

SOLVATOCHROMIC EFFECT IN
A BENZIMIDAZOLE-BASED BETAINES:
DETERMINATION OF THE DIPOLE MOMENTS
AND SECOND-ORDER HYPERPOLARIZABILITY

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*Dedicated to Professors Krzysztof Pigoń, Józef W. Rohleder
and Zdzisław Ruzewicz on the occasion of their 70th birthdays**

Results of measurements of the solvent-dependent shift of the low-energy absorption band solvatochromic effect in a benzimidazole-based betaine are reported in the paper. Measurements of absorption spectra in several solvents of different polarities were performed. The solvatochromic shift of the low-lying absorption band was found to exceed 3000 cm^{-1} ; the results obtained were then employed to calculate the ground- and excited-state dipole moment of the molecule. The spectroscopic measurements were supplemented by measurements of the ground-state dipole moment. A remarkable change in the charge distribution was found to occur upon the electronic excitation: both the experimental results and the calculations indicate that the ground-state dipole moment is close to 13 D, whereas in the excited state it amounts to ca. 3 D. The second-order hyperpolarizability of the molecule was calculated from the measurements; its off-resonance value amounts to ca. $20 \times 10^{-40} \text{ m}^4/\text{V}$ ($4.8 \times 10^{-30} \text{ esu}$), depending on the solvent used.

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1. Introduction

Interest in optically nonlinear molecular systems growing over two recent decades resulted in the discovery of several classes of organic molecules of this type, and in establishing some general principles governing their molecular architecture (e.g. [1, 2] and references therein). In general, the molecules should exhibit ability of re-arrangement of the electronic system upon excitation, manifesting itself, e.g. in a large difference between the dipole moments of the ground and excited state. Additionally, an important ground-state dipole moment is also desirable for some purposes (e.g., facilitating the field-induced orientation of active molecules in matrices). Consequently, a complete description of the electronic properties of the molecules requires the knowledge of the ground- and excited-state dipole moments, as well as of the polarizabilities (linear and of the higher orders). While the parameters characterizing the ground state of the molecule are in many cases readily available (e.g., the ground-state dipole moment can be easily determined from standard dielectric measurements [3]), those of excited states have been scarcely known. Among several existing methods allowing one to obtain such information, the simplest (although not the most reliable) one is that making use of the solvatochromic effect (e.g. [4, 5] and references therein).

In this paper, we report on use of the solvatochromic method to determine the ground- and excited-state dipole moments, as well as the second-order hyperpolarizability in an imidazole-based betaine [1(1-H-benzimidazol-2-yl)-2,4,6-triphenylpyridinium] (hereafter referred to as BTTP — cf. Fig. 1). The molecule under study belongs to the family of zwitterionic molecules, its best known representative being so-called Reichardt's betaine [6], often used to scale the polarity of solvents [5, 7]. The structures of both betaines are shown in Fig. 1.

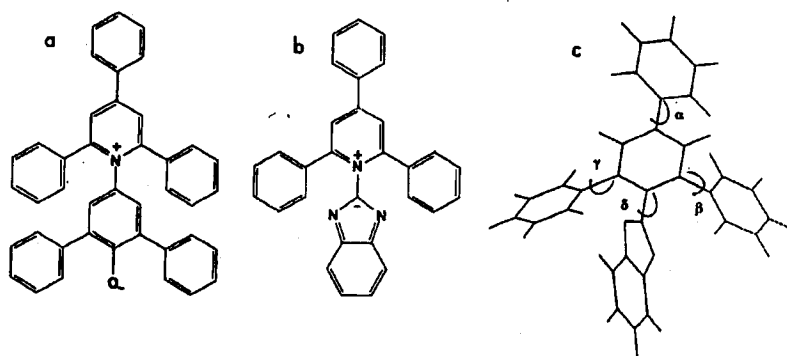


Fig. 1. Formulae of betaines; the systematic chemical names are given in the brackets. (a) Reichardt's betaine [2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinium)phenoxide]; (b) the betaine used in this study (BTTP) [1-(1H-benzimidazol-2-yl)-2,4,6-triphenyl-1-pyridinium]; (c) optimized geometry of BTTP. The calculated values of dihedral angles are given in Sec. 4.

