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Thermal Cis-Trans Isomerization of Solvatochromic Merocyanines: Linear Correlations between Solvent Polarity and Adiabatic and Diabatic Transition Energies

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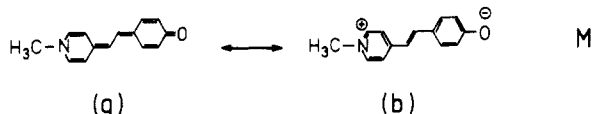
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The correlation between solvatochromy and the solvent-polarity-dependent rate constant k_{ct} of thermal cis-trans isomerization (solvatokinetic behavior) has been investigated for a stilbazolium-type merocyanine and an amphiphilic analogue in a polarity series of eight neat solvents (protic and aprotic). At room temperature k_{ct} varies over 7 orders of magnitude, decreasing with increasing solvent polarity. It has been demonstrated that the first transition energy ΔE_{max} and the free activation enthalpy ΔG^*_{ct} of thermal cis-trans isomerization are linearly correlated with each other and with Dimroth's solvent polarity parameter E_T . These observations and the solvent-polarity-dependent increase of absorption band width are explained in terms of a model emphasizing the strong coupling between molecular conformation, electronic charge distribution, and solvent polarization.

Introduction

The solvatochromism of merocyanine dyes was first reported in 1951 by Brooker et al.¹ The extraordinary sensitivity of the electronic absorption spectra of these compounds to medium effects permits their use as sensitive probes of solvent polarity, which may be applied, e.g., for spectrophotometric determination of water in organic solvents.² They have been used as sensitizers in color photography,³ and due to their extreme hyperpolarizability,^{4,5} they are promising materials for nonlinear optics.⁶ Among this class of compounds particularly the stilbazolium betaine M has continued to be the subject of extensive experimental and theoretical investigation.⁷⁻¹⁶



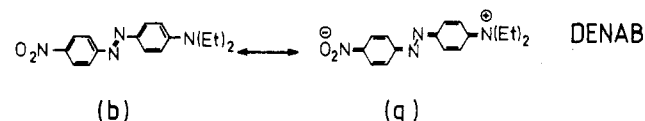
Whereas earlier solvatochromic studies had been carried out in mixed-solvent solutions,^{1,14} only recently a comprehensive investigation in 26 different solvents has been reported by Jacques.¹² The strongly negative solvatochromy (increase of electronic transition energy ΔE_{max} with solvent polarity) was shown to be linearly correlated with Dimroth's empirical solvent polarity parameter E_T for solvents with $E_T \geq 36$. Moreover, a linear two-parameter correlation with Taft's π^* (nonspecific solvent polarity) and α (hydrogen-bond-donor ability)¹⁷ has been established.

Negative solvatochromy is generally indicative of a decrease of dipole moment upon electronic excitation. However, the extremely strong effect in the case of compounds like M involves an additional enhancement due to an increasing ground-state dipole moment with increasing solvent polarity.^{4,10} This may be attributed to an increasing participation of the benzenoid, zwitterionic structure M(b) in polar solvents, which has been borne out by several quantum chemical calculations of various levels of sophistication.¹⁴⁻¹⁶

One should expect that, in parallel with an increasing contribution of resonance structure M(b), an increasing double-bond character of the central C-C bond should develop, which should be reflected in a "solvatokinetic" behavior of cis-trans isomerization around this bond. An indication of such an effect is the largely different rate of cis-trans isomerization that we reported previously for M and its protonated form MH^+ in water.¹⁸ In fact, MH^+ , where the oxygen atom in M is protonated, represents a limiting case of the $q \leftrightarrow b$ resonance, with a predominant b

contribution. In a recent MNDOC calculation by Tavan and Schulten,¹⁶ who compared the isomerization potential of M and MH^+ , this feature was clearly reproduced.

An example of a correlation between solvatochromy and solvent-dependent kinetics (solvatokinetics) has been previously reported by Whitten and collaborators¹⁹ for the solvatochromic compound 4-(diethylamino)-4'-nitroazobenzene (DENAB).



