

previous report.⁹ The maximum at the first peak of the anodic current versus voltage occurs at 0.59 V and corresponds to the one-electron oxidation of DEH to DEH⁺; the second is at 1.04 V and corresponds to the two-electron oxidation of DEH to DEH²⁺. Only one peak at 1.08 V is found in the electrochemical oxidation of BDPH which corresponds to the one-electron oxidation to BDPH⁺; furthermore, as indicated by the large difference between the areas under the curves for the anodic current and cathodic current versus voltage, respectively, this one-electron oxidation-reduction process is not reversible. Thus the oxidation of BDPH to its radical cation requires more energy than for DEH and clearly is not the same process as the one-electron oxidation in DEH. In fact, electrochemical studies on aniline derivatives¹⁹ show that *N,N*-dimethylanilines form radical cations, under the same conditions at ≈ 0.7 V, and that when good electron-donating

groups are substituted in the para position of the phenyl in the aniline structure the anodic oxidation potential decreases to ≈ 0.5 V. As a consequence, we conclude that the theoretical work discussed above explains and supports the electrochemical results that the oxidation of DEH to DEH⁺ should be viewed as a one-electron oxidation of an aniline derivative; thus, a better picture for the radical cation of DEH is where the unpaired electron is localized on the aniline nitrogen with some delocalization into the aniline phenyl ring. The oxidation of BDPH is best described as a one-electron oxidation out of the hydrazone group. The best description for the structure of the BDPH radical cation is one where the unpaired electron resides on the amine nitrogen of the hydrazone group with some delocalization on the C=N double bond and the phenyl ring attached to the amine nitrogen.

Registry No. DEH, 68189-23-1; DEH⁺, 123701-13-3; DEH²⁺, 123701-14-4; BDPH, 966-88-1; BDPH (radical cation), 123805-62-9; formaldehyde hydrazone, 6629-91-0; formaldehyde hydrazone (radical cation), 123805-61-8.

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Photoinduced Intramolecular Charge Transfer and Trans-Cis Isomerization of the DCM Styrene Dye. Picosecond and Nanosecond Laser Spectroscopy, High-Performance Liquid Chromatography, and Nuclear Magnetic Resonance Studies

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The photoexcitation of 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4*H*-pyran (DCM) induces a large intramolecular charge transfer (ICT) from the dimethylamino electron-donor group to the dicyanomethylene acceptor group. The dramatic effect of the solvent polarity on the absorption and fluorescence spectra on the one hand and the competition between the nonradiative $S_1 \rightarrow S_0$ deactivation and trans \rightarrow cis isomerization processes on the other hand has been examined. Our results clearly show that DCM isomerization efficiency is very low in the more polar solvents. The $S_1 \rightarrow S_0$ internal conversion may intervene at a torsional angle smaller than 90° before reaching the perpendicular configuration.

Introduction

The compound 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4*H*-pyran (DCM) is a very efficient arylidene laser dye.¹ DCM laser properties are remarkable as regards the weak overlap between its absorption and emission spectra, broad tunability, high conversion efficiency, and low pumping threshold.² The DCM large Stokes shift in poly(methyl methacrylate) (PMMA) is also valuable in luminescent solar concentrators.³

The DCM spectral shift of the absorption and fluorescence spectra with solvent polarity⁴ is related to charge transfer properties in the molecule, which possesses a dimethylamino electron donor chromogen linked to two cyano electron acceptor chromogens by an unsaturated bridge.⁵ The fact that cyano groups give rise to highly polar merocyanine-type structures is well-known.⁵ From the DCM Stokes shift values ($\nu_A - \nu_F$) in 25 solvents, the Lippert and Mataga theory,⁶ and a vectorial analysis of the DCM ground-state dipole moment, $\mu_g = 6.1$ D, we have estimated the dipole moment of the DCM fluorescent singlet excited state, $\mu_e = 26.3$ D.^{4c} A dual fluorescence has been observed by Hsing-kang et al. in polar solvents and attributed to two emitting states in dynamic equilibrium maintained during their decay which was found to be single-exponential and wavelength independent.^{4a} Drake et al. also concluded to a single exponential.^{4b} However these findings were obtained with a single photon counting system and a nanosecond discharge lamp. Recently using a better time

resolution and picosecond laser excitation, we have concluded that the "intriguing"^{4b} photophysical picture of DCM should include the trans-cis equilibrium under ambient light.^{4f} We showed indeed that the fluorescence temporal profile could be fitted with a sum of two exponential decays attributable to the trans and cis isomers,

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which have been first identified by Drake et al.^{4b} Therefore the trans isomer cannot be considered as the solely fluorescent species and the photoisomerization process has to be taken into account if one wants to further analyze the photophysical properties of DCM and get temporal information on its fluorescence solvatochromism and photoisomerization mechanism which may involve a twisted internal charge transfer state (TICT).

