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Relationship between the Molecular Structure of Merocyanine Dyes and the Vibrational Fine Structure of Their Electronic Absorption Spectra

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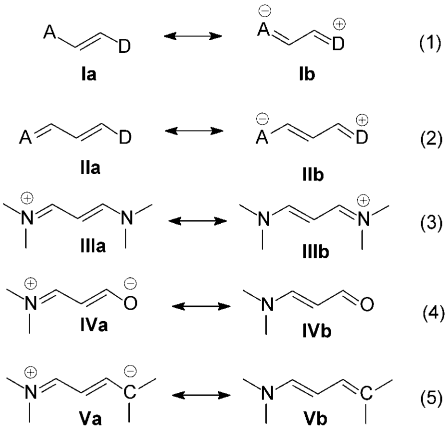
Merocyanines are of widespread interest for different applications[1–5] and have attracted considerable attention owing to their intense absorption bands and the outstanding sensitivity of these bands to solvents. The solvent sensitivity of the absorption bands is discussed in terms of a simple valence bond (VB) model, which assumes that the electronic ground (S_0) and excited state (S_1) of merocyanines can be approximated as a linear combination of a non-charge-separated polyene-like and a charge-separated polyene-like limiting form.[1–6] The net balance is influenced by the nature of the solvent, passing through the "cyanine limit". Several parameters have been suggested for quantifying the contribution of the two limiting forms to the equilibrium structure of the ground state. The concepts of the average bond-length alternation (BLA),[7] and the closely related average π-bond order alternation (BOA),[8] between adjacent bonds in the hydrocarbon chain are most popular.[4,6,9–12] Surprisingly, within the same concept merocyanines have been described by two quite different models, namely Equations (1),[7a,c,8b,c] and (2),[7b,8a] in which A (electron acceptor) and D (electron donor) are capable of charge exchange. Polymethines are characterized by a chain of conjugated double bonds with an odd number n of π centers and $(n+1)$ π electrons, whereas polyenes are characterized by an even number of π centers and the same number of π electrons. Therefore, polyenes and polymethines differ considerably in electronic structure and light absorption,[1–6] and, consequently, polymethines cannot be viewed as acceptor/donor-substituted polyenes. Equation (1) describes two possible limiting forms of acceptor/donor-substituted polyenes and, therefore, cannot be used for merocyanines. Equation (2) represents polymethines; $A=N^{(+)}$ and $D=N$ corresponds to a cyanine [Eq. (3)], $A=O$ and $D=O^{(-)}$ to an oxonole, and $A=N^{(+)}$ and $D=O^{(-)}$ or $A=N^{(+)}$ and $D=C^{(-)}$ to merocyanines [Eqs. (4) and (5)]. The structure labeled **b** in Equations (4) and (5) do not represent polyene-like forms as often claimed,[4,6,9–12] but are equivalent to structure **b** in Equation (3) for cyanines and are polymethines.



We have shown recently that the VB model with the two equivalent limiting forms is an oversimplification for the description of symmetrical cyanines.[13] To test our theoretical understanding further, it is important to establish whether the electronic structures of merocyanines can be adequately described with two limiting forms.

Recently, it was reported that all five spin–spin coupling constants ^3J(H,H) along the hydrocarbon chain of **1a** in [D$_6$]DMSO are equal, whereas in $CDCl_3$ they are markedly different.[12] From these results and observations of solvent effects in the electronic absorption spectra it was concluded that a "polymethine state" dominates in polar solvents and a "polyene state" in less polar solvents. As polyenes and polymethines differ in their electronic structure, and thus a switch between states is not possible, this conclusion cannot be correct. Our own measurements of **1a** do not confirm equal ^3J(H,H) values in [D$_6$]DMSO.[14] Because of the low solubility of **1a** in low-polarity solvents, it is difficult to study NMR spectra as a function of solvent polarity, and thus we synthesized the more soluble dye **1b**. We were then able to measure the NMR spectra of **1b** in [D$_6$]DMSO as well as in CD_2Cl_2 and [D$_8$]-1,4-dioxane. The ^3J(H,H) values in these solvents are presented in Table 1.

According to the simple VB model, the electronic structure of the ground state of **1** can be represented by

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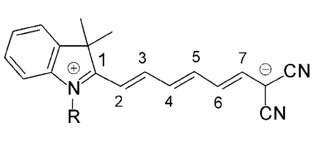
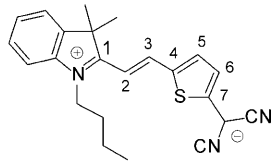
Table 1: ^3J(H,H) coupling constants of the H atoms of the polymethine chain in **1b** and **2**.