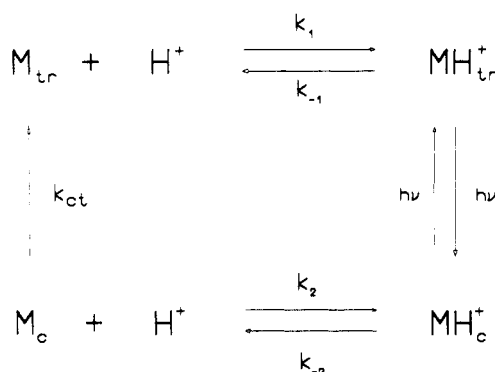
Here, however, the dipolar properties of q and b resonance structures are opposite from the case of merocyanine M, and, in fact, it was observed that in polar solvents, which energetically favor the dipolar resonance form q and cause a hypsochromic shift of the first absorption band, the activation free enthalpy ΔG^*_{ct} has a low value.

In view of the general interest in the properties of merocyanine M and to generalize the reported findings for DENAB, we investigated the relation between solvatochromic and solvatokinetic

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SCHEME I



behavior for the merocyanine M and an amphiphilic derivative C₁₆M (where CH₃ is replaced by C₁₆H₃₃), which had been synthesized as a special polarity probe for micellar systems.

Experimental Section

Materials and Instrumentation. The merocyanines M and C₁₆M were synthesized according to literature procedures.^{20,21} The methylated compound M was recrystallized several times from water, the cetyl-substituted compound C₁₆M from ethyl alcohol containing traces of ammonia. The purity of the dyes was checked by thin-layer chromatography and elemental analysis. According to the latter and to the results of H₂O determination with a Mitsubishi moisturemeter the crystal water content corresponded to 3H₂O for M and 2.5H₂O for C₁₆M.

Organic solvents (Merck) were of reagent grade and used without further purification. Buffer materials used were piperidine (Merck, p.A.), 1,5-diazabicyclo[4.3.0]non-5-ene (DBU; (Merck, >97%) H₂SO₄ (95–97%, Merck, p.A.), 1 N NaOH (Merck, Titrisol), and phthalic acid (Fluka, 99.5%). Sodium methylate was prepared freshly from metallic sodium and methanol.

Absorption spectra were recorded on a Perkin-Elmer Lambda 5 spectrometer, with 1.0-cm matched quartz cells with a cuvette holder connected to a thermostat. The slow kinetic runs in ethylene glycol and methanol were followed in the UV spectrometer after photochemical trans-cis isomerization by irradiation with light from the 365-nm line of a high-pressure Hg lamp (Osram HBO 200W/2) selected by a 365-nm interference filter. The fast kinetic runs in other organic solvents were carried out in a flash photolysis apparatus (Applied Photophysics Model KR-1), with double-wall cylindrical cuvettes of 10-cm path length connected to a thermostat.

Method of Investigation. As reported previously¹⁸ the cis isomer of the basic merocyanine M cannot be obtained in a direct photochemical process, e.g., as in the case of DENAB, since the photochemical quantum yield $\Phi_{\text{ct}}(\text{M})$ is close to zero. On the other hand, the protonated form MH⁺ can be efficiently photoisomerized. Thus, to measure the rate constant k_{ct} of the process $\text{M}_{\text{c}} \rightarrow \text{M}_{\text{tr}}$, we made use of the previously investigated protolytic-photochemical-thermal reaction cycle depicted in Scheme I. If it is assumed that the protolytic equilibria are rapidly established, the mixtures $\text{M}_{\text{c}}/\text{MH}_{\text{c}}^+$ and $\text{M}_{\text{tr}}/\text{MH}_{\text{tr}}^+$ will kinetically behave as quasiespecies, and their thermal turnover following the precedent obverse photochemical turnover, will be a first-order process with an effective rate constant of

$$k_{\text{eff}} = \alpha_{\text{c}} k_{\text{ct}} \quad (1)$$

where α_{c} is defined as

$$\alpha_{\text{c}} = \frac{[\text{M}_{\text{c}}]}{[\text{M}_{\text{c}}] + [\text{MH}_{\text{c}}^+]} \quad (2)$$

Thus α_{c} has to be known to determine k_{ct} from k_{eff} . Our previous investigations in aqueous solution have shown that α_{c}

