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Solvent effects on the spectroscopic properties of triarylmethane dyes

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Abstract

The spectroscopic characteristics of two highly symmetric triarylmethane dyes, Crystal Violet and Ethyl Violet, and two triarylmethanes displaying lower symmetry, Victoria Blue R and Victoria Pure Blue BO, were investigated in a variety of polar solvents. The solvent effects observed on the electronic spectra of the highly symmetric dyes add momentum to previous objections to the rotamers model, a model traditionally used to explain the appearance of a shoulder in the short-wavelength side of the maximum absorption band of Crystal Violet in ethanol. We have found that, in polar solvents the magnitude of the splitting between the overlapped absorption bands of Crystal Violet is dependent on the solvatochromic properties of the media. The nature of this dependence suggested the existence of specific interactions between Crystal Violet and the surrounding solvent molecules. We hypothesize that these solute-solvent interactions represent the symmetry-breaking event that lowers the symmetry of Crystal Violet in solution, and gives rise to the appearance of the spectroscopic shoulder at the short-wavelength side of its maximum absorption band. Analogous results were obtained for Ethyl Violet. The solvent effects observed on the absorption spectra of the triarylmethanes displaying lower symmetry were different from those observed for the highly symmetrical compounds. This difference was rationalized in terms of the distinct nature of the overlapping absorption bands characteristic of these two distinct sets of dyes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Solvent effects; Electronic spectroscopy; Crystal Violet; Ethyl Violet; Victoria Pure Blue BO; Victoria Blue R

1. Introduction

Triarylmethane dyes are suitable for a large variety of technological applications. They have been extensively used as textile dyes for silk, wool and cotton, in the preparation of inks and to surface-coat and dye paper [1], as colorants in foods, drugs, and cosmetics [2], as biological stains [3], and as anti-infective, antimicrobial and anthelmintic agents [1]. They have also been employed for in vitro cleansing of blood from flagellate parasites such as *Trypanosoma cruzi* [4], in application of dye-assisted laser inactivation of enzymes [5–7] and several of them are presently under investigation for use in photochemotherapy of neoplastic diseases [8–14]. The effect of molecular structure and symmetry on the electronic spectra of cationic triarylmethanes (TAM$^+$) in solution has been under investigation and debate for more than five decades, since Lewis and co-workers [15,16] hypothesized the existence of two ground-state

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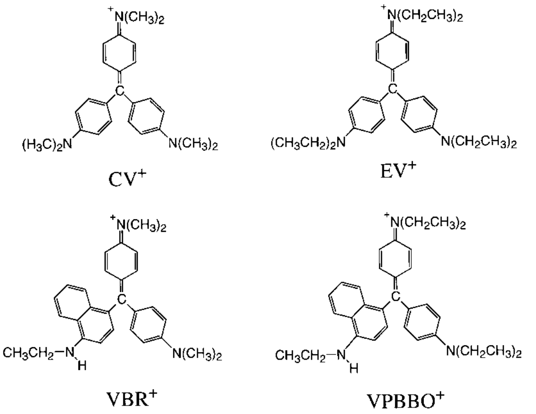

Fig. 1. Triarylmethane dye cations involved in this study.

rotational isomers in rapid equilibrium with one another to explain the appearance of a shoulder in the short-wavelength side of the maximum absorption band of Crystal Violet (CV^+) in ethanol. The structure of CV^+ and other TAM^+ dyes resembles a three blade propeller (Fig. 1) in which the aromatic blades are forced out of the molecular plane that contains the central carbon atom as consequence of steric restrictions. The Lewis model proposes the existence of one rotamer in which all blades rotate in the same direction in equilibrium with another rotamer in which one of the aromatic rings rotates in opposite direction with respect to the rotation of the other two aromatic rings. However, the absorption spectrum of CV^+ in ethanol has been alternatively rationalized in terms of the occurrence of specific interactions of the CV^+ cation with the solvent molecules [17,18] and the existence of solvated isomers instead of rotational isomers in solution [19,20]. In this last case, a rapid equilibrium between a planar and a pyramidal isomer controlled by specific solute–solvent interactions would be the reason for the appearance of the shoulder in the absorption spectrum of CV^+ in ethanol. Here we compare solvent effects on the spectroscopic characteristics of two highly symmetrical TAM^+ dyes, CV^+ and Ethyl Violet (EV^+), with those of other representative TAM^+ dyes displaying lower symmetry, Victoria Blue R (VBR^+) and Victoria Pure Blue BO ($VPBBO^+$). A comprehensive list of extinction coefficients for these four TAM^+ dyes in all solvents investigated is also provided.

