

Relationship between the Molecular Structure of Cyanine Dyes and the Vibrational Fine Structure of their Electronic Absorption Spectra

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Dedicated to Professor Joachim Sauer on the occasion of his 60th birthday

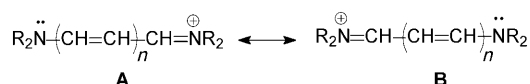
Electronic absorption spectra of symmetrical cyanine dyes show vibronic sub-bands, attributed to the symmetric C–C valence vibration of the polymethine chain in the electronic excited state. Displacements in the equilibrium configuration between electronic ground and excited states of cyanine dyes lead to longer C–C bonds in the excited state. Additionally, in the electronic ground state, a small degree of bond localisation

always remains in the chain depending on the different heterocyclic terminal groups. Our investigations suggest that we can use ³J(H,H) coupling constants in the polymethine chain to characterise the bond localisation within the chain. Based on these values and the Franck–Condon principle, the intensity distribution among the vibrational sub-bands can be explained.

1. Introduction

In addition to the prospect of advanced technical applications,^[1–7] cyanine dyes also provide an ideal model for advancing and testing our theoretical understanding of the electronic structure of conjugated systems.^[8–10] For special applications in advanced technologies, colour filters with small absorption bands are required. However, the electronic absorption spectra of cyanine dyes show prominent short-wavelength sub-bands, attributed to vibronic transitions associated with the long-wavelength electronic transition.^[11–18]

On the other hand, the most widely used model of the “cyanine limit”^[19] leads to the conclusion that in the absorption spectra of symmetrical cyanine dyes only the 0–0 transition should be observed, and thus it offers, at least theoretically, the possibility to obtain spectra without any additional vibrational band. The Dähne model of the ideal cyanine state assumes perfectly uniform delocalisation of the π electrons over the whole π system, leading to 1) alternating π -electron densities and 2) equal π -bond orders in the ground state.^[20] Based thereon, Marder et al. assumed that due to the absence of bond localisation, C–C bond lengths are all the same in both the ground and excited states and thus should not change on excitation (the so-called “cyanine limit”).^[19] These considerations are based on a valence-bond model with only the two equivalent limiting forms **A** and **B**.^[6–10] According to this, a



symmetrical cyanine dye can be represented as a linear combination of **A** and **B**. The coefficient c in Equations (1) and (2) in-

dicates the relative contributions of the two equivalent limiting forms to the electronic ground (S_0) and excited state (S_1) and $c^2=0.5$ represents an equal contribution of **A** and **B** to the electronic ground and excited states, which results in equal π -bond orders in both states:

$$\Psi(S_0) = c\psi_A - \sqrt{1 - c^2}\psi_B \quad (1)$$

$$\Psi(S_1) = \sqrt{1 - c^2}\psi_A + c\psi_B \quad (2)$$

The intensity distribution among the vibrational sub-bands can be explained by the Franck–Condon principle. According to this, during electronic excitation there is no change in the internuclear geometry, and thus light absorption involves so-called “vertical transitions”. The concept of vertical transitions can then be used in conjunction with the wavefunctions for the different vibrational states to predict the probability of a vibronic transition. Application of the Franck–Condon principle is most simply illustrated by examining a diatomic molecule. The potential energy of a diatomic molecule as a function of the bond length R can be approximated by a Morse curve. The value of R at the minimum of the Morse curve is the equilibrium bond length R_e . In general, the potential energy curve for the electronic excited state $R_e(S_1)$ will be displaced relative to