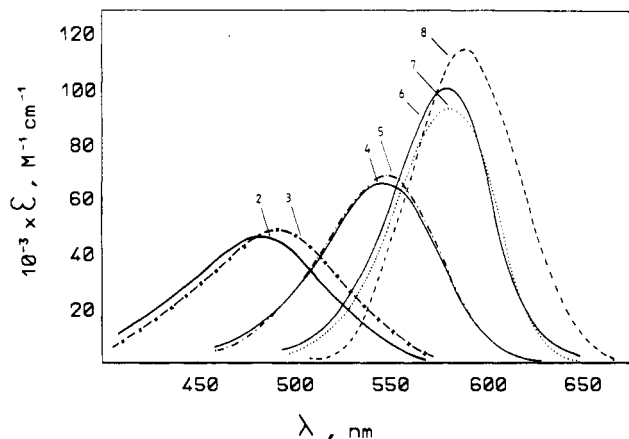


Figure 1. Absorption spectra of C₁₆M in various solvents: 2, ethylene glycol; 3, methanol; 4, 2-propanol; 5, acetonitrile; 6, *N,N*-dimethylformamide; 7, dimethyl sulfoxide; 8, acetone.

and α_{tr} are virtually identical. We assumed this equality also to hold for other solvents. The α value in a given solution was determined as the ratio of the long-wavelength absorption maximum to that of a solution with the equilibrium completely on the side of the M form. For observation of the pure M spectra, the MH^+/M equilibrium had to be completely shifted to the M form, which was achieved by adding between 10^{-3} and 10^{-2} M of piperidine or DBN in aprotic solvents or 10^{-2} M NaOH in protic solvents. To fix α_{tr} at a value of about 0.5 in each solvent investigated, we added suitable amounts of piperidine and sulfuric acid at a total concentration on the order of 10^{-3} M as a buffer system. In the case of methanol a standard buffer of pH* 11.6 according to Broser and Fleischhauer²² was used. The precise value of α_{tr} was checked spectrophotometrically for each solvent and at each temperature where kinetic runs were performed.

With the buffer concentrations used, the protolytic equilibria are expected to be established within microseconds, whereas the highest value of k_{eff} measured was about $4 \times 10^4 \text{ s}^{-1}$. So the validity of eq 1 can be safely assumed.

The kinetics of thermal cis \rightarrow trans isomerization was investigated at seven temperatures ranging between 15 and 55 °C. The reaction rate corresponds to a first-order rate law. From the temperature dependence of the rate constant the Arrhenius and Eyring activation parameters have been obtained.

In concluding the Experimental Section we point out that some kinetic data for thermal cis-trans isomerization of M, reported a few years ago by Abdel-Mottaleb et al.,²³ were based on experiments where the role of α was not adequately taken into account. Therefore the rate parameters obtained in that work have no well-defined relation to the cis-trans isomerization process and should be disregarded.

Results and Discussion

The absorption spectra and the solvent dependence of the first absorption band are very similar for the merocyanines M and C₁₆M. The spectra of the amphiphilic derivative are depicted in Figure 1 to demonstrate the general character of the spectral change. The ϵ_{max} and λ_{max} values of both dyes are listed in Table I. Here are also given the Eyring activation parameters and the rate constants at 25 °C of the thermal cis \rightarrow trans isomerization process.

The results for M in water have been adopted from our previous work.¹⁸ The long-chain merocyanine C₁₆M is actually insoluble in water, at least in a monomolecularly dispersed form. Experiments where methanolic stock solutions have been diluted with more than 50% of water show a drastic change of the absorption spectrum (a strong hypsochromic shift of λ_{max} and a drastic de-

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TABLE I: Spectroscopic^a and Kinetic Data for Thermal Cis-Trans Isomerization of Merocyanines M and C₁₆M^b