2. Materials and methods

Chloride salts of Ethyl Violet (EV^+), Victoria Blue R (VBR^+), Victoria Pure Blue BO ($VPBBO^+$) from Aldrich, and Crystal Violet (CV^+) from Sigma were recrystallized from methanol and dried under vacuum. The purity of recrystallized triarylmethanes was assessed by thin-layer chromatography (silica gel, methanol–acetic acid 95:5, v:v). Acetone, acetonitrile, methanol, and 1-propanol form Fisher, ethanol from AAPER Alcohol and Chemical Co., 2-propanol from Aldrich, 1-butanol from Mallinckrodt, and *t*-butanol from Baker were all of high purity grade and used as supplied. Water was distilled, deionized, and filtered prior to use (Millipore Milli-Q system; resistivity, 18 MΩ cm). The spectrophotometric studies were performed with a Shimadzu UV-2101PC spectrophotometer using cuvettes with either a 10 or 100 mm optical path length. The effects of the Kamlet–Tafts' solvent solvatochromic parameters π^*, α, and β [21] on the electronic spectra of TAM^+ dyes were analyzed in terms of the magnitude of the solvent-dependent splitting between two overlapped TAM^+ visible absorption bands observed in different media. The magnitude of splitting between overlapped electronic transitions was evaluated through the measurement of the difference in frequency ($\Delta\nu$) between the maximum and shoulder of the respective absorption band (or between two maxima for spectra showing better resolution). Accurate frequency values were taken from the first derivative of the electronic spectra, although the parameter $\Delta\nu$ represents a phenomenological (approximated) spectroscopic parameter rather than a precise difference in energy between two distinct vertical electronic transitions. Unless otherwise stated the measurements were carried out at 25°C.

3. Results

The spectral profile of TAM^+ dyes in different media is presented in Fig. 2. The overall observation was that for the symmetric dyes, CV^+ and EV^+, the solvent effect on the structure of the maximum absorption band was modest, while more pronounced effects were observed for the cases of VPBBO$^+$ and VBR$^+$. To facilitate visual inspection, the spectra shown in Fig. 1 represent solutions containing a different dye concentration for each specific solvent (1–5 μM range). Values of extinction coefficient at λ_{max} are given in Table 1. For VPBBO$^+$ and VBR$^+$, the splitting of a single well defined absorption maximum into two well defined maxima was observed upon going from aqueous to organic media, as can be clearly seen through the comparison of the electronic spectra of these dyes in water and in *t*-butanol (Fig. 2).

The absorption spectra of diluted solutions of the symmetrical tri-*para*-amino-substituted dyes CV$^+$ and EV$^+$ display a characteristic shoulder on the short-wavelength side of the visible absorption band. The difference in frequency between the maximum absorption and the shoulder's inflection point (Δv; values in wavenumber taken from the first derivative of the electronic spectrum, see methods) tended to increase upon increasing solvent dipolarity/polarizability (π^* scale) and hydrogen-bond donor acidity (α scale), but with decreasing solvent hydrogen-bond acceptor basicity

