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Theoretical Study of Solvent Effect on the Structure, First Electronic Excited State, and Nonlinear Optical Properties of Substituted Stilbazolium Cations

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ABSTRACT: Molecular structure, first excited state properties and charge distribution of a series of substituted stilbazolium cations in different media are theoretically investigated. First static hyperpolarizability (β_0) of considered compounds is studied by both finite-field and two-state model methods. In contrast to the recent theoretical studies, in present contribution the mutually consistent description of solvent polarity dependence of β_0 calculated by both employed approaches is achieved. It is shown that the ground-to-excited state intramolecular charge-transfer is significantly affected by the solvent that provides the hyperpolarizability variation. Taking into account both solvent polarity and substituent effect the peculiarities of β_0 behavior of stilbazolium derivatives are re-examined. The effect of molecular geometry on the calculated electronic excitation properties is investigated.   © 2010 Wiley Periodicals, Inc. Int J Quantum Chem 111: 780–787, 2011

Key words: quantum chemistry; nonlinear optics; stilbazolium dye

1. Introduction

Substances that exhibit highly nonlinear optical (NLO) responses are currently of great scientific and technological interest because of their potential use in communication and optical information processing [1–3]. Traditional inorganic materials such as lithium niobate ($LiNbO_3$) are difficult to create and possess the relatively slow response time. In contrast, organic compounds are easier to produce, faster response times, lower dielectric constants, and enhanced NLO responses relative to the traditional inorganic solids [1]. Since the NLO response of these organic molecular crystals is ultimately governed

by the NLO characteristics of the constituent molecular chromophores, the search of novel molecules capable of manipulating electric fields, especially photonic signals, is currently intense area of research. The focus of recent researches has been on organic molecules having the large quadratic NLO activities typically contain electron donor (D) and acceptor (A) groups connected via polarizable π-conjugated spacer. The NLO properties of such polarizable dipolar compounds are caused by intense, low-energy $D(\pi) \rightarrow A(\pi^*)$ intramolecular charge-transfer (ICT) transitions. The excellent second harmonic generation efficiency had been reported for an ionic stilbazolium salt 1-methyl-4-(2-(4-(dimethylamino) phenyl) ethenyl) pyridinium p-toluenesulfonate [4]. However, more effective crystals are desired for devices with higher efficiency and stilbazolium derivatives are very attractive for this purpose.

Typically, the values of molecular hyperpolarizability are reported to be based solely on measurements made in one particular solvent. The accurate modeling of the NLO properties of a chromophore in a solvent is essential for the efficient development and evaluation of novel compound design strategies. Moreover, accurate modeling of the NLO properties by taking into consideration environmental interactions will permit investigators to make a theoretical prediction of the merit of such systems and thus avoid the high cost associated with a hit or miss synthetic approach.

NLO properties of substituted stilbazolium cations (Fig. 1) were investigated both experimentally and theoretically [5–9]. The experimental values of molecular hyperpolarizability of these compounds were evaluated by the hyper-Rayleigh (HR) scattering method with methanol solutions [5, 6]. Compound **8** was investigated in butyronitrile glass by electroabsorption (EA) spectroscopic study and detailed description of first excited state properties was obtained [7]. The static (off-resonance) first hyperpolarizability was estimated from these experiments by application of two-state (TS) model introduced by Oudar and Chemla [10]. Sainudeen and Ray verified the applicability of TS model to study the NLO responses of substituted stilbazolium cations by calculation of the frequency-dependent hyperpolarizabilities using the coupled perturbed Hartree-Fock (CPHF) method [9]. Taking into account the solvent effect, they also demonstrated by ZINDO/CV approach that the solvent polarity plays an important role in the first hyperpolarizability of stilbazolium cations and also provided the aggregation effect study. An effects of N-arylation of pyridinium group in stilbazolium
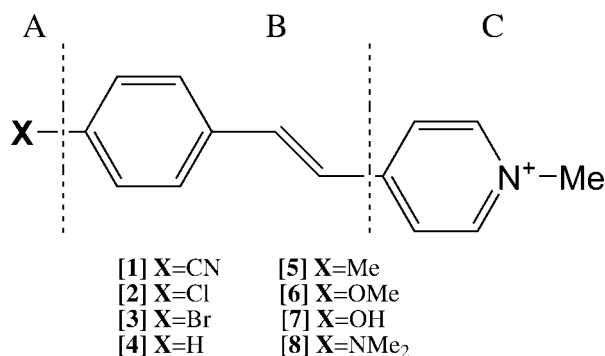
FIGURE 1. Substituted stilbazolium cations investigated.

dyes and dependence of NLO response on conjugation path length in different media was theoretically studied in Refs. [11, 12].