solvent	λ_{\max}^a	ϵ_{\max}^a	k_{ct}^c	$\Delta G_{ct}^{*,d,e}$	$\Delta H_{ct}^{*,d,e}$	$\Delta S_{ct}^{*,e,f}$
water ^g	442	39.0	7.4×10^{-5}	23.1	28.0	16.5
ethylene glycol	474	46.3	3.4×10^{-3}	20.3	20.8	0.1
	(480)	(40.4)	(6.0×10^{-3})	(20.5)	(17.3)	(-10.9)
methanol	484	50.2	4.5×10^{-2}	19.3	20.6	4.2
	(487)	(47.4)	(7.7×10^{-2})	(19.0)	(20.8)	(6.2)
2-propanol	544	67.0	8.0	16.2	18.6	7.9
	(549)	(65.6)	(1.1×10^1)	(16.0)	(19.3)	(10.9)
acetonitrile	547	73.2	5.3×10^1	15.1	19.0	13.2
	(550)	(68.0)	(1.3×10^2)	(14.5)	(21.8)	(24.2)
dimethyl sulfoxide	573	99.4	1.2×10^{-2}	14.6	12.0	-8.8
	(577)	(101.0)	(1.9×10^{-2})	(14.3)	(11.0)	(-11.1)
N,N-dimethylformamide	580	99.5	5.7×10^2	13.7	14.7	3.2
	(585)	(93.2)	(7.9×10^2)	(13.1)	(14.4)	(2.4)
acetone	585	107.0	1.6×10^3	13.1	11.7	-4.6
	(588)	(114.0)	(3.3×10^3)	(12.7)	(13.3)	(2.1)

^a λ_{\max} (nm) and ϵ_{\max} ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$) of the first absorption band of the basic trans isomer. ^bValues for C₁₆M are given in parentheses. ^cs⁻¹, value actually determined at 25 °C. ^dKilocalories. ^eCalculated for 25 °C from Arrhenius parameters. ^fcal/(mol K). ^gData from ref 18.

crease in ϵ_{\max} , along with a completely different band shape; similar spectra have been described by Donchi et al.²¹), which may be an indication of micellar aggregation.

Solvatochromism. An extensive investigation of solvatochromism of M has been recently reported by Jacques.¹² Our results for λ_{\max} of M are in very good agreement with his, except for acetonitrile, where our value of 547 nm is markedly shifted with respect to the value of 571 nm reported in his work. This discrepancy may be explained by the high sensitivity toward small amounts of protic solvents, reported for λ_{\max} of M in very dry acetonitrile.¹² In our case the necessity of using buffered systems precluded the usage of solvents completely free of traces of protic cosolvents. Since we wanted to correlate spectral and kinetic behavior, we used the same quality of solvents for both types of investigations.

For C₁₆M we found that the λ_{\max} values are consistently at 3–6 nm longer wavelength than for M. With respect to the large solvatochromic shifts this is only a minor change, indicating that the spectroscopic behavior of the chromophore is very slightly dependent on the alkyl substituent. However, the shift is systematic and indicates that the effect of the long chain is to render the environment of the chromophore a little less polar than it is for M in the same solvent. A purely electronic effect of the alkyl substituent on the ring nitrogen (enhanced inductive shift) would be expected to cause a spectral shift in the same direction as if protonating the phenolic oxygen, which is known to cause a hypsochromic shift. This electronic effect must be obviously overcompensated for by the general environmental polarity effect exhibited by the long alkyl substituent. As is shown in Figure 2 the first electronic transition energy ΔE_{\max} of M and C₁₆M correlates very well with the empirical solvent parameter E_T . This is not too surprising since Dimroth's reference compound, a pyridinium-*N*-phenolate betaine,²⁴ is closely related in electronic structure to the merocyanines investigated here. Taking the data for M and C₁₆M together, we obtain correlation 3:

$$\Delta E_{\max} = 0.803E_T + 14.15 \text{ kcal} \quad (r = 0.991) \quad (3)$$

with similar coefficients as reported by Jacques¹² for M only:

$$\Delta E_{\max} = 0.799E_T + 14.56 \text{ kcal} \quad (r = 0.989) \quad (3\text{-J})$$

In Figure 2 we have also plotted the solvatochromic data reported for DENAB.¹⁹ With these the correlation has a slope opposite to that of M. Furthermore, the correlation shows much more scatter. On the other hand, it has been reported by Schanze, Mattox, and Whitten¹⁹ (SMW) that when Taft's π^* polarity scale is used, the DENAB data correlate fairly well:

$$\Delta E_{\max}(\text{kcal}) = -6.88\pi^* + 63.00 \quad (r = 0.986) \quad (4\text{-SMW})$$