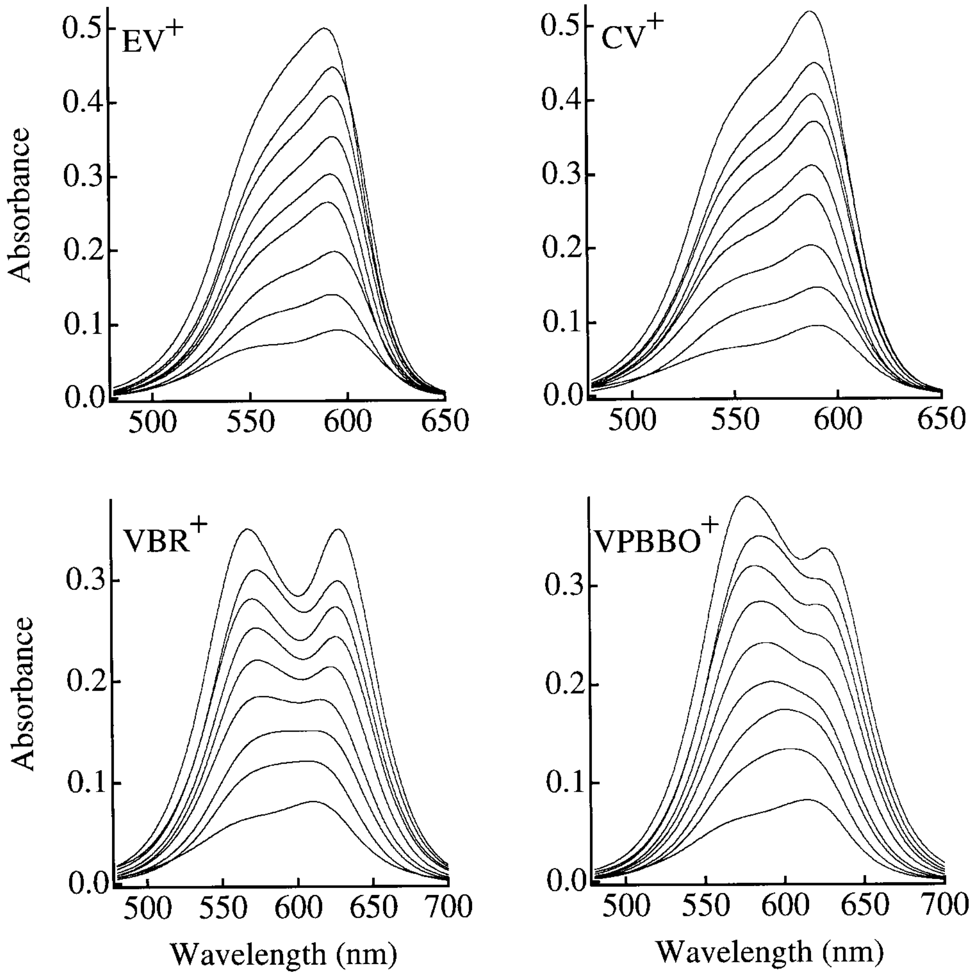

Fig. 2. Absorption spectra of EV$^+$, CV$^+$, VBR$^+$, and VPBBO$^+$ in different solvents. From the bottom of each panel the solvents and dye concentrations (in micromolar units) were water (1.0), acetonitrile (1.5), acetone (2.0), methanol (2.5), ethanol (3.0), 1-propanol (3.5), 2-propanol (4.0), 1-butanol (4.5), and *t*-butanol (5.0).

Table 1
Solvent effects on spectroscopic parameters of TAM$^+$ dyes[a]

				λ_{max} (nm) [$\varepsilon_{max}\times 10^{-4}$ (M^{-1} cm^{-1})]			
Solvent	π^*	α	β	EV$^+$	CV$^+$	VBR$^+$	VPBBO$^+$
Water	1.09	1.17	0.18	595(9.2)	590(9.5)	611(8.1)	614(8.3)
Acetonitrile	0.75	0.19	0.31	592(9.4)	588(9.8)	607(8.1)	604(9.0)
Acetone	0.71	0.08	0.48	593(9.9)	590(10.2)	611(7.6)	601(8.7)
Methanol	0.60	0.93	0.62	590(10.6)	586(10.9)	578(7.4)	592(8.8)
Ethanol	0.54	0.83	0.77	591(10.1)	589(10.4)	574(7.4)	589(8.1)
1-Propanol	0.52	0.78	–	592(10.1)	589(10.6)	573(7.2)	586(8.1)
2-Propanol	0.48	0.76	0.95	592(10.2)	588(10.2)	570(7.0)	582(8.0)
1-Butanol	0.47	0.79	0.88	593(9.9)	589(10.0)	573(7.1)	585(7.9)
t-Butanol	0.41	0.68	1.01	590(9.8)	588(10.4)	568(6.9)	578(7.5)

[a] Solvatochromic parameters (π^*, α and β values) from [21].