As has been known from earlier reports [8], imidazole-based betaines are characterized by important ground-state dipole moments, exceeding 10 D[†]. Moreover, BTTP was expected to behave similarly to Reichardt's betaine, in which the dipole moment significantly decreases upon excitation. For this reason, the molecule appeared to be a suitable candidate for a more thorough study.

2. The solvatochromic effect

The solvatochromic effect manifests itself as a shift of the position of a low-energy band in electronic absorption and/or emission spectra of solute molecules resulting from interactions with solvents of various polarities. For the purpose of this paper, we shall focus our attention on polar molecules (i.e., those with non-zero ground-state dipole moments). In this case, the dominant effect associated with the shift is related to changes of the dipole moments upon excitation [4, 5].

All existing theories relate the solvent shift to weak interactions between a solute molecule and a solvent, usually treated as an isotropic dielectric medium characterized by its static relative electric permittivity (ϵ) and refractive index (n). The parameter taken as a measure of the shift is either the difference between the positions of the lowest-energy absorption bands of an isolated molecule and that dissolved in a given solvent [9], or the difference between the positions of the lowest-energy bands in absorption and fluorescence [10, 11]. Differences in the equations describing the solvatochromic shift result also from assumptions concerning the local field, polarizability of solute molecules, etc. (cf., e.g. [4, 5, 12] and references therein). In the analysis of the results reported in this paper, we shall employ the equations resulting from the theory put forward by Abe [9].

According to Abe [9], the solvatochromic shift in the absorption spectra is given by the equation

$$hc(\bar{\nu}_a^e - \bar{\nu}_a^0) = -\frac{1}{4\pi\epsilon_0 a^3} \{2(\bar{\mu}_e - \bar{\mu}_g)\bar{\mu}_g [\phi(\epsilon) - \phi(n)] + (\mu_e^2 - \mu_g^2)\phi(n)\}, \quad (1)$$

where $\phi(\epsilon) = (\epsilon - 1)/(\epsilon + 2)$, $\phi(n) = (n^2 - 1)/(n^2 + 2)$, $\bar{\nu}_a^0$ and r are the wave numbers corresponding to a transition occurring in 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. Apart from an obvious oversimplification made on approximating the actual shape of molecule by a sphere, the estimation of a itself may be a source of significant errors. A plausible approximation for a , valid for $1/2r_u < r_s < 2r_u$, is [4]

$$a = r_u + \frac{1}{2}r_s, \quad (2)$$

where r_u and r_s are the radii of the solute and solvent molecules, respectively, estimated from appropriate densities (ρ) and molar masses (M)

$$r_i = \left(\frac{3M_i}{4\pi\rho_i N_A} \right)^{\frac{1}{3}} \quad (i = u, s), \quad (3)$$

[†]1 D = 1 Debye unit = 3.33×10^{-30} C m.

N_A being Avogadro's number. In Eqs. (2) and (3), the subscripts "u" and "s" refer to the solute and solvent, respectively. Another assumption made on deriving Eq. (1) is the collinearity of μ_g and μ_e ; as will be shown in the forthcoming sections, this condition is well fulfilled in the betaine under study.

The methods based on the solvatochromic shift allow, in principle, for determination of μ_g , μ_e and $\bar{\nu}_a^0$ from the spectroscopic measurements only. However, more reliable results are often obtained if the ground-state moment is determined independently. This is the route which we followed in the experiments reported in this paper: the ground-state dipole moment was additionally calculated from the results of measurements of static electric permittivity, following the procedure described in Ref. [3].