Although the compounds investigated in present contribution have been extensively studied, analysis of recent theoretical results indicate that on the one hand the CPHF approach demonstrate about 50% enhancement of first static hyperpolarizability (β_0) in methanol solute comparing with the gas phase one [9]. However, assessment of the β_0 via two state model employing the gas phase and acetonitrile solute time-dependent (TD) B3P86 calculated parameters reveals only about 10% increasing of hyperpolarizability and decreasing of β_0 for the INDO/SCI calculations [11].

In this article two different approaches, to estimate the value of β_0, were used: (i) finite-field (FF) method [13] and (ii) TS model approach [10]. In comparison with the previous studies, we make these methods mutually consistent and present a systematic quantum chemical investigation of donor-acceptor properties and solvent polarity effect on the first excited state properties, β_0 and molecular geometry of substituted stilbazolium cations. An accuracy of results calculated by differently optimized molecular geometries was examined. Calculated data are compared with experimental values from HR scattering and EA spectroscopy measurements reported in the literature [5–7]. Excites state properties analysis was carried out by employing the TD density functional theory.

2. Methods and Calculations

In general, the total energy of a molecule can be expanded as the Taylor series of the applied external static electric field **F**:

$$E_{\text{tot}}(\mathbf{F}) = E_{\text{tot}}(0) - \sum_i \mu_i F_i - \frac{1}{2!} \sum_{ij} \alpha_{ij} F_i F_j$$
$$- \frac{1}{3!} \sum_{ijk} \beta_{ijk} F_i F_j F_k - \dots, \quad (1)$$

where μ_i are the components of the permanent dipole moment and α_{ij} and β_{ijk} are the components of linear polarizability and first hyperolarizability tensors, respectively. The squared component of the HR scattering first hyperpolarizability was calculated as follows [14, 15]:

$$\left(\beta_{\text{FF}}^{(0)}\right)^2 = \frac{6}{35} \sum_i \beta_{iii}^2 + \frac{16}{105} \sum_{i \neq j} \beta_{iii} \beta_{ijj} + \frac{38}{105} \sum_{i \neq j} \beta_{iii} \beta_{ijj}$$
$$+ \frac{16}{105} \sum_{i,j,k,\text{cyclic}} \beta_{iij}^2 + \frac{20}{35} \beta_{xyz}^2. \quad (2)$$

The TS model allows one to represent β as product of "intrinsic" hyperpolarizability $\beta_{\text{TS}}^{(0)}$ and frequency-dependent dispersion function as

$$\beta = \beta_{\text{TS}}^{(0)} \left(1 - \frac{(\hbar\omega)^2}{E_{\text{ge}}^2}\right)^{-1} \left(1 - \frac{4(\hbar\omega)^2}{E_{\text{ge}}^2}\right)^{-1}, \quad (3)$$

$$\beta_{\text{TS}}^{(0)} = \frac{3\Delta\mu_{\text{ge}}\mu_{\text{ge}}^2}{E_{\text{ge}}^2}, \quad (4)$$

where E_{ge} is the resonance energy of ICT, μ_{ge} is the transition dipole moment between ground (g) and excited (e) states, and $\Delta\mu_{\text{ge}}$ is the difference between excited and ground state dipole moments. Perturbation (B) convention is used in Eq. (4)[16].

