu}_A^0) = -\frac{1}{4\pi\varepsilon_o a^3}\left(2(\bar{\mu}_e - \bar{\mu}_g)\cdot\bar{\mu}_g\cdot[\phi(\varepsilon)-\phi(n)] + (\mu_e^2-\mu_g^2)\cdot\phi(n)\right) \quad , \quad (1)$$

where $\phi(\varepsilon)=(\varepsilon-1)/(\varepsilon+2)$, $\phi(n)=(n^2-1)/(n^2+2)$, $\bar{\nu}_A^0$ and $\bar{\nu}_A^s$ are the wavenumbers corresponding to the absorption of an isolated solute molecule, and the solute molecule in a solvent, respectively, and μ_g and μ_e are the permanent dipole moments of the molecule in its ground and excited states, respectively. The parameter *a* stands for the radius of a spherical cavity occupied by the solute molecule. To increase the reliability of the measurements, the ground-state moment was determined independently from measurements of the static electric permittivity, following the standard procedure consisting in determining the molar polarizability (Π_{sol}) of diluted solutions of the solute in a non-polar solvent[9]. Assuming Π_{sol} to be an additive function of the properties of the solute and solvent ,one can determine the molar polarizability of the solute at the infinite dilution ($\Pi_{u,o}$)

$$\Pi_{u,o} = \frac{N_A}{3\varepsilon_o}\left(\alpha_{dis} + \frac{\mu_g^2}{3kT}\right) \quad , \qquad (2)$$

where N_A is the Avogadro number, ε_o is the permittivity of the free space and α_{dis} is the distortion polarizability of the solute molecule which can be estimated from molar increments.

Basing on results of the spectroscopic measurements, one can also estimate the second-order hyperpolarizability of the molecule. The two-state quantum-mechanical model[10] predicts the following expression for the vectorial part of the hyperpolarizability tensor, directed along the direction of the charge transfer

$$\beta_{CT}(-2\bar{\nu},\bar{\nu},\bar{\nu}) = \frac{3}{2\varepsilon_o h^2 c^2}\frac{(\bar{\nu}_A^s)^2}{\left((\bar{\nu}_A^s)^2-4\bar{\nu}^2\right)\left((\bar{\nu}_A^s)^2-\bar{\nu}^2\right)}\left|\bar{\mu}_e-\bar{\mu}_g\right|\cdot\mu_{eg}^2 \quad , \qquad (3)$$

where μ_{eg} is the transition moment between the ground and excited states, related to the strength of the transition, which can be calculated from the integral absorbance[11] .

EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

IB1 and IB2 were synthesized at the Department of Organic Chemistry, Prague Institute of Chemical Technology[12], and kindly placed to our disposition by Professor J. Kuthan and Dr S. Böhm. All organic solvents were of spectroscopic grade and were dried before use. The absorption spectra and the relative electric permittivities of the solutions of IB1 and IB2 were measured at room temperature.

The ground state geometries of the IB1 betaine were optimized using the AM1 method of Dewar et. al.[13], other parameters (electronic transitions, polarization, dipole moments etc.) were evaluated using the GRINDOL method[14]. The calculations were carried out both for an isolated IB1 molecule and for a molecule embedded in a solvent. In the latter case, the solvent effect was included by using the Monte Carlo sampling technique[15];details of the calculations will be published elsewhere[16].

RESULTS AND DISCUSSION

The ground-state dipole moments of IB1 and IB2 were determined from the measurements of the static electric permittivities of solutions of BTPP in 1,4-dioxane. The values calculated from these measurements were found equal to 13.4 D and 13.8 D for IB1 and IB2, respectively.

The absorption spectra of IB1 and IB2 are shown in Fig. 2. The main features appearing in the spectral region covered by the measurements are an intense band peaking at ca. 320 nm, accompanied by a band at longer wavelengths - very weak in IB1 and much stronger in IB2. While the former peak is practically uninfluenced by the nature of the solvent, the position of the long-wavelength (CT) band is strongly solvent-dependent: a significant hypsochromic shift of the CT band is observed in IB1 on increasing the solvent polarity, whereas a batochromic shift of a similar magnitude occurs

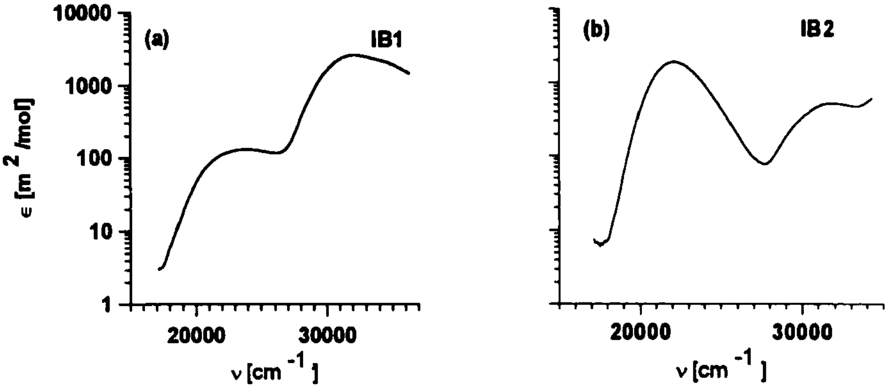

FIGURE 2 Absorption spectra of the betaine solutions in methyl sulfoxide: (a) -IB1; (b) - IB2

in IB2.