The study of the DCM photoisomerization in different solvents is also important for the understanding of its laser properties, because a laser dye photoconversion under the excitation of the pumping laser affects the laser action for several reasons: the absorption coefficient of dye molecules at the pump wavelength is modified during the trans-cis photoconversion;^{2c} the sterically hindered and less planar cis isomer is expected to show lower fluorescence and lasing capability; the fluorescence spectrum of the cis isomer should be different from that of the normal species as their absorption spectra are different.^{4b}

The aim of the present paper is the study of the photophysical properties of the two DCM isomers with the hope of obtaining a clear understanding of the trans-cis photoisomerization mechanism. In that respect, some current ideas should be remembered. The presence of electron-donating and electron-withdrawing groups on each side of an ethylenic bond is known to diminish the double bond character.⁷ The solvent effect should also play an important role through a markedly different solvation of polarized ethylenes in the transition state.^{7a} The zwitterionic nature and the strong stabilization of the perpendicular singly excited $^1\pi\pi^*$ state of unsymmetrical olefins in highly polar solvents are indeed well established theoretically.⁸ Recently the rate constant of the trans-cis photoisomerization of a pyrenyl-substituted styrene has been shown to increase with the solvent polarity due to the lower of the energy of the perpendicular configuration with charge transfer structure.⁹

Experimental Section

The picosecond transient absorption kinetics were obtained with the experimental setup previously described.¹⁰ The second harmonic (532 nm) of a mode-locked Nd³⁺:YAG laser was used for excitation and a picosecond continuum of white light was the analyzing light.

The nanosecond absorption spectroscopy setup has already been described.¹¹ The DCM triplet was populated via triplet-triplet energy transfer from naphthalene which was excited by the 4th harmonic of a Q-switched Nd:YAG laser. The efficiency of the intersystem crossing to the triplet state and the photoisomerization of DCM were investigated by using the 2nd (532 nm) or the 3rd (355 nm) harmonic. Narrow band interference filters and band-pass filters were inserted between the xenon arc lamp and the DCM solution to avoid photoisomerization prior to the laser pulse excitation.

Fluorescence decay profiles were obtained by using the single photon counting technique. The laser source consisted of a cavity-dumped, mode-locked rhodamine 6G dye laser (Coherent Model 701-3) synchronously pumped by the second harmonic of a continuous wave (CW) actively mode-locked Nd:YAG laser (Quantronix Model 416). The dye laser repetition rate was 1 MHz and the pulse duration was shorter than 10 ps, as measured with a home built noncollinear autocorrelator. The emitted fluorescence was analyzed with an Edinburgh Instruments, Ltd., Model 199 spectrometer equipped with a red-sensitive RTC PM 2254 B photomultiplier, two ORTEC Model 584 constant fraction discriminators, an ORTEC Model 567 time to amplitude converter, and an ORTEC Model 7450 multichannel analyzer interfaced to a DEC Micro PDP-11/73 computer. The experimental decay

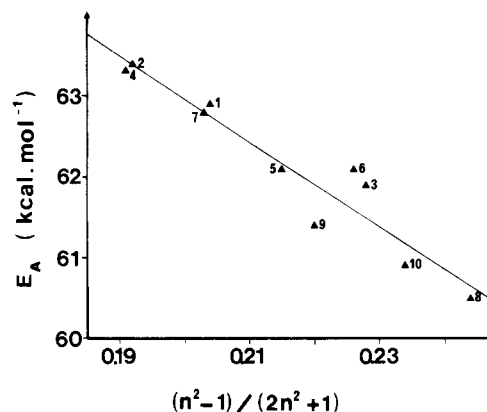


Figure 1. DCM absorption transition energy E_A versus $(n^2 - 1)/(2n^2 + 1)$ in nonpolar solvents.

curves were first fitted to a monoexponential decay function. In the case of a poor statistical fit, a sum of two exponentials based on the simultaneous excitation of two species improved satisfactorily the fit to the data.^{4f}

UV-visible absorption spectra were measured with a Beckman UV 5240 spectrophotometer and fluorescence spectra with a Perkin-Elmer MPF 66 spectrophotofluorometer.

The high-performance liquid chromatography (HPLC) analyses were performed with a Millipore Waters apparatus which includes a Waters 510 pump, a UK6 injector, and a UV-visible absorption spectrophotometer equipped with a photodiode array detector (Model 990). The three-dimensional analysis (optical density wavelength and retention time) was treated with a PC AT compatible calculator (NEC APC IV). The amounts of the two isomers were calculated from the percent area of the elution peaks of the chromatogram displayed at the isosbestic point determined for the eluting solvent. The reverse-phase chromatography separation was operated with a 15-cm microbondapak CN column using a 60/40 methanol-water mobile phase.

The NMR experiments were run at 500 MHz using a Bruker WM 500 spectrometer upgraded with a process controller and an array processor. All spectra were collected at room temperature using a 45° pulse and a 5-s recycling delay to ensure a proper relaxation of all the signals and a correct integral determination.

Products. DCM supplied by Lambda Physik and Exciton were used alternatively without showing any difference. Naphthalene (BDH), methanol (Merck UVASOL for spectroscopy), chloroform (Merck pro analysi), and DMSO- d_6 and $CDCl_3$ (Commissariat à l'Énergie Atomique) were used without further purification. For the nanosecond laser experiments, DCM solutions were deaerated by purging with argon.