(β scale). Better linear relationships between $\Delta\nu$ and the Kamlet–Taft solvatochromic parameters π^*, α, and β [21] were obtained when taking into consideration only solvents of the same family, e.g. the C_1–C_4 alcohol series (Fig. 3). Water typically gave anomalous results with regard to the dominant linear trends observed for Δν as a function of the solvents' solvatochromic properties, while the non-hydroxylated solvents, acetone and acetonitrile, afforded a pronounced deviation when the dependence of $\Delta\nu$ on the hydrogen-bond donor acidity character (α scale) was taken into consideration. The behavior of acetone and acetonitrile is not surprising, since these two solvents can not act as proton donors in solvent-to-solute hydrogen-bond interactions. The dominant trends observed for the solvent effect on the absorption spectra of VPBBO$^+$ and VBR$^+$ (Fig. 4) exhibited opposite character as compared to those noticed for the cases of CV$^+$ and EV$^+$ (Fig. 3). For the Victoria Blue dyes, the dominant trend was clearly characterized by a *decrease* in $\Delta\nu$ upon increasing π^* and α, and decreasing β (Fig. 4).

All triarylmethanes considered in this investigation are known to form dye aggregates in aqueous media upon increasing dye concentration [22]. The formation of these aggregates is attested by the appearance of a hypsochromically shifted absorption band that overlaps with the spectral shoulder of the respective dye monomer observed in diluted solutions [23]. For example, the formation of EV$^+$ and VPBBO$^+$ aggregates in water can be easily characterized in 30 μM solutions, since the shoulder at the short-wavelength side of the maximum absorption band becomes slightly more prominent in 30 μM solutions than in more dilute solutions (e.g. 10 μM). That is, the $A_{max}/A_{shoulder}$ ratio decreases upon increasing dye concentration in the concentration range in which dye aggregation takes place. For dilute aqueous solutions of these TAM$^+$ dyes (ca. 5 μM and lower) the $A_{max}/A_{shoulder}$ ratio is constant, and the normalized spectra of dilute solutions containing different concentrations are identical. Identical normalized spectra (or constant $A_{max}/A_{shoulder}$ ratio) indicate that below the 5 μM concentration range dye aggregation does not occur to any detectable extent in pure water.

We have carried out a series of control experiments designed to explore the possibility that the formation of dye aggregates might explain, at least in part, the pronounced spectral changes observed for the cases of VBR$^+$ and VPBBO$^+$ as a function of the nature of the solvent. One set of experiments was carried out using 10, 1.0, and 0.1 μM solutions of VBR$^+$ in 1-propanol, 2-propanol, and 1-butanol and of VPBBO$^+$ in 1-propanol and 1-butanol. The normalized spectra of the different VBR$^+$ and VPBBO$^+$ solutions in the individual solvents showed exactly the same spectral profile. These results indicate that dye aggregation does not contribute to a measurable extent to the spectral changes observed in VBR$^+$ and VPBBO$^+$ solutions upon changing from aqueous to organic