The TS model is very fruitful for theoretical study of NLO compounds, as it allows make the detailed analysis of electronic stucture of investigated chromophores, while the FF approach does not provide a microscopic interpretation of the obtained results. This model was modified to account for details expected to become important on or near resonance, including the finite lifetime of the charge-transfer state, inhomogeneous broadening and the vibronic structure of the electronic transition [17–20]. Evidently, there is value in using both FF and TS model calculation methods to obtain as full a picture as possible of the molecular hyperpolarizabilities of chromophores investigated here. The Eqs. (2) and (4) describe the same value of static molecular hyperpolarizability. To distinguish hyperpolarizabilities calculated by FF calculations and TS model we marked these values by $\beta_{\text{FF}}^{(0)}$ and $\beta_{\text{TS}}^{(0)}$, respectively.

3. Computational Details

Calculations were carried out using the Gaussian 03 package of quantum chemical programs [21]. Effect of molecular geometry obtained by different optimization techniques on electronic properties of cation **8** is reported in Ref. [12]. It was found that MP2 method gives the best agreement for calculated structures with X-ray crystallographic data [22]. At the same time, first excited state properties and NLO response calculated using geometries optimized by Hartree-Fock (HF) and MP2 approaches give results close to each other. By this reason and due to the high computation cost, in this article full geometry optimization was performed only at the B3P86 and HF levels within the 6-311++G(d,p) basis set.

Excited electronic states were analyzed by TD-B3P86 approach using the same basis set and the molecular geometries previously optimized. The differences of dipole moments between ground and m-th excited states were estimated as follows [12, 23]:

$$\Delta\mu_{\text{ge}}^{(m)} = \frac{E_{\text{ge}}^{(m)}(0) - E_{\text{ge}}^{(m)}(F)}{F}, \quad (5)$$

where $E_{\text{ge}}^{(m)}(F)$ is the mth band resonance energy calculated at the presence of external electric field F parallel to molecular dipole moment. The unidirectional ICT was assumed. In the framework of TS model, we focus our attention on the electronic properties of the first excited state. Use of Eq. (5) to estimate the $\Delta\mu_{\text{ge}}$ values is more preferable, as it takes into consideration electronic correlations that are neglected in frequently employed one-particle RhoCI density excited state dipole moment calculations. The FF calculations were carried out using B3P86 method too.

The effect of solvent polarity is often discussed within the methods, which represent the solvent as a continuum medium of dielectric constant ϵ. Among the classical continuum models, the polarizied continuum models (PCM), first proposed by Tomasi and coworkers [24], probably are the most widely used for the description of solute-solvent interactions. In present contribution, the solvent effect was estimated by performing calculations within the framework of the integral equation formalism PCM [25]. Net atomic charges were calculated using the natural population analysis (NPA) included in the natural bond orbital algorithm proposed by Weinhold and co-workers [26–28]. NPA analysis was carried out for the HF optimized structures. Excited state

TABLE I

Results of TD-B3P86 analysis of Compounds 1–8 in different media.

Cation	Gas			CHCl$_3$			MeOH			Experiment		
	E_{ge} (eV)	μ_{ge} (D)	$\Delta\mu_{ge}$ (D)	E_{ge} (eV)	μ_{ge} (D)	$\Delta\mu_{ge}$ (D)	E_{ge} (eV)	μ_{ge} (D)	$\Delta\mu_{ge}$ (D)	E_{ge} (eV)	μ_{ge} (D)	$\Delta\mu_{ge}$ (D)
1	3.13	8.93	9.21	3.37	9.69	9.22	3.49	9.59	7.89	3.70[a]	—	—
							3.33[b]	10.16[b]	6.48[b]			
							3.40[c]	9.86[c]	7.66[c]			
2	2.96	9.00	8.78	3.19	9.42	11.80	3.35	9.16	11.73	3.58[a]	—	—
							3.22[b]	9.73[b]	9.99[b]			
3	2.83	8.86	10.63	3.13	9.49	13.21	3.31	9.26	12.90	3.56[a]	—	—
							3.18[b]	9.85[b]	11.12[b]			
4	3.16	6.04	10.96	3.28	8.99	9.78	3.41	8.75	10.43	3.57[a]	—	—
							3.29[b]	9.22[b]	8.83[b]			
5	3.05	9.10	6.54	3.16	9.44	10.51	3.30	9.15	11.35	3.43[a]	—	—
							3.17[b]	9.70[b]	9.57[b]			
6	2.86	9.78	5.82	2.93	9.89	11.23	3.08	9.49	12.64	3.25[a]	—	—
							3.00[b]	10.12[b]	10.38[b]			
7	2.95	9.37	5.50	2.97	9.69	10.48	3.09	9.31	11.87	3.17[a]	—	—
							3.00[b]	9.94[b]	9.73[b]			
8	2.61	10.98	4.00	2.51	11.12	9.80	2.61	10.55	12.03	2.62[a]		
							2.60[b]	11.37[b]	9.36[b]	2.58[d]	9.1[d]	16.3[d]
							2.56[e]	10.63[e]	11.88[e]			