Results

Solvent Effects on the DCM Absorption and Fluorescence Spectra. In a previous paper we showed that the red shift of the DCM absorption transition energy with increasing solvent polarity correlated excellently with the χ_R solvent property indicator of Brooker over 25 χ_R values.¹² The advantage of the χ_R indicator is to predict empirically the effect of solute-solvent interactions in the case of weakly polar merocyanines. In the case of more polar merocyanines, an opposite behavior is observed, i.e., a blue shift characterized by a χ_B value.¹²

If one intends to describe more precisely the solute-solvent interactions, one must consider the electronic polarization of the surrounding solvent medium. Following the theory based on the reaction field of Onsager that Bayliss applied to merocyanines in apolar solvents,¹³ we found that the plot of the DCM transition energy E_A (in kcal mol⁻¹) versus the $(n^2 - 1)/(2n^2 + 1)$ function of the solvent refractive index in ten apolar solvents is a straight line with a correlation coefficient of 0.954 (Figure 1). In fact

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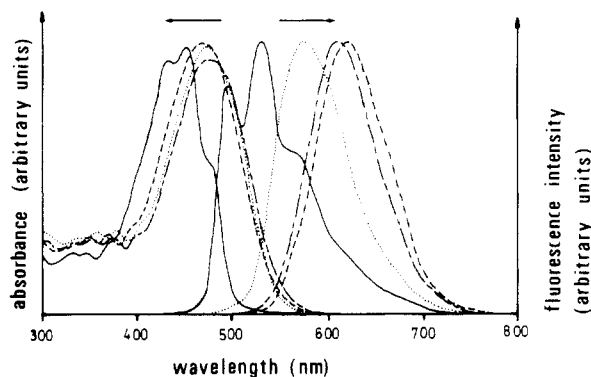


Figure 2. DCM absorption and emission spectra in (—) isooctane, (···) chlorobenzene, (---) methanol and (- - -) pyridine.

this dispersion term applies to the general red shift of the absorption spectrum of nonpolar solutes in nonpolar solvents. More refined treatments¹⁴ similar to the Ooshika¹⁵ treatment consider the orientation polarizability of the solvent molecules and include the static dielectric constant and the absorption wavenumber of the solvent. However they do not take into account short range interactions such as hydrogen bonding, charge transfer, etc., which obviously affect the vibrational structure of the DCM absorption spectrum as shown in Figure 2. The clearly apparent vibronic structure in the nonpolar isooctane, heptane, cyclohexane, and carbon tetrachloride is blurred in polar solvents. Moreover, the fluorescence spectrum structure, which is even better defined than that of the absorption spectrum in isooctane, completely disappears in polar solvents. This behavior is clearly related to the degree of solute-solvent interaction.¹⁶ In the case of DCM in polar solvents, the dipole-dipole forces are very strong, inhibiting thereby the vibrational structure. It also disappears in benzene, chlorobenzene, and bromobenzene as expected from the dipole-induced dipole interactions between DCM and highly polarizable aromatic solvents.^{16,17} The well-structured fluorescence spectrum in isooctane is also characteristic of a planar nuclear geometry both in the ground and excited states.¹⁸

Figure 2 also shows a weak overlap of the absorption and emission spectra and a red shift of the fluorescence spectrum with solvent polarity, which is even greater than that of the absorption spectrum. They result from an increased dipole moment in the fluorescent excited state. The plot of the Stokes shift values ($\nu_A - \nu_F$) versus the solvent Δf parameter

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$$

where n is the refractive index and ϵ is the dielectric constant, enabled us to calculate this dipole moment increase, $(\mu_e - \mu_g) = 20.2$ D, using the Lippert and Mataga theory.^{6,14} We also estimated the dipole moment of the DCM ground state, $\mu_g = 6.1$ D, using a vectorial analysis. This value is only a crude estimation since the dipole moment of the solute largely depends on the solvent.^{6b,17,19} Pawelka et al. noted for example that the dipole moment of a merocyanine considerably increased in chloroform, which exhibits proton-donor properties and induces an additional charge displacement.¹⁷ The high dipole moment increase of DCM is due to a large charge transfer occurring from the dimethylamino donor group to the dicyano acceptor group in the excited singlet state. A complete localization of the electronic charges +e and -e on the donor and acceptor groups distant by 12.5 Å would lead to a dipole moment value of 60 D. The DCM electronic excitation thus leads to a $\pi\pi^*$ state which undergoes a partial charge transfer.