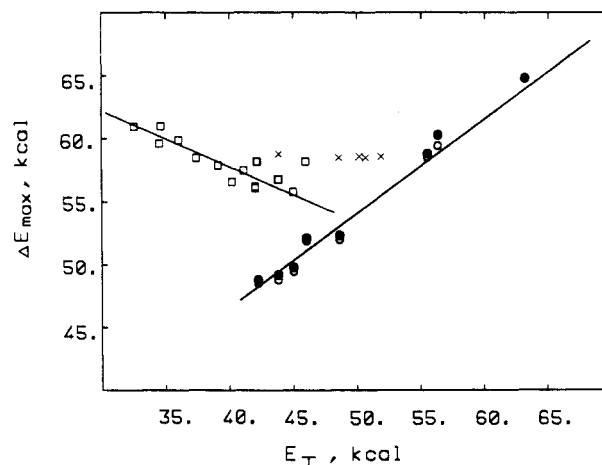


Figure 2. Plot of transition energy ΔE_{\max} versus Dimroth's solvent parameter E_T : ●, M; ○, C₁₆M; □, DENAB in aprotic solvents; ×, DENAB in protic solvents (DENAB data after Schanze et al.¹⁹).

This is not so in the case of M and C₁₆M. Analyzing the ΔE_{\max} data for M, Jacques showed that these are similarly sensitive to π^* and the hydrogen-bond-donor ability parameter α :

$$\Delta E_{\max}(\text{kcal}) = 9.69\pi^* + 11.13\alpha + 41.01 \quad (r = 0.992) \quad (4\text{-J})$$

From our data, including those for both M and C₁₆M, we obtain the following correlation:

$$\Delta E_{\max}(\text{kcal}) = 9.78\pi^* + 11.45\alpha + 40.69 \quad (r = 0.973) \quad (4)$$

Thus we may note here that with respect to their solvatochromism, M and C₁₆M differ from DENAB not only in the sign of the effect but also in their specific sensitivity to solvent hydrogen-bond-donor effects.

Looking at the band shapes, yet another feature of the merocyanine solvatochromism is borne out. In the series of solvents investigated there is a monotonic increase of ϵ_{\max} with decreasing solvent polarity parameter. But in the same series the width of the absorption bands decreases in such a way that the oscillator strength, which has been found to vary in the range between 0.9 and 1.1, is almost constant. Such a relation has been suspected by Jacques¹² from a comparison of two solvents, namely, CHCl₃ and CH₃OH. We shall provide an explanation of this regularity below.

Solvatokinetic Behavior. As is borne out by the data in Table I the rate constant of cis → trans isomerization at 25 °C is increased by about 7 orders of magnitude when going from water to acetone. This behavior nicely parallels the polarity series of the ΔE_{\max} data. The results for M and C₁₆M are very similar, yet with the notable difference that in each solvent the rate constant for C₁₆M is a factor of about 2 larger than for M. We tend to assume that this difference is in itself a microenvironmental

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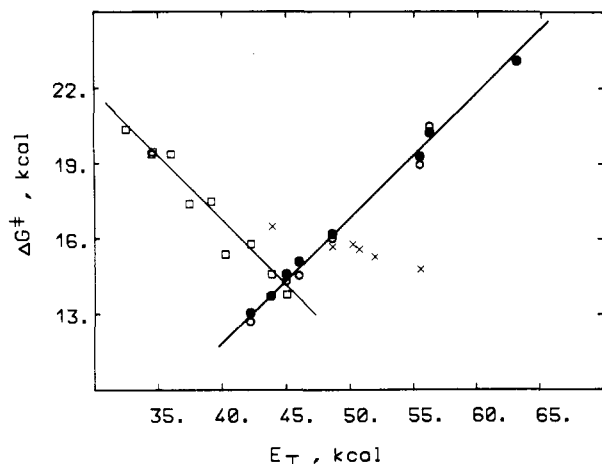


Figure 3. Plot of activation free enthalpy ΔG^\ddagger of thermal cis-trans isomerization versus Dimroth's solvent parameter E_T : ●, M; ○, $C_{16}M$; □, DENAB in aprotic solvents; ×, DENAB in protic solvents (DENAB data after Schanze et al.¹⁹).

polarity effect and systematically reflects the small difference of ΔE_{\max} for both dyes, which we have interpreted as an indication of a somewhat lower polarity in the environment of the $C_{16}M$ chromophore due to the long alkyl-chain substituent.