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the curve for the ground state $R_e(S_0)$. However, if the electronic ground and excited states have exactly the same equilibrium bond lengths, that is, $R_e(S_0) = R_e(S_1)$, the most probable transition will obviously be the 0–0 transition, as the wavefunctions for the two states will have maximum overlap. Under these circumstances, there should be no fluorescence Stokes shift. In addition, as the two electronic states have exactly the same potential energy curves, the vibrational functions of both states will be identical. Since the vibrational functions are orthogonal to one another, the overlap integral between the vibrational function of the electronic ground state ($v=0$) with any vibrational function of the S_1 state with $v' \geq 1$ will be zero, and thus, the electronic absorption band will consist only of the 0–0 transition. Therefore, the traditional cyanine-limit model would require that the visible absorption band of a symmetrical cyanine dye should be extremely sharp, consist only of the 0–0 transition, and should show no vibrational fine structure. Thus, the appearance of vibronic bands in the spectra of many symmetrical cyanine dyes is inconsistent with the cyanine-limit model. This prompted us to carry out a systematic investigation of the influence of molecular structure on the relative intensity of vibronic transitions in the electronic absorption spectra.

2. Origin of Vibrational Fine Structure

A prerequisite to this discussion is that the sub-bands seen in the absorption spectra of cyanine dyes should belong to the same electronic transition, and this has been confirmed by polarisation spectra.^[12] In addition, any vibrational fine structure observed in an absorption band must be due to vibrational modes active in the electronic excited state. To understand more fully the influence of structure on the intensity of these shorter wavelength sub-bands, one must determine the vibrational mode contributing to the observed vibronic transitions.

As discussed above, vibrational fine structure will only occur for a diatomic molecule if the equilibrium bond length $R_e(S_1)$ differs from $R_e(S_0)$. However, in a polyatomic molecule, the number of possible vibrations will be large ($3N-6$ or $3N-5$ for linear molecules), and each will involve changes in the size and the shape of the molecule. If the initial vibrational state ($v=0$) is totally symmetric, only a totally symmetric vibrational state will have a nonzero overlap integral with it; with any non-totally symmetric vibration, the overlap integral must be zero. Therefore, within a symmetry-allowed (intense) electronic transition in a polyatomic molecule, vibrations can appear as a progression only if the symmetry is the same in the excited state as in the ground state; that is, it can couple only with totally symmetric vibrations, which change the size but not the shape of the molecule, just as for a diatomic molecule. The concentration of intensity of absorption^[11–18] and fluorescence in the 0–0 vibronic band of cyanine dyes and the small Stokes shift of the fluorescence spectrum^[4,8,15,16] all serve to indicate that the shape of the molecule does not greatly change on excitation.

Furthermore, if many vibrational modes are connected with the electronic excited state of a polyatomic molecule, the vari-

ous progressions will overlap and the band envelope is then observed as a smooth absorption curve. Usually it is assumed that only if one unique vibrational mode is dominant in the excited state does vibrational structure become evident in the absorption band. In this case one must identify this vibration in order to discuss structural influences on the vibrational fine structure of the absorption spectra. Regarding this question, most experimental data pertain to pseudoisocyanine, whose absorption spectrum exhibits vibrational structure with a spacing of about 1375 cm^{-1} .^[12b] Resonance Raman spectroscopy has determined the vibrational mode frequency in the excited state to be 1365 cm^{-1} .^[13] Additionally, the vibrational quantum beat at 1310 cm^{-1} measured by femtosecond pump-probe spectra of the indotricarbocyanine HDITC supports this assignment.^[17] Thus, it can be safely assumed that the prominent progression of the absorption band of pseudoisocyanine is associated with a vibrational mode having a frequency of about 1370 cm^{-1} in the excited state. In support of this, it was found that a rigidised derivative of pseudoisocyanine exhibits an absorption band with a shape typical of pseudoisocyanine in general, but with better resolution of the vibrational structure. Here, the difference between the two vibrations was determined to be 1370 cm^{-1} .^[14] In the fluorescence spectrum a corresponding main progression appears in approximate mirror symmetry with a difference between the sub-bands of 1550 cm^{-1} .^[14,15] Thus, it was suggested that the vibrational mode of 1370 cm^{-1} in the excited state corresponds to the 1550 cm^{-1} vibrational mode in the ground state. This is an experimental hint that the equilibrium bond lengths in the excited electronic state differ from those of the ground state.