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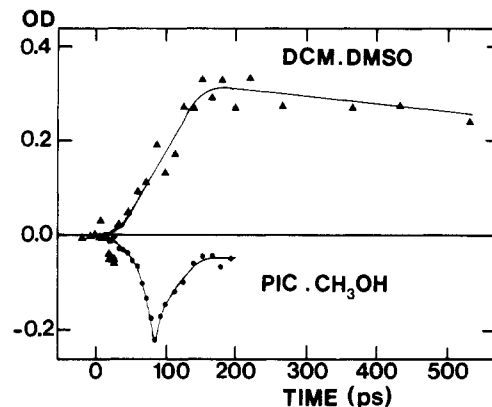


Figure 3. Build up and decay of the DCM first singlet excited state absorbance at 460 nm in dimethyl sulfoxide. Photobleaching and recovery of the ground state PIC absorbance at 460 nm in methanol.

DCM Excited Singlet State S_1 . The DCM excited singlet state generated in a DCM methanolic solution by using nanosecond laser excitation at 532 nm presented an absorption maximum at $\lambda_{\max} = 450$ nm with a molar extinction coefficient $\epsilon_{450\text{nm}}^{S_1 \rightarrow S_n} = (6.5 \pm 0.6) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ which is greater than the molar extinction coefficient of the ground state $\epsilon_{465\text{nm}}^{S_0 \rightarrow S_1} = 4.2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.^{4c}

In order to characterize the stabilization of the excited singlet state which follows DCM $\pi\pi^*$ excitation, we investigated the build up and decay time of the S_1 state absorbance at the 460-nm wavelength, which is close to the S_1 absorption maximum. One needs indeed to describe both the intramolecular charge transfer and the resulting solvent orientational cage relaxation which lower the S_1 energy level and induce the fluorescence solvatochromism of meropol stilbenes as evidenced in time-resolved experiments at low temperature.²⁰⁻²²

A $2 \times 10^{-4} \text{ mol dm}^{-3}$ DCM solution in dimethyl sulfoxide was excited at room temperature in a 1-mm cell using a single laser pulse at 532 nm of 27-ps duration (fwhm). The induced 460-nm absorbance change was probed by using the picosecond continuum of white light generated in the middle of a 4-cm cell containing a mixture of water and orthophosphoric acid (60/40). The temporal profile of the 460-nm transient absorbance signal was compared to the 460-nm photobleaching and absorption recovery of a methanolic solution of pseudoisocyanine (PIC) resulting from the same laser excitation conditions (Figure 3). The fast recovery time constant of the PIC ground state, $\tau \approx 8$ ps, is in good agreement with the literature values found in methanol for the homologous cyanine series PIC,²³ pinacyanol,^{11,24} and DDI.²⁵ The incomplete absorbance recovery is probably due to the formation of a short-lived photoisomer.^{11,23b,26}

The 460-nm absorbance profile of DCM shows a fast increase which follows closely the integration of the pulse shape and a slow decay with a time constant $\tau \approx 2.2$ ns, identical with the fluorescence lifetime of the singlet excited state in dimethyl sulfoxide.⁴ We thus believe that the overall vibrational relaxation of S_1 is too fast at room temperature to be observed under our present time resolution. The intramolecular charge transfer

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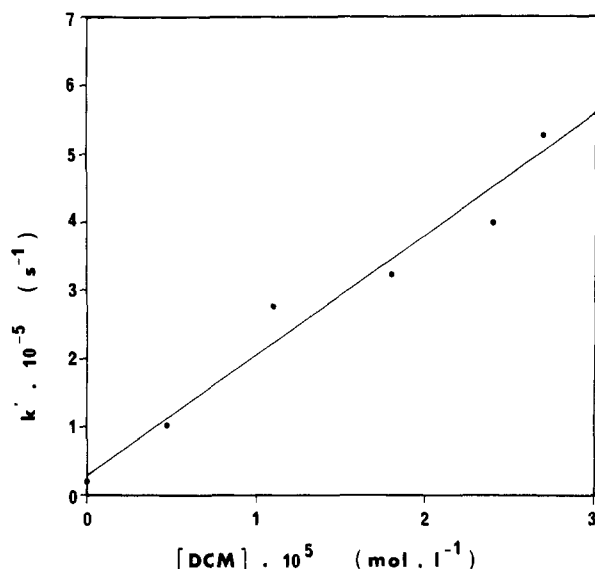
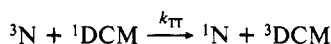


Figure 4. Plot of the pseudo-first-order decay rate constant k' of the naphthalene triplet state versus the DCM concentration.

certainly occurs in the subpicosecond time range and the orientational relaxation of dimethyl sulfoxide expected to be in the range of a few tens picoseconds does not affect the transient absorbance rise time assumed from the laser pulse integration.

Intersystem Crossing to the Triplet State. Nanosecond laser excitation of a deaerated methanolic solution of DCM at 532 nm gave no transient absorbance attributable to a triplet state. To populate the DCM triplet state, we thus used naphthalene as a sensitizer for triplet-triplet energy transfer.^{27,28} Deaerated solutions containing $1.8 \times 10^{-4} \text{ dm}^{-3} \text{ mol}$ naphthalene (N) and a DCM concentration ranging from 4.8×10^{-6} to $2.7 \times 10^{-5} \text{ dm}^{-3} \text{ mol}$ were excited at 266 nm where the DCM direct excitation is negligible. The naphthalene triplet decays were analyzed at 415 nm



The plot of the pseudo-first-order rate constant k' of the naphthalene triplet versus the DCM concentration (Figure 4) gave the second-order rate constant $k_{\text{TT}} = (1.8 \pm 0.1) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is diffusion limited.