The solvatochemical behavior of M and $C_{16}M$ is almost clearly represented in Figure 3, where we have plotted the activation free enthalpy ΔG^\ddagger_{ct} as a function of solvent polarity parameter E_T . A good linear correlation is obtained. Including both the data for M and $C_{16}M$, the correlation parameters are

$$\Delta G^\ddagger_{ct} = 0.491E_T - 7.760 \text{ kcal} \quad (r = 0.996) \quad (5)$$

Again it is interesting to compare the merocyanine case with the DENAB case, which is also depicted in Figure 3. With DENAB in aprotic solvents there is also a good correlation with E_T , the slope corresponding approximately to the negative value of the correlation for M. The DENAB data for protic solvents (a series of alcohols) strongly depart from the main correlation line and seem to be distributed along another straight line. This has been noted previously by Whitten and co-workers²⁵ for a plot using Kosowers Z instead of E_T . Since, however, Z is linearly correlated with E_T ,²⁶ the conclusions are equivalent.

As discussed above, a linear correlation with E_T indicates the importance of hydrogen-bond-donor properties of the solvents if protic solvents are included in the correlation. Correspondingly the correlation with Taft's π^* polarity parameter alone is very poor and needs improvement by a two-parameter correlation, including also the α parameter. In the case of ΔG^\ddagger_{ct} we obtain

$$\Delta G^\ddagger_{ct}(\text{kcal}) = 6.34\pi^* + 7.11\alpha + 8.16 \quad (r = 0.991) \quad (6)$$

whereas Whitten's results for DENAB were

$$\Delta G^\ddagger_{ct}(\text{kcal}) = -6.33\pi^* + 20.77 \quad (r = 0.935) \quad (6a\text{-SMW})$$

for aprotic solvents and

$$\Delta G^\ddagger_{ct}(\text{kcal}) = -6.33\pi^* - 2.38\alpha + 20.80 \quad (r = 0.991) \quad (6b\text{-SMW})$$

for protic solvents. Thus from a comparison of DENAB with M and $C_{16}M$ in Figure 3 and eq 6 we see, that not only the solvatochromic but also the solvatochemical behaviors of these compounds are of different sensitivity with respect to the specific solvent-solute interaction of hydrogen-bond formation.

As compared to ΔG^\ddagger_{ct} the activation parameters ΔH^\ddagger_{ct} and ΔS^\ddagger_{ct} for M and $C_{16}M$ show considerable scatter in a polarity correlation. The correlation parameters for ΔH^\ddagger_{ct} are

$$\Delta H^\ddagger_{ct} = 0.58E_T - 11.00 \text{ kcal} \quad (r = 0.80) \quad (7)$$

which indicates that, on the average, the solvent-polarity dependence of ΔH^\ddagger_{ct} is similar to that of ΔG^\ddagger_{ct} .

When discussing the reasons for the observed solvatochemical behavior of M and $C_{16}M$ in more detail, we may certainly rely on the assumption that in these compounds the mechanism of thermal cis-trans isomerization is an *adiabatic rotation around the central C-C bond*. No other path connecting cis and trans form of our compounds, e.g., a motion analogous to the planar N-inversional mechanism in azo compounds, suggests itself in our stilbene-type compounds. Furthermore, a diabatic change from the lowest singlet potential surface to the lowest triplet surface as discussed for some styryl pyridines²⁷ seems to be highly improbable in view of the high-frequency factors which we found to be larger than 10^{11} s^{-1} in all solvents investigated.

Some quantum chemical data obtained by Tavan and Schulten¹⁶ on the change of electronic structure during cis-trans isomerization of M and MH^+ are of special interest in relation to our work. The protonated form MH^+ , while corresponding to b-type resonance structure in its planar trans conformation and its approximately planar cis conformation, obtains a good deal of q-type resonance character in the 90° rotated conformation (henceforth denoted as M_q), which is borne out in a pronounced charge migration from the phenyl group to the pyridyl group. This is just what would be expected by chemical intuition.