Basing on results of the spectroscopic measurements, one can also estimate the second-order hyperpolarizability of the molecule. The sum-over-states quantum-mechanical model [13] predicts the following expression for the vectorial part of the hyperpolarizability tensor, directed along the direction of the charge transfer (the long axis of the molecule, in our case collinear with the directions of μ_g and μ_e)

$$\beta_{CT}(-2\bar{\nu}, \bar{\nu}_i, \bar{\nu}) = \frac{3}{2\varepsilon_0 h^2 c^2} \sum_i \frac{(\bar{\nu}_{a,i}^s)^2}{[(\bar{\nu}_{a,i}^s)^2 - 4\bar{\nu}^2][(\bar{\nu}_{a,i}^s)^2 - \bar{\nu}^2]} |\bar{\mu}_{e,i} - \bar{\mu}_g| \mu_{eg,i}^2, \quad (4)$$

where the sum is taken over low-lying charge-transfer (CT) states, and $\mu_{eg,i}$ is the transition dipole moment between the ground and an i -th excited states. In many cases it is sufficient to take into consideration only a dominant excited state. Thus one obtains the usual two-state expression [13, 14]

$$\beta_{CT}(-2\bar{\nu}, \bar{\nu}_i, \bar{\nu}) = \frac{3}{2\varepsilon_0 h^2 c^2} \frac{(\bar{\nu}_a^s)^2}{[(\bar{\nu}_a^s)^2 - 4\bar{\nu}^2][(\bar{\nu}_a^s)^2 - \bar{\nu}^2]} |\bar{\mu}_e - \bar{\mu}_g| \mu_e^2. \quad (4a)$$

The parameter μ_{eg} is related to the strength of the transition, and can be calculated from the integral absorbance [14, 15]

$$\int_{\text{band}} \epsilon(\bar{\nu}) d\bar{\nu} = \frac{2\pi^2 \bar{\nu}_a^s N_A f^2}{3 \ln 10 \varepsilon_0 c h n} \mu_{eg}^2, \quad (5)$$

where $\epsilon(\bar{\nu})$ is the molar absorbance appearing in the Lambert-Beer equation and f is the local field factor, taken here in the Lorenz approximation [16]

$$f = \frac{n^2 + 2}{3}. \quad (6)$$

3. Experimental and computational procedures

BTTPP was synthesized following the procedure described in detail in Ref. [17], and purified by multiple crystallization from chloroform and by chromatography on alumina. The composition was checked by NMR and mass spectroscopy.

The concentrations of solutions of BTTPP used in the experiments reported in this paper ranged from 10^{-4} to 10^{-5} mol/dm³. All organic solvents were of spectroscopic grade and were used without further purification. Unfortunately, the number of solvents which could be used in the experiments described in this paper was limited by almost a total lack of solubility of BTTPP in several non-polar solvents.

The absorption spectra were recorded using a UV-VIS spectrophotometer Shimadzu 2101-PC. The relative electric permittivities of BTTP solutions in 1,4-dioxane were determined using a Tesla BM559 RLCG automatic bridge operating at 1 kHz. All measurements were carried out at room temperature.

To optimize the ground state geometry of BTTP, we used the quantum-chemical AM1 method of Dewar et al. [18]. Other parameters of BTTP (electronic transitions, polarization, dipole moments, etc.) have been evaluated using the GRINDOL method [19] being a modified version of an INDO-like approach, including the configuration interaction (CI), with 500 singly excited configurations included. The method enables calculation of parameters of ground and excited state of isolated molecules, molecular complexes and transition metal compounds within a unified parametrization scheme, in a reasonable agreement with relevant experimental results. In additional calculations we also included the solvent effect via the virtual charge method (VCM) of Constanciel and Tapia [20–22]. These results will be reported elsewhere [23].

4. Results

4.1. Ground-state properties

4.1.1. Quantum-chemical calculations

BTTP molecule can be represented to a good approximation by a set of five rigid planar fragments (cf. Fig. 1): central pyridinium (Py) moiety, to which a benzimidazolyl (BI) and three phenyl (Ph1-Ph3) groups are attached. Thus the conformation of BTTP is characterized by four dihedral angles: α (Py-Ph1), β (Py-Ph2), γ (Py-Ph3) and δ (Py-BI). The optimization procedure yields the following values for the minima of these parameters: $\alpha = -36.6^\circ$, $\beta = 103.2^\circ$, $\gamma = 99.1^\circ$, and $\delta = 69.5^\circ$. However, it should be pointed out that the potential energy curves are quite flat across each angle thus local minima can exist in the space of these variables. Moreover, the equilibrium conformation of the molecule can be readily modified by external factors (e.g., polarity and shape of the solvent molecules, temperature, etc.). The optimized geometry of the molecule is shown in Fig. 1c, the details will be discussed elsewhere [23].