The DCM triplet-state differential spectrum (400–840 nm) was calculated after the naphthalene triplet decay in a deaerated solution containing $1.9 \times 10^{-4} \text{ dm}^{-3} \text{ mol}$ naphthalene and $2.3 \times 10^{-5} \text{ dm}^{-3} \text{ mol}$ DCM (Figure 5). The transient absorbance with a maximum at 560 nm decayed with first-order kinetics and a time constant $\tau = (31 \pm 5) \mu\text{s}$. We also checked that no significant 560-nm absorbance was generated in the absence of naphthalene. The DCM triplet molar extinction coefficient was calculated by assuming a complete energy transfer, and using the literature²⁷ molar extinction coefficient of the naphthalene triplet $\epsilon^{415\text{nm}} = 4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. From the differential absorption spectrum of the DCM triplet state and the corresponding ground-state photobleaching spectrum, we deduced the DCM triplet absorption spectrum which presents an absorbance maximum at $\lambda = 530 \text{ nm}$ with a molar extinction coefficient $\epsilon^{530\text{nm}} = (1.9 \pm 0.2) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Figure 6 gathers the absorption spectra of the DCM ground state ($S_0 \rightarrow S_n$), first singlet excited state ($S_1 \rightarrow S_n$) and triplet state ($T_1 \rightarrow T_n$), superimposed on the same graph.

The DCM intersystem crossing quantum yield $\phi_{S_1 \rightarrow T_1}$ was calculated using 3,3'-diethyloxadiazobenzene iodide (DODCI) for actinometry.^{27,28} DODCI ($4.1 \times 10^{-6} \text{ dm}^{-3} \text{ mol}$) and DCM ($2.7 \times 10^{-5} \text{ dm}^{-3} \text{ mol}$) were excited alternatively in deaerated methanolic solution at 532 nm. By monitoring the DODCI

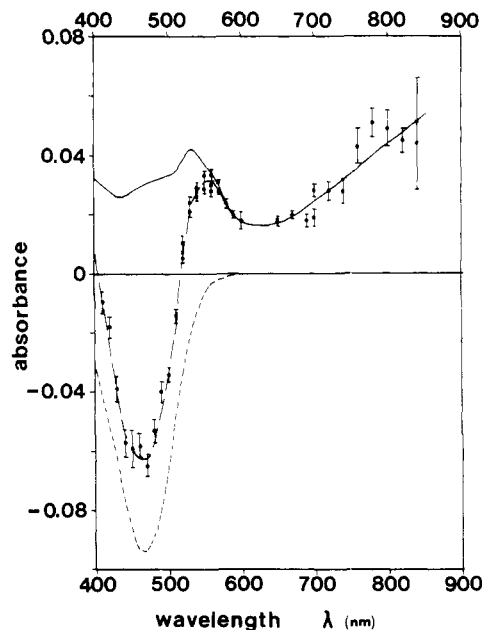


Figure 5. Differential absorption spectrum of DCM triplet state (---); DCM ground state photobleaching spectrum (---); calculated DCM triplet state absorption spectrum (—).

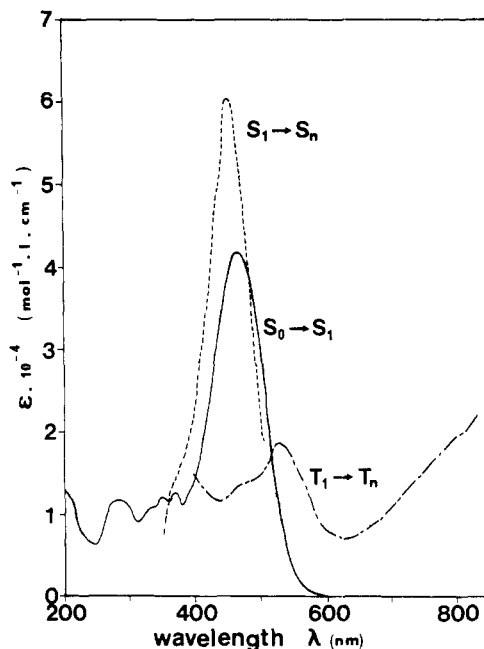


Figure 6. DCM ground state and singlet and triplet excited states absorption spectra.

photoisomer absorbance ($d = 0.24$) at 620 nm ($\epsilon^{620\text{nm}} = 1.84 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)²⁷ and that of the DCM triplet at 560 nm ($d < 10^{-3}$) and using the DODCI photoisomerization quantum yield in methanol, $\phi_p = 0.07$,^{10,29} we estimated a higher limit, $\phi_{S_1 \rightarrow T_1} < (3 \pm 1) \cdot 10^{-3}$ for DCM.