Bond	^3J(H,H) [Hz] [D$_6$]DMSO **1b**	^3J(H,H) [Hz] [D$_6$]DMSO **2**	^3J(H,H) [Hz] CD$_2$Cl$_2$ **1b**	^3J(H,H) [Hz] CD$_2$Cl$_2$ **2**	^3J(H,H) [Hz] [D$_8$]-1,4-dioxane **1b**	^3J(H,H) [Hz] [D$_8$]-1,4-dioxane **2**[a]
2–3	12.9	14.0	12.8	13.3	12.6	–
3–4	13.1	–	13.3	–	13.6	–
4–5	12.6	–	12.0	–	11.7	–
5–6	13.1	–	13.4	–	13.8	–
6–7	12.4	–	12.3	–	12.1	–

[a] Not sufficiently soluble for NMR measurement.

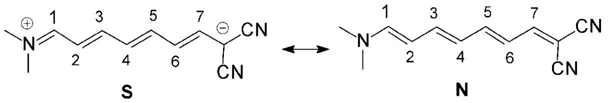


1a R = Me
1b R = *n*Bu



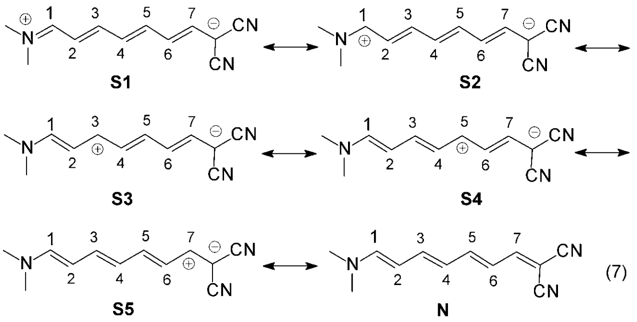
2

different contributions of the charge-separated limiting form **S** and the non-charge-separated limiting form **N** [Eq. (6)]. It is generally assumed that polar solvents stabilize charge separation and would hence increase the contribution of **S** to the ground state. All five coupling constants ^3J(H,H) along the hydrocarbon chain seem to provide evidence for support of this assumption. With increasing polarity of the solvent, the ^3J(H,H) values of bonds 2–3, 4–5, and 6–7 increase, whereas those of bonds 3–4 and 5–6 decrease.



(6)

The general weak point in this approach is that it is limited to consideration of the bond-length changes only. Cyanines and merocyanines are also characterized by alternating π-charge densities along the hydrocarbon chain, as shown experimentally by variations of their chemical shifts in the ^{13}C NMR spectra.[1–6] The simple VB model cannot account for the alternating π- charge densities in the chain! In a complete VB treatment all limiting forms would be considered. Developing a model with minimum complexity, Pauling, Herzfeld, and Sklar considered the resonance of a positive charge throughout the whole chain between A and D, that is, taking into account all limiting forms with a positively charged carbon atom in the chain [Eq. (7)].[15]



(7)

According to this model, with increasing polarity of the solvent the contribution of all charge-separated limiting forms **S1**–**S5** to S$_0$ increases, whereas that of **N** decreases; in other words, the various limiting forms tend to contribute more equally to S$_0$. Experimental data derived from NMR spectroscopy confirm these predictions. The shifting of the methanide carbanion signal from $\delta = 74.5$ ppm in [D$_8$]-1,4-dioxane to $\delta = 66.2$ ppm in [D$_6$]DMSO indicates a reduced contribution of **N** in polar solvents. The δ values within the carbon chain of **1b** (see Table S1 in the Supporting Information) can be explained by invoking variable contributions of the limiting forms **S1**–**S5** and **N**. The absolute value of the difference in δ values between adjacent C atoms in the hydrocarbon chain ($\Delta\delta = |\delta_i - \delta_{i+1}|$) is a measure of π- charge density alternation. With increasing polarity of the solvent, $\Delta\delta$ increases (see Table S2 in the Supporting Information). The difference between CH=CH and CH−CH average coupling constants (ΔJ) was suggested for an estimation of BLA in solution.[7a] For the alternating diene *trans*-butadiene with an even number of carbon atoms ^3J(H,H) was determined to 17.1 Hz (CH=CH) and 10.4 Hz (CH−CH),[16] and $\Delta J = 6.7$ Hz. For **1b** ΔJ is 1.6 Hz in 1,4-dioxane and drops to 1.0 Hz in CH$_2$Cl$_2$ and 0.5 Hz in DMSO; that is, in **1b** bond-length alternation decreases with increasing polarity of the solvent, but there is no change from a "polyene state" to a "polymethine state".