[a] Obtained by absorption spectra measurements in methanol [5, 6].
[b] Obtained using the B3P86 optimized structure.
[c] Obtained using the B3P86 optimized structure with the carbon-carbon interatomic distances in polymethine backbone forced to be the same with the HF optimized ones.
[d] Obtained by EA measurements in butyronitrile [7].
[e] Obtained using the MP2 optimized structure. From Ref. [12].
For each chromophore theoretical data were obtained by using the HF optimized structures, except otherwise denoted.

charge distribution was analyzed by employing the one-particle RhoCI density. The default Gaussian 03 parameters were used in every case.

4. Results and Discussion

As it had been demonstrated both experimentally and theoretically [29, 30], the bond length alternation (BLA) and bond order alternation are the molecular structure parameters that are strongly influence on the values of hyperpolarizability of π-conjugated donor-acceptor systems. Following to article [30], the value of BLA is defined as the difference between the average carbon-carbon single and double bond lengths in the polymethine backbone. It had beed shown that, in the case of cation **8**, the most accurate value of BLA can be obtained for the MP2 solute optimized structure and the B3P86 optimized one gives the worst agreement [12]. The HF gas phase optimized geometries underestimates the

BLA, whereas the solute one overestimates it. For the HF and B3P86 solute optimized geometries the absolute deviation of the BLA value from the experimental one is quite same. Comparison of calculated E_{ge}, μ_{ge}, and $\Delta\mu_{ge}$ with the EA data indicates with employing HF and MP2 optimized structure give results close to each other and better agreement with experiment.

The results of TD-B3P86 analysis for all optimized structures in different media are summarized in Table I. It is seen that for all investigated compounds calculations using the HF optimized geometries reveal the best agreement with experiment for the absorption energies measured in methanol. So, for Compound **7** the experimental value of the BLA is 0.168 Å [31], whereas this value calculated in the gas phase (methanol solute) equal to 0.104 (0.128) Å and 0.067 (0.086) Å for the HF and B3P86 optimized structures, respectively. For Compound **8** calculations using the HF optimized structures demonstrate the best agreement of E_{ge}, μ_{ge}, and $\Delta\mu_{ge}$ with the results

TABLE II

Results of gas phase TD-B3P86 analysis for the HF/MeOH optimized structures.

Cation	E (eV)	μ (D)	$\Delta\mu$ (D)
1	3.12	8.00	9.81
2	2.95	8.66	9.79
3	2.81	8.49	11.78
4	3.13	5.05	12.11
5	3.02	8.74	7.50
6	2.80	9.31	7.04
7	2.90	9.01	6.45
8	2.48	10.40	5.01

Data for Compound **8** are from Ref. [12].

of EA experiment [7]. Use of the B3P86 optimized geometries strongly underestimates the E_{ge} and $\Delta\mu_{ge}$ and simultaneously overestimates the μ_{ge} values relatively results obtained by the HF optimized ones.

To evaluate the effect of BLA variation on the calculated properties, we forced the carbon-carbon interatomic distances in polymethine bridge for the B3P86 structure of Cation **1** to be the same as in the HF optimized one. Obtained results demonstrate that such geometry variation reduce the discrepancy between data obtained by different geometries on the values about 50% for the E_{ge} and μ_{ge} and on 85% for the $\Delta\mu_{ge}$ (Table I). Thus, modification of only three bonds in the molecule leads to the critical change of the excited state properties. This allows us to consider the BLA as the most important geometry parameter. As the HF optimized structures reveal the best agreement with experiment for the E_{ge} values for all considered chromophores and the best agreement with the EA experiments, all the following analysis will be performed for the HF optimized geometries.