DCM Photoisomerization. The DCM photoisomerization has been found to be more efficient in chloroform by Drake et al.^{4b} They clearly separated two DCM species using HPLC and demonstrated that the photoproduct was a cis isomer through proton NMR spectroscopy. We thus undertook an extensive study of the DCM photoisomerization first in chloroform and then in other solvents in order to understand the photoisomerization efficiency. Under the effect of an increasing number of 532-nm laser pulses in a $8 \times 10^{-6} \text{ dm}^{-3} \text{ mol}$ DCM solution in chloroform prepared and stored in the dark, we observed the gradual decrease of the ab-

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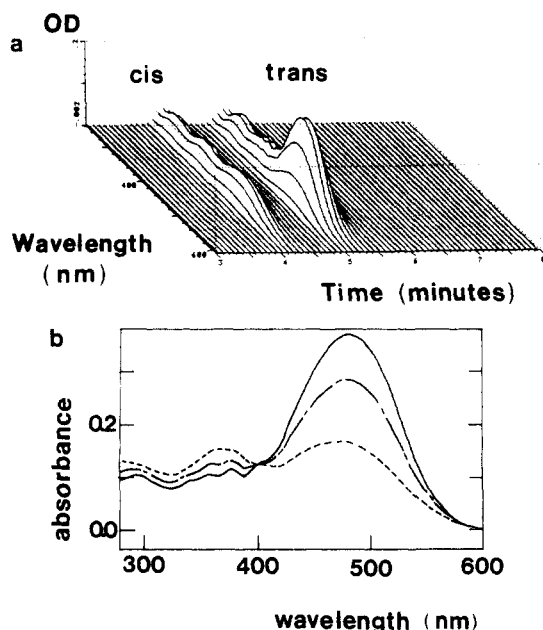


Figure 7. (a) 3D analysis of the HPLC separation of the DCM trans and cis isomers. (b) Absorption spectra of DCM (—) trans isomer, (---) cis isomer, and (-.-) 57/43 trans-cis mixture.

sorption between 400 and 550 nm and a simultaneous absorption increase between 300 and 400 nm, which were stable and irreversible when the solution was kept in the dark for several hours. They result from the trans-cis photoisomerization.^{4b}

After equilibration in room light of a DCM solution in chloroform, the separation of the two isomers through HPLC chromatography using a methanol-water solution (60/40% in volume) as eluting solvent enabled us to fully characterize their absorption spectra and retention times as depicted in the 3D analysis of Figure 7a. In Figure 7b, the absorption spectra of the trans and cis isomers (each being calculated for 100%) are superimposed together with the sum of the spectra of the two isomers obtained as eluted (57/43 trans-cis). The percentages of the two isomers are calculated from the integrals of the absorbances of the elution peaks at the isosbestic point, $\lambda = 400$ nm for the methanol-water (60/40) eluting solvent.

It is worth mentioning that the characteristic absorption band of the DCM trans isomer with a maximum around 470 nm is much less intense in the case of the cis species as expected from the steric hindrance which destroys the planarity of the π system and lowers the oscillator strength.¹⁸ However the absorbance of the cis isomer is greater in the UV.

A nanosecond laser study was also performed by exciting alternatively at 532 nm two 1.3×10^{-5} mol DCM solutions in chloroform. The first one was prepared and kept in the dark while the second one was exposed for about 3 min to the xenon arc light filtered with a combination of two optical filters (Schott BG25 and GG 435), $428 < \lambda < 474$ nm. The resulting transient signals monitored at 460 nm are given respectively in parts a and b of Figure 8. A photobleaching is observed at 460 nm in the solution kept in the dark. It extends from 395 to 550 nm and a simultaneous absorption increase is noticed below 395 nm (Figure 9a). The differential absorption spectrum is well explained by the photoconversion from the trans isomer to the cis isomer. Excitation of the solution exposed to the light leads to an absorbance increase at 460 nm (Figure 8b), which extends from 395 to 550 nm and to a photobleaching below 395 nm (Figure 9a). These absorbance changes can be explained by a preliminary trans \rightarrow cis photoconversion under the continuous irradiation leading to simultaneous laser excitation of the two isomers. Since the relative absorbance of the cis isomer at 532 nm is not dominant, the more important cis \rightarrow trans photoconversion must be explained by assuming that the cis \rightarrow trans photoconversion efficiency is greater than that of the trans \rightarrow cis photoconversion. This assumption is realistic if one takes into account the steric hindrance

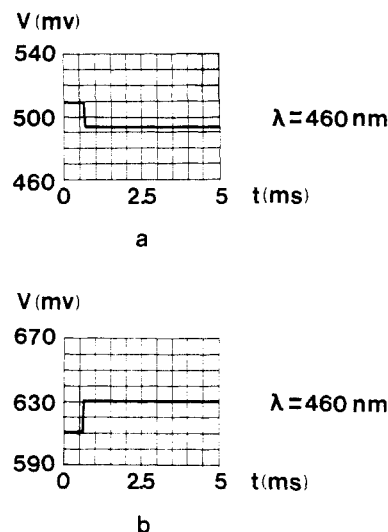


Figure 8. Transient signals monitored at 460 nm in a 1.3×10^{-5} mol DCM solution in chloroform: (a) light-protected solution, (b) light-exposed solution.