The VB approach with two limiting forms is very popular for the interpretation of solvent effects on the electronic absorption spectra of merocyanines.[1–12] The weak point in these discussions lies in the fact that the easily measured and most often recorded solvent effect is the shift of the absorption maximum λ_{max}. However, theoretical considerations of electronic energy states should be related to the shift of the 0–0 band, which is not necessarily affected in the same way as λ_{max}. It is incorrect to use λ_{max} to analyze the solvent effects of compounds, which present in some circumstances structured absorption bands. First, one has to analyze the solvent influences on the structure of the absorption band. The electronic absorption spectra of cyanines and some merocyanines show prominent short-wavelength subbands, attributed to the totally symmetric C=C valence vibration of the chain in S$_1$ (see reference [13] and references therein). After light absorption the electron in the antibonding orbital weakens the bonds in S$_1$, and, therefore, the equilibrium bond lengths in the electronic excited state R_e(S$_1$) are larger in comparison to those in the ground state R_e(S$_0$). Decreasing bond alternation in the ground state results in smaller changes of R_e(S$_1$) in comparison with R_e(S$_0$), that is, low slope on both the ground- and excited-state Morse curves. Then, according to the Franck–Condon principle, the intensity of the absorption band will be concentrated in the 0–0 at the expense of the higher 0–v' vibronic transitions. Conversely, solvent-induced increasing bond alternation in S$_0$ of **1b** should increase the intensity of the 0–v' at the expense of the 0–0 transition. Compound **1b** exhibits the lowest ΔJ value in [D$_6$]DMSO, indicating that it has the lowest bond alternation in S$_0$ in DMSO and the absorption band shows a well-resolved vibrational structure (Figure 1). However, in low-polarity solvents the vibrational structure is less defined, and a hypsochromic shift of λ_{max} (relative to that in DMSO) is observed in these solvents, which can be due to higher 0–ν' transitions. Unfortunately the spectral evidence is not clear.

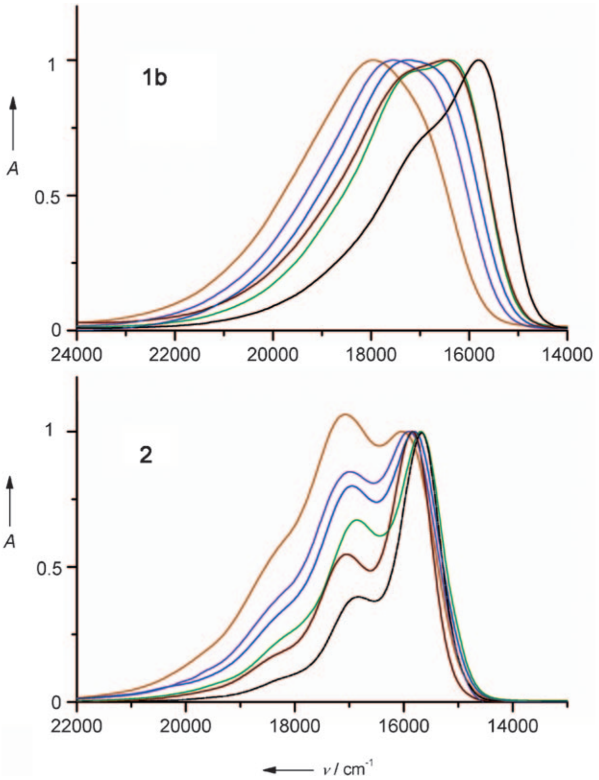


Figure 1. Normalized absorption spectra of the merocyanines **1b** and **2** in DMSO (black), acetone (red), CH_2Cl_2 (green), THF (light blue), ethyl acetate (dark blue), and 1,4-dioxane (orange).

To overcome this problem, we have designed the new merocyanine **2** whose absorption spectrum does not lose its vibrational fine structure in a wide range of solvents. As shown by the δ values (see Table S1 in the Supporting Information), increasing solvent polarity increases the contribution of the charge-separated limiting forms to the electronic ground state, which leads to an increased π-charge density alternation (see Table S2 in the Supporting Information). In a similar manner to **1b** the ^3J(H,H) values of bond 2–3 in **2** indicate reduced bond-length alternation in polar solvents (Table 1). Therefore, in DMSO dye **2** exhibits the highest relative intensity of the 0–0 subband and in 1,4-dioxane the lowest. Thus, we are able to demonstrate with **2** that the ratio of the intensity of the 0–1 subband relative to the 0–0 subband reflects the solvent-induced bond-length alternation in the ground state, and it is more likely that the hypsochromic shift of the absorption band of **1b** in low-polarity solvents is due to higher 0–ν' transitions.

In conclusion, we have shown that the electronic structure of the merocyanines cannot be adequately described by a linear combination of the two limiting forms **N** and **S**. The alternating π-charge densities in the chain can be described only by taking into account all limiting forms with a positively charged carbon atom in the polymethine chain. Moreover, we have provided a new theoretical model for understanding solvent effects on electronic absorption spectra of merocyanines.

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