Moreover, some 90 different cyanines and merocyanines all show an energy spacing between their two sub-bands of $(1200 \pm 200) \text{ cm}^{-1}$.^[18] The vibrations are independent of the cyanine or merocyanine structure, which leads to the conclusion that these sub-bands arise from the totally symmetric C–C valence vibration of the polymethine chain in the electronic excited state.

All these observations are consistent with the following explanation for the vibronic fine structure: An observed sub-band is a vibronic transition from $v=0$ to v' , where v is the vibrational quantum number of the totally symmetric C–C valence vibration of the polymethine chain in the electronic ground state and v' is that in the electronic excited state. The intensity distribution among the vibrational sub-bands can then be explained by the Franck–Condon principle.

3. Results and Discussion

Within this framework, we synthesised a series of nine cyanine dyes 1–3 (Table 2) with absorption maxima ranging from 491 to 774 nm in dimethyl sulfoxide (DMSO, see Figure 1). In previously reported conformational studies, a value of $^3J(\text{H,H}) \approx 13 \text{ Hz}$ was taken to indicate quasi-planar all-*trans* cyanine dye structures.^[21–25] Protons at symmetry-related positions for the all-*trans* structure are equivalent, and all spin–spin coupling constants $^3J(\text{H,H})$ are in the range of 12.6 to 13.5 Hz (Table 1), representative of an all-*trans* configuration of the

lution it is not possible to measure the bond lengths within the polymethine chain in a direct way to obtain an indication of the bond localisation. However, NMR investigations and related quantum chemical calculations on a number of cyanines, merocyanines and polyenes have revealed an almost linear correlation between the $^3J(\text{H,H})$ coupling constants for *trans* vicinal protons in the polymethine chain and the C–C bond lengths or π -bond orders.^[12,31–33] Based on this relationship, we suggest to use the coupling constants for *trans* vicinal protons as an indication for bond localisation within the polymethine chain (Table 1).

Conjugated polyenes typically show marked bond alternation in the ground state with essentially single and double bonds. For butadiene, for example, $^3J(\text{H,H})$ was determined to be 17.1 Hz (alternating double bonds, *trans* coupling) and 10.4 Hz (single bond).^[34] Absorption spectra of most of the polyenes show a broad absorption band with low molar extinction coefficient and a very characteristic vibrational structure with a wavenumber spacing of the sub-band maxima of about $(1450 \pm 150) \text{ cm}^{-1}$, attributable to the totally symmetric C=C valence vibration of the polyene chain in the electronically excited state.^[35] On excitation of an electron, the π -bond order of double bonds in the excited state decreases substantially, and so the double bonds get longer. With such a large change in the C=C equilibrium bond lengths in the excited electronic state, that is, $R_e(S_0) \ll R_e(S_1)$, the absorption intensity is spread over higher members of the vibrational progression, and as a result, the absorption band is broad, the molar extinction coefficient is low and the absorption maximum is provided by a vibronic transition other than the 0–0 transition.

The appearance of vibronic bands in the spectra of many symmetrical cyanine dyes is consistent with the effect of an electron in an antibonding LUMO. In confirmation thereof, all quantum chemical calculations (PPP,^[8,27] all-valence-electron,^[8,28] and ab initio procedures^[8]) predict that within the polymethine chain all C–C bond lengths increase in the excited state. This is supported experimentally by the vibrational mode of 1370 cm^{-1} found in the excited state of a rigidified derivative of pseudoisocyanine, which corresponds to the 1550 cm^{-1} progression in the ground state found in the fluorescence spectrum.^[14,15]

Such a change in the molecular geometry of the excited state explains the appearance of vibronic sub-bands (Figure 1) and leads to the conclusion that cyanine-dye structures lacking such shorter wavelength sub-bands are not feasible, because it is not possible for C–C bond lengths to be identical in both the ground and excited states. However, there is no question that the symmetrical cyanines show much smaller changes in the equilibrium bond lengths on electronic excitation [$R_e(S_0) < R_e(S_1)$] compared to the polyenes, and as a consequence they have an absorption band with a higher molar extinction coefficient and narrower bandwidth, and the absorption intensity is largely concentrated in the 0–0 vibronic transition.