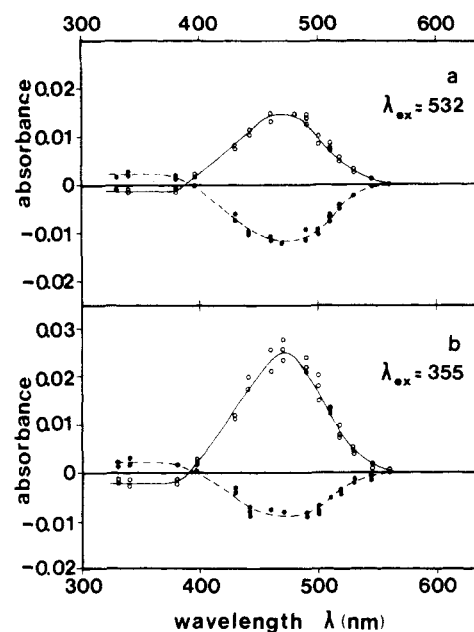


Figure 9. Differential absorption spectra obtained in a 1.3×10^{-5} mol DCM solution in chloroform: (●) light-protected solution, (○) light-exposed solution; (a) $\lambda_{ex} = 532$ nm, (b) $\lambda_{ex} = 355$ nm.

of the cis isomer, which should lower the energy barrier for photoisomerization. The same experiments have been performed by exciting the two solutions at 355 nm, leading to similar observations (Figure 9b). We noticed however that the cis \rightarrow trans photoconversion was more important under 355-nm excitation due to the higher relative absorbance of the cis isomer in the UV.

In order to further characterize the two species present in light-exposed solutions, we undertook proton nuclear magnetic resonance (NMR) experiments. The NMR spectrum of a room-light-exposed 8.2×10^{-4} mol DCM solution in deuterated dimethyl sulfoxide was compared to the NMR spectrum of another DCM solution prepared in the following way. The DCM powder was first dissolved in deuterated chloroform, exposed for 3 h to room light, evaporated to dryness, and then dissolved in deuterated dimethyl sulfoxide. Figure 10 shows the details of the two spectra between 7.8 and 6.2 ppm. The spectrum of the first solution is characteristic of a single DCM species and the doublet with a typical coupling constant $J_{7-8} = 16$ Hz was attributed by Drake et al. to ethylenic protons of the trans isomer.^{4b} The presence of a cis isomer must be rejected. On the other hand, for the second solution, additional peaks and a doublet with a coupling constant $J_{7-8} = 12.6$ Hz similar to that measured by

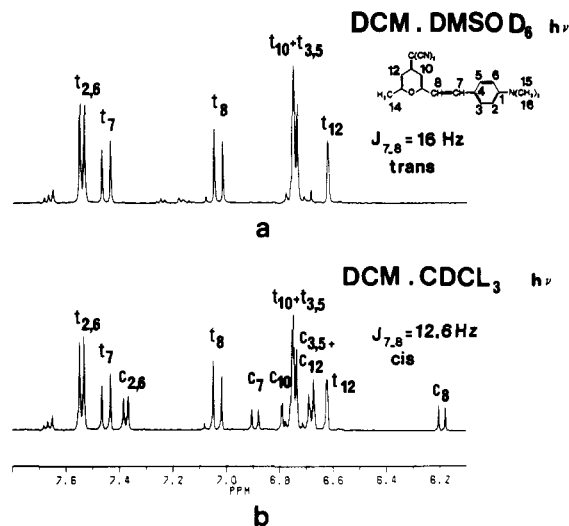


Figure 10. Proton NMR spectra of DCM (a) room-light-exposed $8.2 \times 10^{-4} \text{ dm}^{-3}$ mol DCM in deuterated DMSO and (b) room-light-exposed $8.2 \times 10^{-4} \text{ dm}^{-3}$ mol DCM in deuterated chloroform, taken to dryness and dissolved in deuterated DMSO.

Drake et al are assigned to the DCM cis isomer. Integration of these peaks allows the percentage of the cis isomer to be calculated (29%). Another experiment carried out with protecting the DCM–deuterated chloroform solution from any light exposure showed only the features of the trans isomer. These observations can be interpreted in the following way: (i) The DCM isomerization in chloroform only results from light excitation. (ii) Once formed the DCM cis isomer is thermally stable in all the solvents investigated. (iii) DCM photoisomerization is much less efficient in dimethyl sulfoxide than in chloroform. This latter conclusion is in good agreement with our fluorescence lifetime measurements, which showed the presence of one emitting species in dimethyl sulfoxide and of two emitting species in chloroform.^{4f}