To consider the geometry and solvent polarity effects separately, the TD-B3P86 analysis by the HF/MeOH optimized structures was carried out. The results are presented in Table II. The solvent effect on the molecular geometry itself demonstrates the decreasing of the E and μ and increasing the $\Delta\mu$ values. Further changes of these values in MeOH solute are caused by the solvent polarity.

The magnitude of hyperpolarizability and its dependence on the solvent polarity are closely related to the **X** substituent in each actual cation. Substitution effect is often analyzed using Hammett parameters and the σ_p^+ dependence of investigated stilbazolium derivatives have to be studied. The σ_p^+ parameter [32] is selected because this is used when the electron-acceptor resonantly interacts with substituent **X** in the transition state. Values of σ_p^+ parameter for all considered **X** substituents are summarized in Table III.

The first static hyperpolarizabilities of investigated compounds calculated by both FF and TS model approaches in different media are summarized in Figure 2. The values of $\beta_{FF}^{(0)}$ and $\beta_{TS}^{(0)}$ do not exactly agree but demonstrate the same functional dependence on the media polarity. The values $\beta_{TS}^{(0)}$ for all cations except **2** and **3** are within the 20% experimental error [5, 6]. It should be notified that the HR scattering hyperpolarizability measurement for Cation **8** was also carried out by Coe et al. [33]. The reported hyperpolarizability ($\beta_0 = 25 \times 10^{-30}$ esu) significantly differs from the results of Duan et al. [5, 6, 8] (Fig. 3). As in the present contribution the substituent effect is studied, we will compare out data with the last series of experiment.
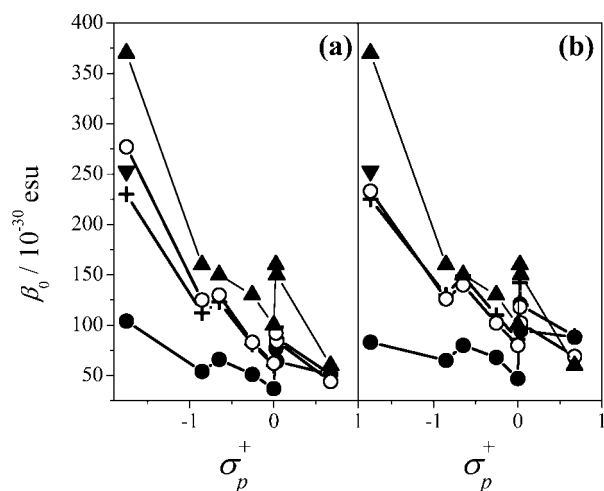
Calculations predict the significant blue shift for E_{ge} values for all compounds except Cation **8**. Halogenated Cations **2** and **3** have the largest values of $\beta_{TS}^{(0)}$ in the gas phase among all considered chromophores but in solute phase the Cation **8** demonstrates the largest values of hyperpolarizability in all solvents. In solute media, the magnitude of static hyperpolarizability is greatly enhanced with decreasing of σ_p^+ parameter and weakly depends on solvent polarity. A slight decreasing of the $\beta_{TS}^{(0)}$ value at large positive σ_p^+ constant for CN substituted stilbazolium changes to significant increasing at large negative σ_p^+ and electron donation of substituent **X** increases in solution comparing with the gas phase.