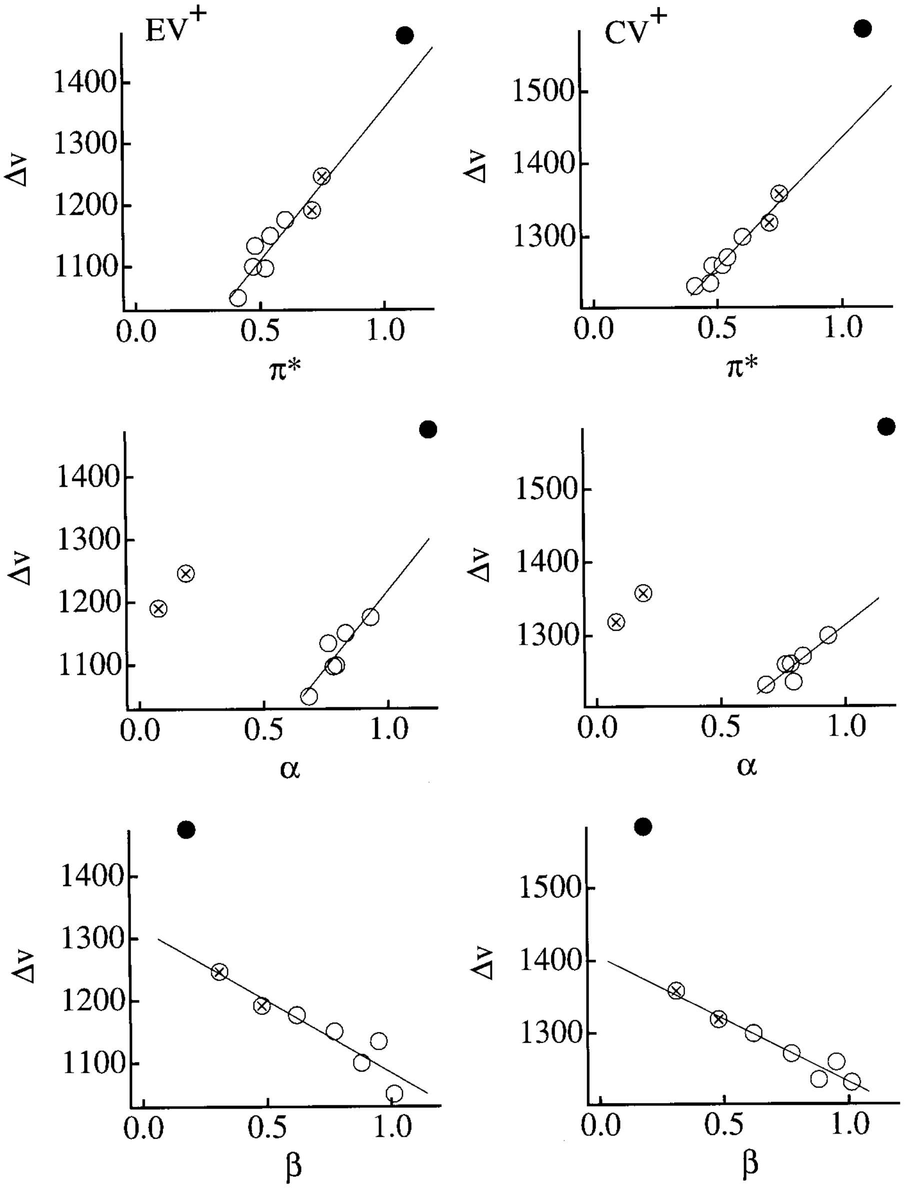

Fig. 3. Solvatochromic effects on the magnitude of the splitting ($\Delta\nu$) between the overlapping absorption bands of EV^+ (left column) and CV^+ (right column) in polar solvents. Empty circles, C_1–C_4 alcohol series; full circle, water; crossed circles, acetone and acetonitrile.

media. Other evidence that supports the hypothesis that dye aggregation does not account for the solvent effects observed with VBR^+ and $VPBBO^+$ was obtained by studying the effect of temperature (5–50°C) on the absorption spectra of 10 and 1.0 μM solutions of VBR^+ in 2-propanol and of $VPBBO^+$ in 1-propanol and 1-butanol. The normalized spectra acquired at different temperatures did not support the formation of VBR^+ and $VPBBO^+$ aggregates in organic media as the cause of the spectral changes observed upon switching from aqueous to organic media.