The ground-state dipole moment, calculated for the optimized geometry of the isolated molecule, was found equal to 12.87 D, being directed along the long axis of the molecule.

4.1.2. Dipole moment

The experimental values of the ground-state dipole moment of BTTP were determined following the procedure described, e.g. in Ref. [3]. The procedure consists in determining the molar polarizability of diluted solutions of the solute in a non-polar solvent (Π_{sol}),

$$\Pi_{\text{sol}} = \frac{\epsilon_{\text{sol}} - 1}{\epsilon_{\text{sol}} + 2} \frac{x_s M_s + x_u M_u}{\rho_{\text{sol}}} = \frac{N_A}{3\epsilon_0} \left(\alpha_{\text{dis}} + \frac{\mu_g^2}{3kT} \right), \quad (7)$$

where ϵ_{sol} is the static electric permittivity of the solution, x_s and x_u are molar fractions of the solvent and the solute, respectively, α_{dis} is the distortion polar-

izability of the solute molecule. Assuming Π to be an additive function of the properties of the solute and solvent

$$\Pi_{\text{sol}} = x_s \Pi_s + x_u \Pi_u, \quad (8)$$

one can determine the molar polarizability of the solute at the infinite dilution: $\Pi_{u,0} = \lim_{x_u \rightarrow 0} \Pi_u$. In order to calculate the permanent dipole moment, the distortion polarizability should be estimated. The latter parameter is not much different from the molar refraction (R); to a first approximation, it is usually taken as $(1 \div 1.15)R$.

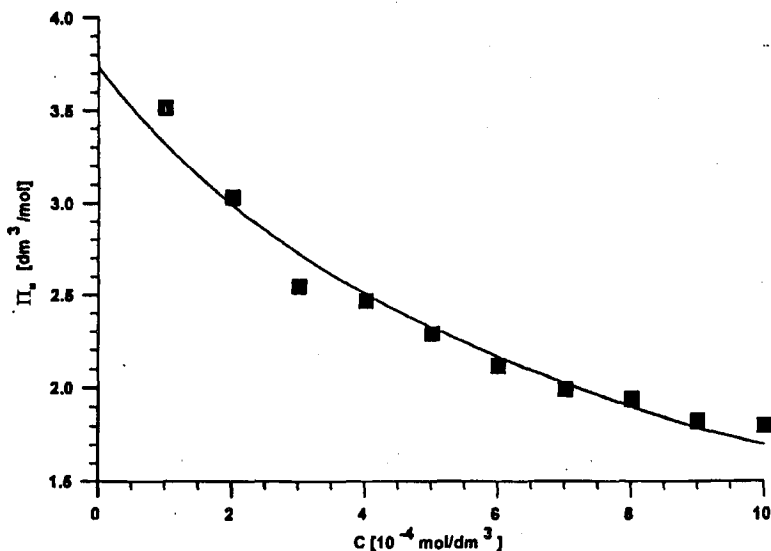


Fig. 2. Concentration dependence of the molar polarizability of BTTP in dioxane.

The molar polarizability of BTTP ($\Pi_{u,0}$) was determined from the measurements of the static electric permittivity of solutions of BTTP in 1,4-dioxane (cf. Fig. 2); the average value amounts to 3.7×10^{-3} m 3 /mol. The molar refraction, estimated as a sum of structural increments [24], was equal to 1.34×10^{-4} m 3 /mol. Thus the ground-state dipole moment of BTTP calculated from these measurements was found equal to (13.5 ± 0.5) D, in a reasonable agreement with both the literature data [8] and the quantum-chemical calculations (Sec. 4.1.1.).