To explain these peculiarities, the BLA dependence of the first static hyperpolarizability of Cations **1–8** is plotted in the Figure 2. Qualitative behavior of $\beta_{TS}^{(0)}$ value on the BLA perfectly agree with results of Meyers and coworkers [29, 30]. BLA values for all
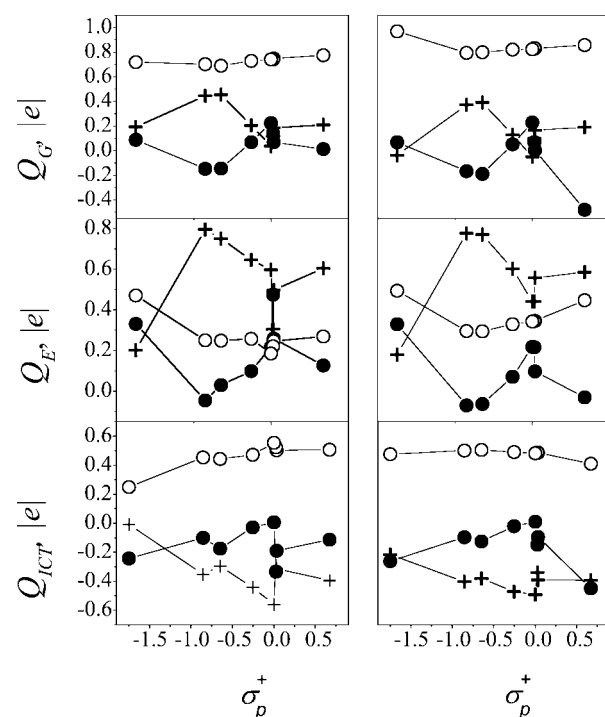
TABLE III

Hammett parameter σ_p^+ for cations investigated.

Cation	1	2	3	4	5	6	7	8
σ_p^+	0.674	0.035	0.025	0	−0.256	−0.648	−0.853	−1.75
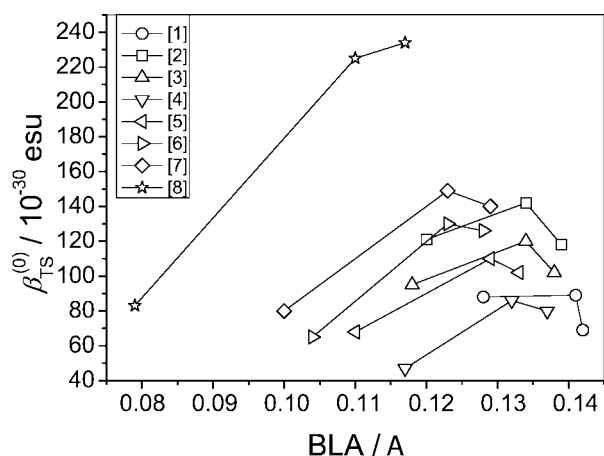
FIGURE 2. The BLA dependence of $\beta_{TS}^{(0)}$ for compounds **1**–**8** calculated in different media.

compounds, except **8**, in methanol are not optimal and their maximal first hyperpolarizability could be observed in solvents with less polarity, for example, in chlorophorm. Large gas phase $\beta_{TS}^{(0)}$ values of halogenated stilbazolium cations can be explained by the fact that BLA for these compounds are close to the optimal. The slow change of first static hyperpolarizability with BLA increasing is caused by the reducing of phenyl ring electron donating ability by halogen

substituent. With decreasing of σ_p^+ constant the BLA values have tendency to decrease too. For Cation **8**, they have the smallest values among all compounds in all media. The small BLA values indicate that the large mixing between ground and resonance canonical forms exists. The large absolute value of the Hammett constant for $N(CH_3)_2$ group leads to high donor electron donating ability. According to results of articles [29, 30], the blue shift usually takes place when the structure of π-conjugated bridge evolves from the cyanine structure (zero BLA) to polyene limit (bond alternated). Such change of the BLA take place for all considered stilbazolium derivatives except Cation **8**. In the last case, the change of media polarity from the gas phase to chlorophorm solute leads to the small red-shifted solvatochromic effect that is altered by the small blue-shifted one. The origin of this phenomena is the fact that the extremum of the E_{ge} as a function of the BLA value is slightly


FIGURE 3. The σ_p^+ dependence of $\beta_{FF}^{(0)}$ (a) and $\beta_{TS}^{(0)}$ (b) calculated in gas phase (●), CHCl$_3$ (+) and MeOH (○) in comparison with experiment. Experimetnal results were obtained using Eq. (3) from the β value measured by the HR scattering method at 1064 nm as a fundamental beam [5, 6, 8] (▲) and using Eq. (4) from the EA measurements in butyronitrile [7] (▼).