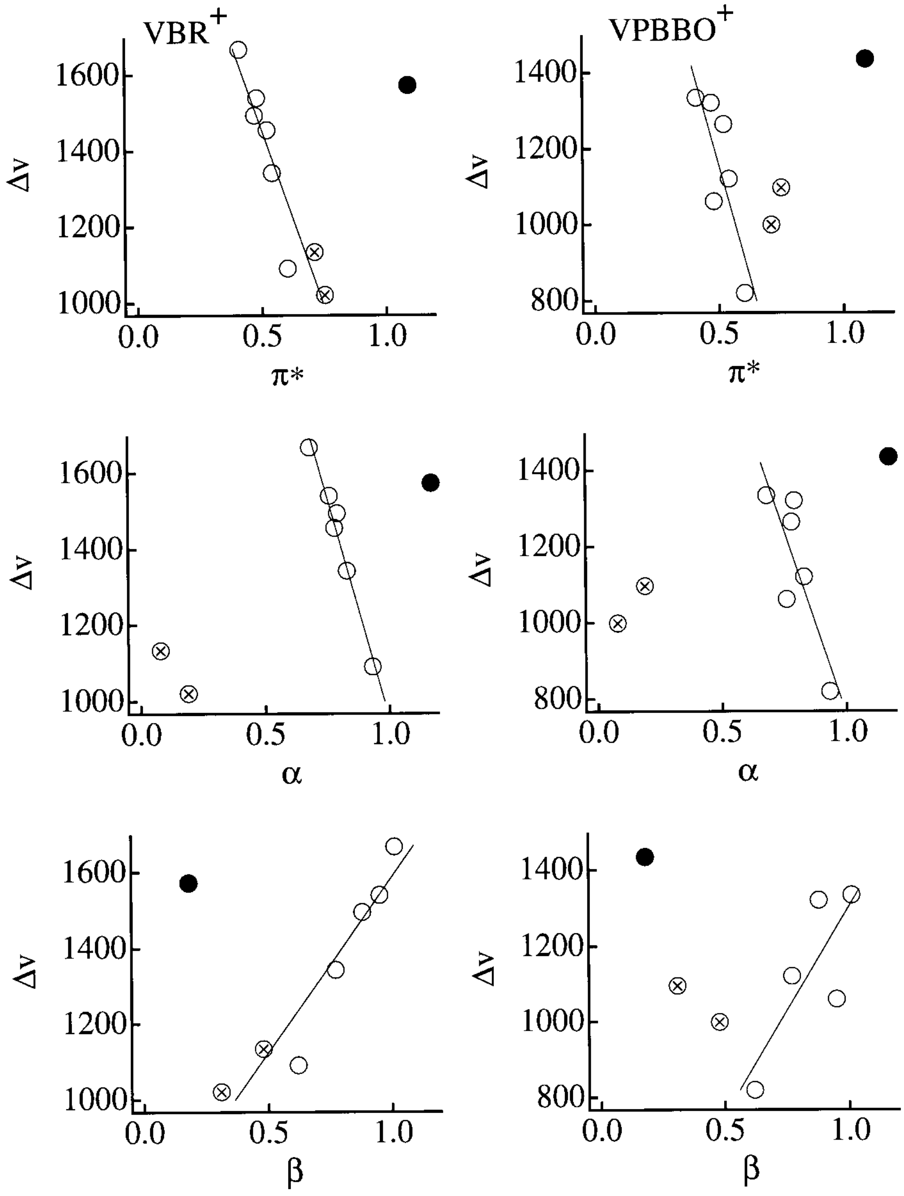

Fig. 4. Solvatochromic effects on the magnitude of the splitting ($\Delta\nu$) between the overlapping absorption bands of VBR$^+$ (left column) and VPBBO$^+$ (right column) in polar solvents. Empty circles, C_1–C_4 alcohol series; full circle, water; crossed circles, acetone and acetonitrile. The poor resolution of the absorption spectra of VPBBO$^+$ in acetone and acetonitrile did not permit the accurate characterization of $\Delta\nu$ for this dye in these solvents.

4. Discussion

Lewis et al. proposed the existence of two CV$^+$ ground state rotational isomers in rapid equilibrium with each other to explain the absorption spectrum of this dye in ethanol. The key observation was that as the temperature was lowered, the 550 nm shoulder in the CV$^+$ absorption spectrum began to disappear, while the intensity of the transition at the wavelength of maximum absorption

(589 nm) increased. This fact rules out the interpretation that the band structure of CV^+ in ethanol represents a partially resolved Franck–Condon progression of a single electronic state. The observed temperature dependence was originally interpreted by Lewis and co-workers as the result of a shift in the equilibrium between two rotational isomers present in solution, in favor of the lower-energy species as the temperature was lowered [15,16].

Due to steric restrictions, the aromatic rings of CV^+ and other cationic TAM^+ dyes are forced out of the molecular plane that contains the central carbon atom. The out-of-plane angle is modulated by both the repulsion between ortho-hydrogen atoms in adjacent aromatic rings and the restoration force that opposes rotation due to the double bond character of the twisted chemical bond. In the case of symmetrical molecules, such as the tri-para-amino-substituted CV^+, the repulsive and restorative forces acting on each distinct ring are expected to be equivalent [15,17]. When the aromatic rings rotate in the same direction and the angles between them are held constant, the resulting three blade propeller has D_3 symmetry. Within the Hückel approximation, the D_3 symmetry gives rise to a doubly degenerate lowest excited state [17,18]. Therefore, the overlapped doublet observed in the absorption spectrum of CV^+ in ethanol can be caused either by the presence of two rotational isomers in equilibrium, or by a solvent-perturbed single CV^+ propeller with symmetry lower than D_3 (giving rise to two nondegenerate states). The model originally developed by Lewis et al. [15,16] proposes the existence of a rotational isomer of CV^+ that is generated when one of its aromatic rings rotates in the opposite direction with respect to the other two rings. This unsymmetrical propeller is represented by a C_2 point group [17,18,24], and because of the nature of the restorative force that opposes the out-of-plane rotation of the aromatic rings, the unsymmetrical rotamer is expected to have higher energy than its symmetrical counterpart. Therefore, the rotamers model predicts that with decreasing temperature, the equilibrium between the two rotamers is shifted in favor of the symmetrical (D_3) species (the species responsible for the stronger absorption band in the visible).