The absorption spectra in Figure 1 are normalised according to the 0–0 sub-band. The relative intensity ratio of 0–1 versus 0–0 sub-bands in the various cyanines 1–3 varies and depends on molecular structure. Dyes 1c, 1d, 2c, 2d and 3 exhibit the

smallest coupling constants (12.6–12.8 Hz) of all dyes (Table 1), which indicates that they have the lowest degree of bond localisation in the ground state. According to the Franck-Condon principle, the lower the degree of bond localisation in the polymethine chain in the ground state, the smaller the changes in the C–C equilibrium bond lengths in the excited state in favour of the 0–0 and at the expense the 0–1 transition. Consequently, in these cyanine dyes the intensity ratio I_{rel} of the 0–1 versus the 0–0 band is about 0.45 (Table 1). On the other hand, increasing the $^3J(\text{H,H})$ coupling constants corresponds to increasing the bond localisation in the ground state, which results in larger changes in the C–C equilibrium bond lengths in the excited state in favour of the 0–1 (and at the expense of the 0–0) transition, as shown by 1a, 1b, 2a and 2b (see Figure 1).

As illustrated in Figure 2, there is an evident relationship between the $^3J(\text{H,H})$ coupling constants and the intensity ratio of the 0–1 versus the 0–0 band. Thus, we are able to demonstrate that within a series of structurally related cyanine dyes, the intensity ratio of the 0–1 versus the 0–0 band reflects the bond localisation in the ground state. The applicability of this relationship to other dye classes is currently under investigation.

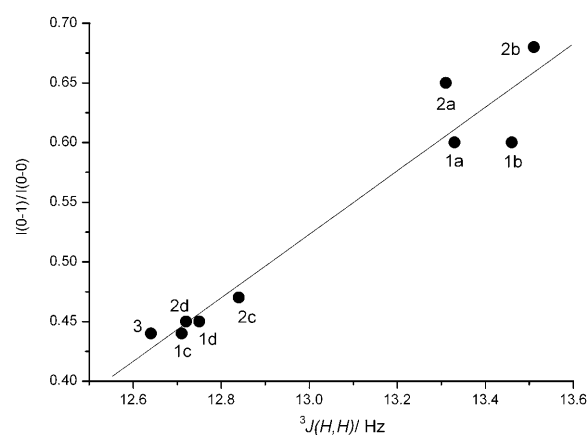


Figure 2. Relation between $^3J(\text{H,H})$ in $[\text{D}_6]\text{DMSO}$ and the relative intensity of the 0–1/0–0 sub-bands in DMSO.

4. Conclusions

The concept of resonance has been fundamental to our understanding of reactivity in conjugated systems. Based on the valence-bond model, resonance theory assumes that the electronic ground (S_0) and excited (S_1) states of cyanine dyes can be approximated as a linear combination of two equivalent limiting forms. The model of the “cyanine limit” assumes that the two equivalent limiting forms contribute equally to the electronic ground and excited states of cyanine dyes. This results automatically in equal π -bond orders in the ground and excited states. As shown by semiempirical and ab initio MO quantum chemical calculations, bond equalisation within the polymethine chain is not complete. The π -bond orders at symmetry-related positions are equivalent, but up to the centre of the polymethine chain a degree of bond localisation always re-

mains in the electronic ground state. This bond localisation is experimentally confirmed by crystal-structure analysis of various types of cyanine dyes. These results clearly demonstrate that reduction to only two equivalent limiting forms is an oversimplification for describing cyanine dyes.

We have used $^3J(\text{H,H})$ coupling constants in the polymethine chain to characterise the bond localisation in the ground state and showed that different heterocyclic terminal groups induce different bond localisations in the electronic ground state.

Usually, it is assumed that the vibronic sub-bands are determined by a unique, dominant vibrational mode. It was shown that it is the totally symmetric C–C valence vibration of the polymethine chain in the electronic excited state. In addition, there are displacements in the equilibrium configuration between electronic ground and excited states of cyanine dyes. Within the polymethine chain the equilibrium C–C bonds are longer in the excited state. This explains the appearance of vibronic bands in cyanine dyes in addition to the 0–0 band. The intensity distribution among the vibrational sub-bands can be explained by the Franck–Condon principle together with the $^3J(\text{H,H})$ coupling constants.