FIGURE 4. Results of NPA charge distribution calculated in gas phase (left panel) and MeOH solute (right panel) calculated ground (Q_G), excited (Q_E) and ground-to-excited state ICT (Q_{ICT}) for A (●), B (+) and C (○) parts of cations investigated. The Q_{ICT} values were obtained by subtraction of excited state net charge on corresponding molecular moiety from the same value in the ground state. The way of partitioning shown in Figure 1.

shifted from cyanine limit to the polyene area [29, 30]. The BLA realized in the Compound **8** is around this value.

To understand the origin of enhancement of the first static hyperpolarizability in solution comparing with the gas phase, the charge distribution in different media was calculated. Figure 4 summarizes the net charge in the ground and excited states of substituent **X** (part A), styryl group (part B) and pyridinium ring (part C). In comparison with the gas phase, solute calculated charge distribution demonstrates additional polarization of investigated chromophores. As a result, the ground state dipole moments of all cations increases as it is shown in Figure 5. Solvent also intensifies the ICT. To illustrate this the ground-to-excited state charge transfer in the gas phase and MeOH solution calculated by subtraction of excited state net charge on corresponding molecular moiety from the same value in the ground state is plotted in Figure 4.

Use of the one-particle RhoCI density for $\Delta\mu_{ge}$ calculation give results different from obtained by Eq. 5 (Table IV). In contrast to the estimation approach used in this article, the one-particle RhoCI density method neglects the electronic correlations. Using Eq. 5, these correlations are effectively taken into account and obtained results are more accurate. By this reason description of the ground-to-excited state ICT estimated by the one-particle RhoCI density is only qualitative.
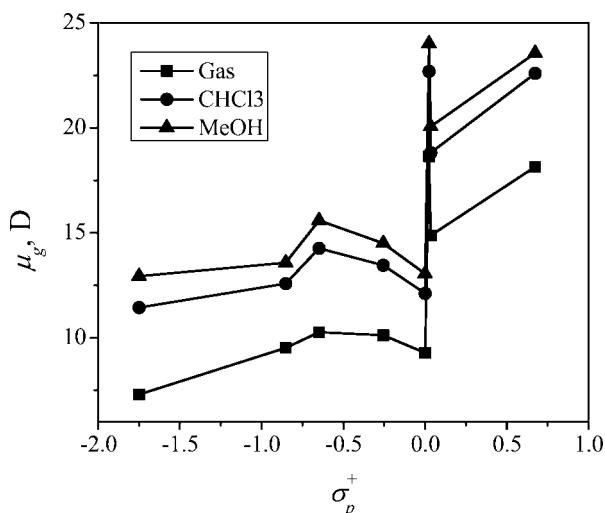
FIGURE 5. The values of ground state dipole moment μ_g (D) calculated in different media using B3P86 functional and the HF optimized structures.

TABLE IV _____

The values of $\Delta\mu_{ge}$ (D) calculated in different media using one-particle RhoCI density.

Cation	Gas	CHCl$_3$	MeOH
1	18.81	13.56	11.31
2	20.27	17.26	15.92
3	17.23	19.10	17.35
4	19.32	14.16	13.43
5	16.30	15.60	14.77
6	18.32	19.09	19.26
7	17.46	18.38	18.58
8	18.42	21.53	22.16

Data for compound **8** are from Ref. [12].

5. Conclusion

The molecular hyperpolarizability of a series of substituted stilbazolium cations in different media are theoretically studied by both the FF and TS model approaches. In contrast to the recent theoretical studies, in present contribution the mutually consistent description of solvent polarity dependence obtained by both of these approaches was provided. The accuracy of electronic excitation properties calculated by different optimized molecular geometries was compared. It was shown that use of the HF optimized structures gives the better agreement with experiment than B3P86 ones. Solvent effect is critical in studies of nonlinear optic response of compounds investigated because of its influence on the molecular geometry and ground-to-excited state ICT. Taking into account both effects of solvent polarity and substituent electron withdrawing (donating) ability the peculiarities of first static hyperpolarizability and electronic excitation energy were explained. The underestimation of solvent effect on the first hyperpolarizability obtained in the previous study [11] was associated with neglect of electron correlations provided by one-particle RhoCI density excited state dipole moment estimation procedure. The calculation procedure used in this study to be useful for the investigation of NLO properties of different push-pull chromophores and for understanding the origin of their NLO activity with high accuracy.

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