According to Eq. (1), the position of the CT band should be simultaneously a linear function of $[\phi(\varepsilon)-\phi(n)]$ and $\phi(n)$. As is shown in Fig. 3, the predictions of the Abe's model[7,8] are reasonably fulfilled. The excited-state dipole moments determined from the solvatochromic shifts amount to (3±1) D in IB1 and (18±1) D in IB2.

The dispersion of the second-order hyperpolarizability calculated from Eq. (3) is

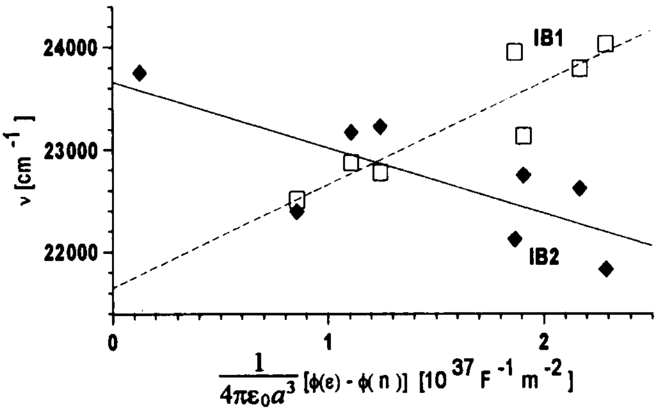

FIGURE 3 Dependence of the position of the CT band on the solvent polarity. The meaning of the functions $\phi(\varepsilon)$ and $\phi(n)$ is explained in the text.

presented in Fig. 4. The calculations were carried out employing the ground-state dipole moments determined from the dielectric measurements, excited-state moments taken from the solvatochromic shifts, and the transition moments calculated from the intensities of the CT bands. The results shown in the figure were calculated for IB1 and IB2 dissolved in chloroform. The off-resonance values of β_{CT} amount to ca. $20\text{x}10^{-40}$ m^4/V ($4.8\text{x}10^{-30}$ esu) for IB1 and $55\text{x}10^{-40}$ m^4/V ($13.8\text{x}10^{-30}$ esu) for IB2.

The quantum-chemical calculations carried out for IB1 yield results consistent with the experiment. The conformation of the betaine is characterized by four dihedral angles

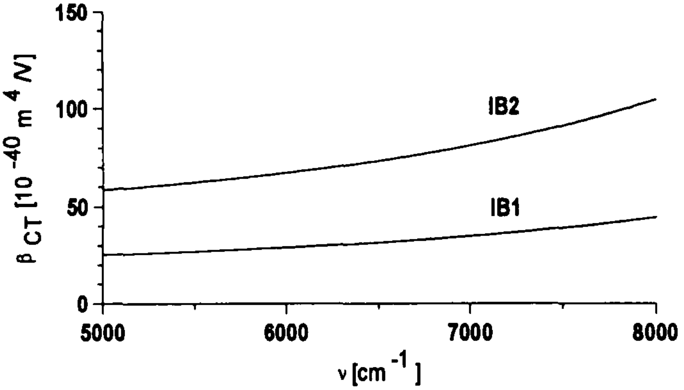

FIGURE 4 The dependence of the second-order hyperpolarizability of the betaine molecules.

between nearly-planar rigid moieties (see Fig. 1b). The optimization procedure yields the following values for the minima of these parameters in an isolated molecule: α = -38°, β = 51°, γ = 51° and δ = 60°. The potential energy curves are, however, quite flat across each angle thus the equilibrium conformation of the molecule can be modified by external factors (e.g., polarity and shape of the solvent molecules etc.). In particular, the calculations[16] carried out for the solvent-embedded IB1 showed that the angle δ, influencing the energies and intensities of the CT transitions allows for the minimum of the potential energy around 60° for the isolated molecule, whereas it shifts to nearly 90° for IB1 in chloroform (a non-polar solvent), and water (a model polar solvent). The ground-state dipole moment, calculated for the optimized geometry of the isolated molecule, was found equal to 12.9 D, being directed along the long axis of the molecule. Our calculations demonstrate that, among possible low-lying CT transitions, only the transitions to S_1 and S_3 states could be observed, the respective excited-state dipole moments amounting to -6.2 D and 1.3 D, respectively. It appears that the experimentally measured absorption might be due to a superposition of the two transitions. The calculated dependences of the oscillator strengths on the dihedral angle (δ) demonstrate that the geometry assumed by the molecule in the gas phase apparently favours the transition to S_1, whereas the transition to S_3 may become more important in solutions.

CONCLUSIONS

The results of measurements described in the preceding sections of this paper yield a consistent picture. In the ground state, both IB1 and IB2 molecules exhibit dipole moments exceeding 13 D. The experimental values are in a very good agreement with the results of calculations obtained using the GRINDOL method. There is a dramatic change of polarity upon excitation: the experimentally determined dipole moments of

IB1 in its lowest-lying excited state decreases significantly, whereas IB2 becomes even more polar. The difference should probably be sought in the presence of electrons in the dimethylammonium group of IB2; appropriate quantum-chemical calculations are in progress.

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