Experimental Section

The solvents used were of commercial grade. ^1H NMR spectra were recorded on Varian Mercury 300 MHz and Varian Mercury 400 MHz spectrometers. IR spectra were recorded on a Spectrometer Scimitar (Digilab), and UV/Vis spectra on a Specord 250 (Analytik Jena).

To determine the relative intensity ratio I_{rel} of 0–1 versus 0–0 sub-bands, the absorption spectra were normalised with respect to the maxima of the 0–0 sub-bands. To determine the maxima of the 0–1 transitions, the wavelength at which the second derivative of the absorption curve has its minimum value in the region of the 0–1 sub-band was estimated, and the intensity of this wavelength was used.

The dyes were synthesised following standard procedures on 0.6 mmol scale.^[36] After filtration, the remaining solid dye was washed three times with cold 2-propanol (6 mL) and diethyl ether (10 mL) and dried for 12 h under vacuum at 50 °C. All dyes were obtained in pure form (≥ 99 area% by HPLC), and no impurities were detected in the ^1H NMR spectra.

3-Ethyl-2-[3-(3-ethyl-3H-benzoxazol-2-ylidene)propenyl]benzoxazolium iodide (1a): Red-violet crystalline powder; 42% yield; m.p. 279 °C; ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 8.29$ (t, $^3J(\text{H,H}) = 13.3$ Hz, 1H), 7.76–7.36 (m, 8H), 6.08 (d, $^3J(\text{H,H}) = 13.3$ Hz, 2H), 4.24 (q, 4H), 1.35 (t, 6H); IR (DRIFT): $\tilde{\nu} = 2975, 1564, 1509, 1459, 1218, 1117, 1084, 970, 916, 737$ cm^{-1} .

1-Ethyl-2-[3-(1-ethyl-3,3-dimethyl-1,3-dihydroindol-2-ylidene)propenyl]-3,3-dimethyl-3H-indolium iodide (1b): Grey-violet crystalline powder; 89% yield; m.p. 277 °C; ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 8.35$ (t, $^3J(\text{H,H}) = 13.5$ Hz, 1H), 7.66–7.28 (m, 8H), 6.56 (d, $^3J(\text{H,H}) = 13.5$ Hz, 2H), 4.18 (q, 4H), 1.69 (s, 12H), 1.33 (t, 6H); IR (DRIFT): $\tilde{\nu} = 2966, 1558, 1487, 1456, 1432, 1252, 1199, 1126, 1079, 925, 779, 679$ cm^{-1} .

3-Ethyl-2-[3-(3-ethyl-3H-benzothiazol-2-ylidene)propenyl]benzothiazol-3-ium trifluoromethanesulfonate (1c): Olive-green powder; 51% yield; m.p. 259 °C; ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 7.99$ –7.37 (m, 9H), 6.58 (d, $^3J(\text{H,H}) = 12.7$ Hz, 2H), 4.36 (q, 4H), 1.33 (t,

6H); IR (DRIFT): $\tilde{\nu} = 3076, 2981, 2809, 1547, 1415, 1260, 1202, 1160, 1130, 1026, 851, 784$ cm^{-1} .

1-Ethyl-2-[3-(1-ethyl-1H-quinolin-2-ylidene)propenyl]quinolinium trifluoromethanesulfonate (1d): Dark-green powder; 34% yield; m.p. 302 °C; ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 8.69$ (t, $^3J(\text{H,H}) = 12.7$ Hz, 1H), 8.30–7.41 (m, 12H), 6.55 (d, $^3J(\text{H,H}) = 12.7$ Hz, 2H), 4.46 (q, 4H), 1.42 (t, 6H); IR (DRIFT): $\tilde{\nu} = 3000, 2971, 2936, 1552, 1465, 1397, 1352, 1316, 1268, 1161, 1029, 957, 825, 746$ cm^{-1} .