On the other hand, the unprotonated M, which corresponds to a q-type structure in its planar trans or its approximately planar cis conformation, does not show such a change during isomerization. This is also in accord with chemical common sense, since the q-type structure with its low double-bond character of the central C-C bridge is the most favorable one for the perpendicular conformation, anyway. Actually, according to the calculation of Tavan and Schulten, who considered isolated molecules devoid of any solvation, the M_c conformation is even higher in energy than the perpendicular one, meaning that in the gas phase M_c would be thermodynamically unstable, i.e., the observability of M_c in itself seems to be a solvent effect. An extension of the quantum chemical calculations to account for solvation would be highly desirable. So far, solvent effects have been taken into account only in a calculation confined to the planar M_t structure.¹⁵

As long as more detailed quantum chemical information is not available, one may assume as a rough approximation that the role of solvent polarity, no matter if it is actually due to hydrogen-bond formation, could be envisaged as being equivalent to exhibiting partial protonations¹⁴ at the oxygen atom, thus inducing a weaker or stronger contribution of resonance structure b in the planar conformations, generating a corresponding molecular dipole moment and causing an energetic stabilization with respect to the nonpolar, q-type structured M_s form.

Such a concept suggests that solvent-polarity-dependent changes of ΔG^\ddagger_{ct} are largely due to changes in the free energy of solvation $\Delta G_{\text{solv}}(M_c)$, viz.

$$\Delta \Delta G^\ddagger_{ct} \approx \Delta \Delta G_{\text{solv}}(M_c) \quad (8)$$

In the activated-state M_s , the solvation must be assumed to be in equilibrium with the actual charge distribution of the molecule. If this charge distribution closely corresponds to the q-type resonance structure, then the solvent will be only weakly polarized. On the other hand, if this unpolarized solvent configuration would be held fixed, a planarization of M_s toward the M_c conformation would be probably only weakly, if at all, exergonic, as can be concluded from Tavan and Schulten's results. Thus it follows that a descent from M_s to M_c or, vice versa, the activation from M_c to M_s will occur along a reaction coordinate corresponding to a highly cooperative motion of C-C bond twist and orientational polarization of the solvent. These cooperative changes may be instigated by independent fluctuations of either the internal rotational vibration of M around the central C-C bond or the orientational polarization of the solvent shell.

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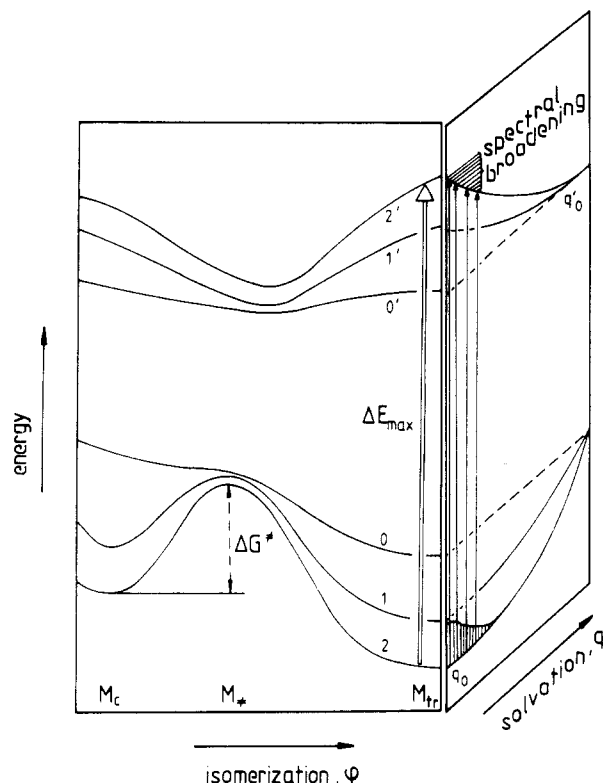


Figure 4. Schematic energy surfaces of *M* versus cis-trans isomerization coordinate φ and solvation coordinate q . The numbers 0, 1, and 2 in S_0 and 0', 1', and 2' in S_1 denote potential curves for increasing polarity of solvent.