Lewis' rotamers model has faced several objections over the years. As observed by Korppi-Tommola and Yip [17], no significant change in the absorption spectra of CV^+ in toluene takes place over the temperature range of +46–50°C, while in methanol the shoulder in the 550 nm region decreases with decreasing temperature, and practically disappears at $-70°C$. These authors suggest that their observations contradict the basis for the rotamers model, since there would be no reason why the equilibrium between the two rotamers would be significantly less temperature dependent in toluene than in methanol. They explain the effect observed in methanol in terms of changes in solvation of CV^+ with temperature. Because methanol tends to self-associate in solution, with decreasing temperature the number of monomeric solvent molecules present in neat methanol also decreases [25]. Following the model of Korppi-Tommola and Yip, if it is assumed that the solvation of CV^+ involves the interaction between dye and methanol monomers, reducing the temperature would decrease the number of solvent molecules capable of solvating CV^+. Eventually, at sufficiently low temperatures, the dye molecule would be "isolated" inside a solvent cavity. The degenerate lower electronic excited states of this "isolated" dye would not be disturbed, in keeping with the observation of practically only one absorption component in the visible region at low temperature. Therefore, the model of Korppi-Tommola and Yip explains the spectroscopic behavior of CV^+ in solution in terms of solvation rather than the hypothetical existence of two rotational isomers in solution.

Lueck et al. also presented results that do not support the rotamers model [18]. Based on semi-empirical molecular orbital calculations carried out using the intermediate neglect of differential overlap (INDO) method, these authors pointed out that the barrier separating the two rotamers is large compared to kT at room temperature. This suggests that it is unlikely that the shoulder observed in the absorption spectra of CV^+ in ethanol can be explained in terms of the presence of the unsymmetrical propeller in solution. Based on a combination of experimental measurements and theoretical calculations, the authors suggested that a solvent-induced symmetry-breaking process may be the cause of the appearance of the overlapped bands in the absorption spectra of CV^+. The proposed model explores the possibility that the loss in degeneracy of the symmetrical D_3 propeller can be produced by the electronic perturbation introduced by a solvent molecule located near one of the amino groups, or by the stabilization of the positive charge in one of the amino groups via a specific interaction with a solvent molecule. In this last case, in terms of resonance structures the amino group which accommo-dates the positive charge would be forced to assume a planar geometry while the other two amino groups would retain the tetrahedral configuration, and this solvent-induced difference in amino group configuration is a symmetry-breaking event.

The experimental results presented in the present paper add momentum to previous objections to the rotamers model, since they indicate that the magnitude of the splitting between the overlapped absorption bands of the highly symmetrical TAM^+ dyes CV^+ and EV^+ is dependent upon solvent solvatochromic parameters. However, since multiple interacting solvent effects may be taking place simultaneously, only qualitative comments can be drawn based on the data shown in Fig. 3. Accordingly, since the π^* scale represents an index of the ability of the solvent to stabilize a dipole or charge due to its dielectric effect [21], the observed increase in $\Delta\nu$ upon increasing π^* is consistent with the hypothesis that an electronic rather than a mechanical perturbation is responsible for the loss in degeneracy of the symmetric D_3 propeller [18]. Besides, the results of semi-empirical molecular orbital calculations carried out by Lueck et al. have indicated that the stronger the dipole located near one of the amino groups of the D_3 propeller the larger the expected splitting between its overlapping bands [18]. This theoretical prediction is in agreement with our experimental data. The linear relationships observed between $\Delta\nu$ and the solvatochromic parameters β and α further emphasizes the solvation dependence of the spectroscopic behavior of CV^+ and EV^+ in condensed phase. Although it is not clear why the data obtained in water typically display anomalous characteristics, the deviations observed in acetone and acetonitrile arise from the fact that these two solvents do not function as proton donors in solvent–solute interactions. More recently Ishikawa et al. [20] have reported a model to explain the absorption spectra of CV^+ in methanol and other alcohols in which they hypothesize the existence of two solvation isomers in fast equilibrium with one another. In this model the symmetric (D_3) propeller is thought to be in equilibrium with a pyramidal (C_3) isomer formed when the central carbon atom is strongly solvated with an alcohol molecule.