4.2. Absorption spectra

4.2.1. Experimental results

The absorption spectrum of BTTP is shown in Fig. 3. The main feature appearing in the spectral region covered by the measurements reported here (above 220 nm, i.e. beyond the absorption region of the solvents) is an intense band peaking at ca. 320 nm, accompanied by a much weaker band at longer wavelengths. While the position of the main peak is practically uninfluenced by the nature of the solvent, the intensity and position of the weak CT band is strongly

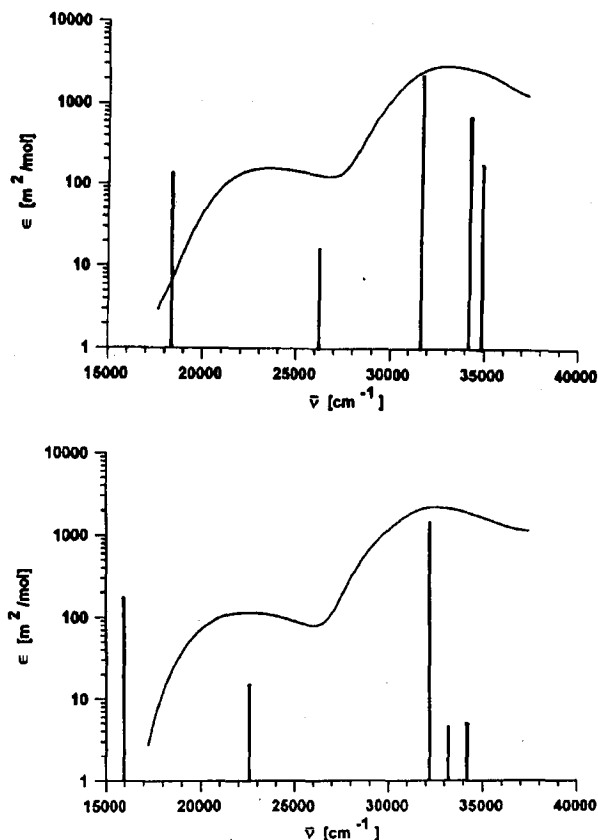


Fig. 3. Absorption spectra of solutions of BTTP in acetonitrile (upper spectrum) and chloroform (lower spectrum), compared with the transition energies determined from the quantum-chemical calculations. The spectra in chloroform are compared with the energies calculated for an isolated molecule, those in acetonitrile — with energies calculated for a molecule embedded in a polar medium. Note: the heights of the bars do not correspond to the oscillator strengths.

solvent-dependent, and in some solvents an additional very weak long-wavelength band can be discerned. In the experiments reported in this paper, we shall focus our attention on the peak centred around 430 nm. A significant hypsochromic shift of the CT band is observed on increasing the solvent polarity thus suggesting that the dipole moment decreases upon excitation. Due to a partial overlap of the two bands, the position of the maximum of the CT absorption band was determined after fitting it with a Gaussian function, and its integral absorbance was then determined as twice the integral of the low-energy half of the experimentally obtained absorbance. The positions of the maxima thus obtained are listed in Table.

The solvatochromic shift of the CT band of BTTP was analysed using the equation derived from Abe's model [9]. Taking into account the collinearity of μ_g

TABLE
Positions of absorption and emission maxima of BTPP in solvents of different polarity.

No.	Solvent	ϵ	n	a [10^{-10}m]	$\bar{\nu}_a^s$ [cm^{-1}]	μ_{eg} [D]
1	carbon tetrachloride	2.22	1.4603	6.97	20517	2.3
2	chloroform	4.81	1.4486	6.86	22512	2.2
3	ethyl acetate	6.11	1.3726	6.97	22873	1.8
4	tetrahydrofurane	7.60	1.4071	6.87	22779	0.6
5	acetone	21.2	1.3591	6.82	23137	2.4
6	acetonitrile	37.5	1.3460	6.66	23798	2.2
7	methyl sulfoxide	46.4	1.4790	6.80	23952	2.3