In the case of DENAB these arguments apply similarly, with, however, the correspondence that here the activated state is the strongly polar one, and eq 8 would take the form

$$\Delta\Delta G_{ct}^*(\text{DENAB}) \approx \Delta\Delta G_{\text{solv}}(\text{DENAB}_*) \quad (9)$$

Such a relation was implicitly assumed by Schanze et al.¹⁹ to estimate the change of dipole moment between the almost planar *cis* and the activated perpendicular conformation.

Correlation of Adiabatic and Diabatic Transition Energies. Traditionally,^{3,8} strongly negative solvatochromy has been interpreted as evidence that there is a strong decrease of the dipole moment on electronic excitation. Furthermore, our previous experimental investigations¹⁸ have shown that M_c photoisomerizes very efficiently, indicating that in the photoreactive state, which is thought to be the S_1 state, the double-bond character of the central C-C bridge must be very low. Thus, with respect to charge distribution and central C-C bond order the electronic structure of *M* in S_1 ought to be very similar to that of the ground-state M_* conformation. In particular this similarity is borne out in the linear correlation of both ΔG_{ct}^* and ΔE_{max} with E_T , implying, of course, that there is a direct linear correlation between ΔG_{ct}^* and ΔE_{max} . The correlation equation is

$$\Delta G_{ct}^* = 0.604\Delta E_{\text{max}} - 15.98 \text{ kcal} \quad (r = 0.989) \quad (10)$$

Altogether our findings are suggestive of an explanation that may be illustrated by means of the schematic diagram depicted in Figure 4. Here the first horizontal axis corresponds to the rotational isomerization coordinate φ , whereby it is understood that along φ the solvent arrangement is always in equilibrium with the actual intramolecular charge distribution in *M*. Let curve

1 represent the situation for a solvent of medium polarity; then changing to a more polar solvent (curve 2) will lower the potential minima at the close-to-planar conformations M_c and M_{tr} , whereas the energy of the weakly polar transition-state conformation M_* should be only weakly solvent dependent.

The potential curves 1' and 2' in the excited S_1 state belong to solvation states corresponding to vertical Franck-Condon (FC) transitions from the corresponding position of the S_0 isomerization potential curves 1 and 2, respectively. Since the electronic charge distribution changes on excitation, the FC solvent configuration is not in equilibrium with the new charge distribution. Thus, even though the S_1 state may have a small dipole moment, its FC energy will strongly depend on solvent polarity. In this way the diagram represents our finding that $\Delta\Delta E_{\text{max}} > \Delta\Delta G_{ct}^*$. On the other hand, the experimentally appearing proportionality of these quantities implies that the stabilization of M_c (and M_{tr}) by increasing the solvent polarity must be proportional to the destabilization of the S_1 FC state.

Finally, to explain the solvent-polarity dependence of the absorption band width and its relation to the solvent dependence of ΔE_{max} , we have extended the potential diagram at a fixed position of the isomerization coordinate corresponding to M_{tr} , by adding the dimension of a representative solvation coordinate q . This coordinate can be defined as corresponding to a solvent configuration that would be established in equilibrium with a molecule (M_{tr})' with a virtual dipole moment of q .²⁸ (One should note that q is not constant along the reaction coordinate φ as defined here.)

In the electronic ground state there will be a thermal distribution along the coordinate q , centered at q_0 , the position of the potential minimum. In the excited state there is a solvent-polarity-dependent slope toward the excited-state equilibrium solvation q_0' . It follows from the FC principle that the q distribution in S_0 is transferred to a ΔE distribution of the corresponding FC transition, which is broader the steeper the slope in the excited-state potential curve. Thus, according to our model, the band width will increase in parallel with the transition energy as the polarity of the solvent increases.

Conclusion

Our experimental results demonstrate that for the merocyanine *M* and its amphiphile derivative $C_{16}M$ the energy and band width of the first electronic transition and the activation free enthalpy ΔG_{ct}^* of thermal cis-trans isomerization are strongly solvent-polarity dependent and correlate closely with each other. All these effects have been suggested to be related to the strong coupling between solvent polarization modes and conformationally induced electronic changes of the molecule going along with major charge redistribution. A detailed quantum chemical study of the relevant potential surfaces in the ground and excited states, including a suitable solvent polarization mode, would be highly desirable to achieve a better understanding of this intriguing situation.

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Registry No. *M*, 23302-83-2; $C_{16}M$, 58346-32-0.

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