3-Ethyl-2-[3-(3-ethyl-3H-1-oxa-3-azacyclopenta[a]naphthalen-2-ylidene)propenyl]-1-oxa-3-azoniacyclopenta[a]naphthalene trifluoromethanesulfonate (2a): Brown powder; 31% yield; m.p. 333 °C; ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 8.62$ (t, $^3J(\text{H,H}) = 13.3$ Hz, 1H), 8.49–7.61 (m, 12H), 6.14 (d, $^3J(\text{H,H}) = 13.3$ Hz, 2H), 4.36 (q, 4H), 1.43 (t, 6H); IR (DRIFT): $\tilde{\nu} = 3075, 2991, 1561, 1498, 1464, 1388, 1336, 1260, 1202, 1143, 989, 804, 748$ cm^{-1} .

3-Ethyl-2-[3-(3-ethyl-1,1-dimethyl-1,3-dihydrobenzo[e]indol-2-ylidene)propenyl]-1,1-dimethyl-1H-benzo[e]indolium tetrafluoroborate (2b): Green crystalline powder; 62% yield; m.p. 283 °C; ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 8.57$ (t, $^3J(\text{H,H}) = 13.5$ Hz, 1H), 8.29–7.50 (m, 12H), 6.58 (d, $^3J(\text{H,H}) = 13.5$ Hz, 2H), 4.30 (q, 4H), 1.99 (s, 12H), 1.39 (t, 6H); IR (DRIFT): $\tilde{\nu} = 2986, 2934, 1554, 1483, 1429, 1354, 1228, 1195, 1128, 1064, 932, 878, 807, 726$ cm^{-1} .

3-Ethyl-2-[3-(3-ethyl-3H-naphtho[2,1-d]thiazol-2-ylidene)propenyl]naphtho[2,1-d]thiazol-3-ium 4-methylbenzenesulfonate (2c): Olive-green crystalline powder; 48% yield; m.p. = 251 °C; ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 8.05$ –7.39 (m, 13H), 6.56 (d, $^3J(\text{H,H}) = 12.7$ Hz, 2H), 4.38 (q, 4H), 1.35 (t, 6H), Anion: 7.49–7.08 (m, 4H), 2.26 (s, 3H); IR (DRIFT): $\tilde{\nu} = 3056, 2978, 1554, 1445, 1423, 1269, 1209, 1137, 999, 879, 814, 753, 677$ cm^{-1} .

4-Ethyl-3-[3-(4-ethyl-4H-benzo[f]quinolin-3-ylidene)propenyl]benzo[f]quinolinium 4-methylbenzenesulfonate (2d): Dark-green powder; 25% yield; m.p. = 323 °C; ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 8.74$ –7.53 (m, 15H), 6.45 (d, $^3J(\text{H,H}) = 12.7$ Hz, 2H), 4.50 (q, 4H), 1.47 (t, 6H); Anion: 7.96–7.46 (m, 4H), 2.26 (s, 3H); IR (DRIFT): $\tilde{\nu} = 3074, 2980, 2936, 1578, 1536, 1456, 1391, 1342, 1290, 1206, 1153, 1062, 1034, 801, 745, 677$ cm^{-1} .

1-Butyl-2-[3-(1-butyl-1H-benzo[cd]indol-2-ylidene)propenyl]benzo[cd]indolium tetrafluoroborate (3): Red-brown crystalline powder; 48% yield; m.p. 266 °C; ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 9.11$ (t, 1H), 8.57–7.67 (m, 12H), 7.13 (d, $^3J(\text{H,H}) = 12.7$ Hz, 2H), 4.32 (t, 4H), 1.84 (quint, 4H), 1.47 (hept, 4H), 0.98 (t, 6H); IR (DRIFT): $\tilde{\nu} = 2960, 2874, 1546, 1445, 1417, 1217, 1174, 1072, 907, 897, 803, 770, 774, 666$ cm^{-1} .

Keywords: absorption · chromophores · cyanine limit · dyes/pigments · vibronic transitions

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