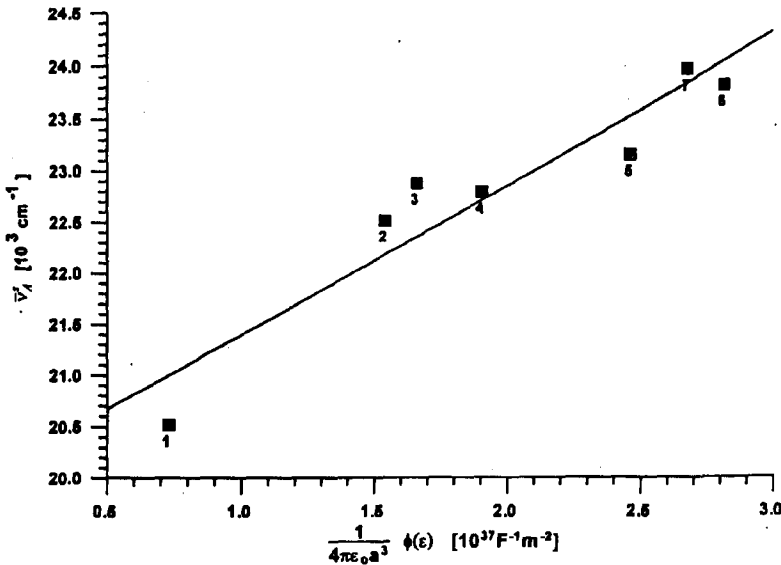


Fig. 4. Dependence of the position of CT bands in absorption spectra of BTPP on the solvent polarity. The function $\phi(\epsilon)$ is defined in Eq. (1). The numbers refer to the solvents as listed in Table.

and μ_e , Eq. (1) after simple manipulations can be rewritten in the form

$$hc(\bar{\nu}_a^s - \bar{\nu}_a^0) = \frac{1}{4\pi\epsilon_0 a^3} [2\bar{\mu}_g(\bar{\mu}_g - \bar{\mu}_e)\phi(\epsilon) + (\bar{\mu}_g - \bar{\mu}_e)^2\phi(n)]. \quad (9)$$

It should be noted that the parameter $\phi(n)$ varies very little: for the solvents used in this work, it assumes values ranging between 0.21 and 0.28. Consequently, to within a reasonable approximation Eq. (9) may be rewritten in the form

$$\bar{\nu}_a^s = \frac{1}{2\pi hc\epsilon_0 a^3} [\bar{\mu}_g(\bar{\mu}_g - \bar{\mu}_e)] \phi(\epsilon) + \text{const.} \quad (9a)$$

The dependence of the positions of the maxima of the CT band on $\phi(\epsilon)$ is shown

in Fig. 4. The excited-state dipole moment, calculated assuming $\mu_g = 13.5$ D (the value taken from dielectric measurements — cf. Sec. 4.1.2.) was determined to amount to (3 ± 1) D. Finally, the position of the CT absorption band of an isolated molecule was calculated to amount to 20200 cm^{-1} .

4.2.2. Calculations

The absorption spectrum of an isolated molecule (gas-phase spectrum) calculated for the ground-state geometry contains several low-intensity transitions above 350 nm. The low-lying electronic states, to which these transitions occur, can be described as intramolecular charge-transfer states. Two transitions with non-negligible oscillator strengths have been marked with vertical bars in Fig. 3. It should be indicated that in both cases the transition moments are parallel to the long axis of the molecule. The first strong absorption appears at ca. 310–320 nm and can be regarded as a superposition of a few closely-lying transitions. The position and intensity of the latter band was found only weakly dependent on the geometry of the molecule, its environment etc.: for the gas-phase spectrum, and for the molecule in a dielectric medium, the most intense transition appears at $31900 \pm 300 \text{ cm}^{-1}$, in a very good agreement with the experiment (cf. Fig. 3). On the other hand, parameters of the CT transitions are strongly dependent on both the conformation and the environment of the molecule. Our calculations [23] indicate that the most important parameter is the dihedral angle δ between the central pyridinium and benzimidazolyl moieties (cf. Fig. 1c). However, as was mentioned above, the potential energy curve is quite flat around the minimum: at room temperature, the angle δ can vary by as much as 77° within the 2 kT energy limit. Thus there is a non-zero probability of the existence of a distribution of molecular