4.1. The spectroscopic behavior of VBR^+ and $VPBBO^+$ in solution

The lower energy levels of the TAM^+ dyes displaying lower molecular symmetry, VBR^+ and $VPBBO^+$, are not degenerate. Consequently, these dyes are expected to display relatively well resolved $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ absorption bands in solution. Indeed, the presence of two well defined absorption bands was readily noticed in the electronic spectra of VBR^+ and $VPBBO^+$ in the C_1–C_4 alcohol series, although the resolution of these bands was diminished in the other solvents considered in this study (Fig. 2). The experiments carried out to explore the effects of dye concentration and temperature on the electronic spectra of VBR^+ and $VPBBO^+$ performed in a variety of solvents have clearly indicated that, within the concentration range investigated, the spectroscopic doublet observed in the electronic spectra of the Victoria Blue dyes cannot be attributed to the formation of dye aggregates in solution. Since the occurrence of aggregation can be easily characterized in water but not in the alcohols investigated herein, the hydrophobic effect can be hypothesized to play an important role in the aggregation phenomena. However, we have also observed that the spectral profiles of VBR^+ and $VPBBO^+$ are concentration dependent in chloroform (1–10 μM range), which is evidence for the formation of dye aggregates in that solvent. As previously reported [23], while the aggregation of tri-*para*-amino substituted dyes is readily observed in aqueous media, the bi-*para*-amino substituted

TAM$^+$ dye Malachite Green (*N,N,N',N'*-tetramethylpararosaniline) does not undergo aggregation to a significant extent in water. These observations indicate that the hydrophobic effect is not the only thermodynamic parameter controlling the aggregation phenomena, and that the contribution of structure to TAM$^+$ aggregation is not completely understood [22,23].

Since the intensity of the overlapping visible electronic transitions in VBR$^+$ and VPBBO$^+$ observed at shorter wavelengths does not increase upon increasing the temperature from 5 to 50°C, their band structures can not be attributed to partially resolved Franck–Condon progressions within single electronic states. Interestingly, as indicated by the difference in frequency between the maximum absorption the two overlapping bands ($\Delta\nu$) as a function of π^*, α, and β, the dominant trends observed for the effects of solvents on the absorption spectra of VPBBO$^+$ and VBR$^+$ exhibit behavior that is opposite of that observed for the highly symmetrical CV$^+$ and EV$^+$ (compare Fig. 3 with Fig. 4). While for EV$^+$ and CV$^+$, $\Delta\nu$ typically increased with increasing π^* and α and decreasing β, in the case of the Victoria Blue dyes, $\Delta\nu$ tended to decrease upon increasing π^* and α and decreasing β. Although this behavior may not represent a general observation, for the TAM$^+$ dyes investigated here, the effect of solvent properties on $\Delta\nu$ can be used to characterize of the nature of the overlapping visible absorption bands.

The question of how molecular symmetry considerations can be combined with other structural aspects of triarylmethanes to allow the prediction of some of the characteristics of the electronic spectra of this class of compounds is a matter of substantial interest. A pertinent observation follows. While the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions in *t*-butanol are well separated in the case of Malachite Green (maxima at 622 nm and 429 nm, respectively), they appear as overlapping bands in VBR$^+$ and VPBBO$^+$. Apparently, for these three compounds the availability (or lack thereof) of the third amino group in the *para*-position of the aromatic rings is an important factor with regard to the control of the energy gap between the first two excited singlet states in these dyes.

5. Concluding remarks

The observed solvent-dependence on the magnitude of the splitting between the overlapping absorption bands indicates that the occurrence of specific interactions involving the TAM$^+$ dyes and the solvent molecules is the event that lowers the symmetry of the D_3 propeller, giving rise to two nondegenerate states or two solvation isomers. The observed solvent effects on the absorption spectra of the TAM$^+$ dyes displaying lower symmetry, VBR$^+$ and VPBBO$^+$, are distinct from those observed for CV$^+$ and EV$^+$, because the nature of the overlapped absorption bands is different in these two distinct sets of TAM$^+$ dyes. The difference in energy between the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic transitions in the non-symmetrical TAM$^+$ molecules is apparently strongly dependent upon the number of amino groups in the *para* position of the aromatic rings, since the lack of one amino group in Malachite Green leads to a much large splitting between these transitions than those observed in the case of VBR$^+$ and VPBBO$^+$.

Acknowledgements

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