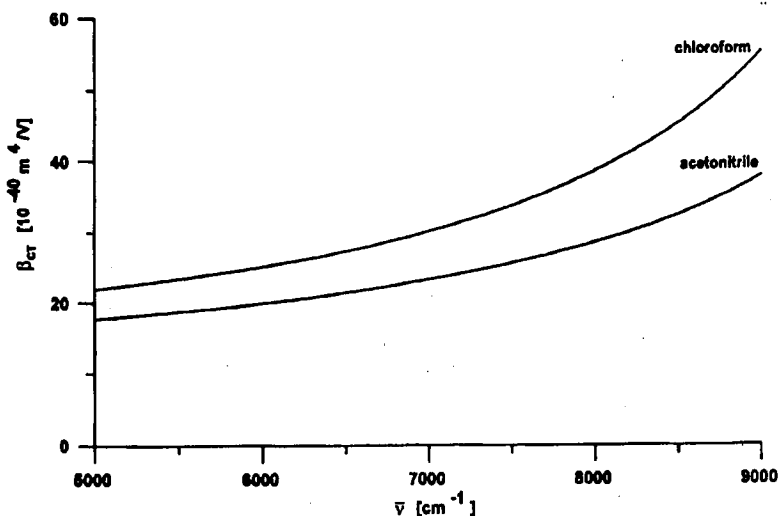


Fig. 5. The dispersion of the second-order hyperpolarizability calculated from Eq. (4a).

conformations influencing the transition energies. These results will be described elsewhere [23].

The dispersion of the second-order hyperpolarizability calculated from Eq. (4a) assuming the applicability of the two-state model, is presented in Fig. 5. The calculations were carried out employing the following set of parameters: $\mu_g = 13.5$ D and $\mu_e = 3$ D. Two curves were calculated, representing the results obtained for BTPP in non-polar and polar solvents (chloroform and acetonitrile, respectively).

5. Final remarks

The results of measurements described in the preceding sections of this paper yield a consistent picture. In the ground state, BTPP molecules exhibit a large dipole moment exceeding 13 D. The experimental value is in a very good agreement with the results of quantum-chemical calculations. There is a dramatic change of polarity upon excitation: the experimentally determined excited-state dipole moment of the molecule is over 10 D smaller, amounting to ca. 3 D. The change is reflected in an important solvatochromic shift of the position of the CT band. The experimental and calculated absorption spectra are in a very good agreement in the region of the most intense band, i.e. around 320 nm. On the other hand, both the spectrum and the excited-state dipole moments are more difficult to reproduce by the quantum-chemical calculations. The explanation of the discrepancy should be sought in an extreme sensitivity of the lowest-lying transitions to the geometry of the molecules and the nature of their environment. On the other hand, the potential energy surface is flat around the minimum thus structures involving large deviations from the optimized structure can be realized quite easily. These two features result in producing a wide band being essentially a convolution of geometry- and environment-dependent transitions.

A closer inspection of the experimental data, and a comparison of the experiment with the results of our calculations (c.f. Fig. 3) does not exclude a possibility of a very weak absorption associated with the existence of a low-energy transition. This, however, does not change the validity of the results presented in this paper and their interpretation: in any case the band observed around 430 nm should be regarded as due to an intramolecular CT transition.

The hyperpolarizability of BTPP, estimated from the two-state model, is about 2–3 times lower than the respective value determined for typical molecules exhibiting efficient second-order nonlinearity [14]. As can be inferred from Eq. (4), high hyperpolarizabilities can be achieved in molecules in which a high transition moment is accompanied by an important change of the dipole moments upon transition. This is not the case in BTPP: while the latter condition is indeed fulfilled, the intensity of the CT band (and hence the transition moment) are far too weak. Thus the effort should be now concentrated on a functionalization of the benzimidazole-based betaine resulting in increase in the intensity of the CT band.

Acknowledgments

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