We then investigated the DCM photoisomerization efficiency in various solvents. The DCM solutions were submitted to irradiation by a xenon arc lamp through optical filters ($453 < \lambda < 468 \text{ nm}$) in a 1-mm path-length cell. Their concentrations were low enough to ensure an homogeneous irradiation and adjusted for equal absorbances at the average wavelength of the excitation band. The DCM photoisomer formation was calculated by integrating the cis-isomer elution peak of the HPLC chromatogram obtained for each DCM solution. The exposure time was kept sufficiently short to avoid a photoconversion greater than 10%, and the concentration of the DCM photoisomer generated was always proportional to the exposure time. Under our experimental conditions, we never observed surprising results such as the percent cis decrease with increasing DCM concentration reported by Drake et al.^{4b}

Relative yields of photoisomerization in various solvents normalized to that found in chloroform are gathered in Table I. They confirm the general observations of Drake et al. even though their percent cis values only represent the cis-isomer percentage present in the solution without any reference to the light exposure. The highest photoisomerization efficiency is found in chloroform, and tetrahydrofuran and is smaller by 1 order of magnitude in methanol, dimethyl sulfoxide, and dimethylformamide which possess a higher static dielectric constant and induce a more important Stokes shift.

Discussion

The decay rate constant of the first singlet excited state of the DCM trans isomer is the sum of the rate constants of the ($S_1 \rightarrow S_0 + h\nu$) radiative process, ($S_1 \rightarrow S_0$) internal conversion, ($S_1 \rightarrow T_1$) intersystem crossing to the triplet state, and (trans \rightarrow cis) photoisomerization. It is given by the measurement of the fluorescence decay kinetics of the pure trans isomer of DCM. We showed indeed in a previous paper that great care was necessary to avoid simultaneous excitation of the two DCM isomers, i.e.,

TABLE I: Solvent Viscosity η and Static Dielectric Constant ϵ , DCM Maximum Absorption Energy E_A , Stokes Shift ($\nu_A - \nu_F$), Fluorescence Lifetime of the DCM Trans Isomer τ^F , and Trans \rightarrow Cis Photoisomerization Normalized Relative Yields ϕ_{t-c}

solvent	η^{20° , cP	$\epsilon^{20^\circ C}$	$E_A(4C)$, kcal/mol	$\nu_A - \nu_F$, cm^{-1}	τ^F , ns	ϕ_{t-c}
acetonitrile	0.36 ^a	36 ^b	61.8	5.41	1.93	0.05
tetrahydrofuran	0.46 ^b	7.4 ^b	61.8			0.5
chloroform	0.58 ^a	4.81 ^b	60.8	3.55	1.38	1
methanol	0.597 ^a	33.7 ^b	61.4	5.37	1.36	0.07
dimethylformamide	0.845 ^b	38.3 ^b	60.2	5.08	2.19	0.05
dimethyl sulfoxide	2.47 ^b	48.9 ^b	59.4	5.02	2.24	0.04

^a Handbook of Chemistry and Physics, 56th ed.; CRC Press: Cleveland, OH, 1975. ^b Janz, G. J.; Tomkins, R. P. T. *Non Aqueous Electrolytes Handbook*; Academic Press: New York, 1972; Vol. I, p 35.

that the DCM solution should be freshly prepared and kept in the dark.^{4f} The interference of a small amount of the cis isomer in the solution can be minimized by exciting the solution around the maximum of the trans-DCM absorption band since the oscillator strength of the cis isomer is small in this wavelength region. Moreover a two-exponential decay analysis enabled the measurement of the fluorescence lifetimes of both isomers. For the trans isomer, shorter lifetimes are found in chloroform and methanol and longer lifetimes in acetonitrile, dimethyl sulfoxide,^{4f} and dimethylformamide (Table I). Our nanosecond laser investigation shows that intersystem crossing to the triplet state is not efficient and cannot influence significantly the S_1 decay rate. The radiative lifetime is dependent on the solvent through the square of the refractive index and the displacements of the absorption and fluorescence spectra which affect the theoretical calculation using the Strickler–Berg equation.³⁰ The radiative lifetime in methanol should be greater than in chloroform by 20% if one considers the solvent refractive index only. A more extended analysis is underway.

The rate constants k_{ic} of internal conversion back to S_0 and k_p of the conformational change to a perpendicular state are also expected to play an important role in the deactivation of the fluorescent state. Various schematic representations of the energy levels of the trans, cis, and perpendicular conformations of stilbene-like molecules as a function of the twist angle about the central bond^{7a,8,31} have been proposed. In the Salem's picture of olefin isomerization, upon rotation around the double bond the ground state leads to an orthogonal singlet diradical (D) while the singly excited $^1\pi\pi^*$ state leads to an orthogonal zwitterionic singlet (Z) which lies below (D) in a highly polar solvent. A type B avoided crossing of the potential surfaces and a double well minimum for the excited state are thus created.⁸ In the Orlandi and Siebrand model for the direction photoisomerization of stilbene,³¹ an additional low-energy singlet state S_2 is introduced. An internal conversion $S_1 \rightarrow S_2$ and a crossing between the two surfaces with an energy barrier $\approx 1000 \text{ cm}^{-1}$ are then hypothesized to account for the experimental observations. The S_2 state can then relax toward the perpendicular electronic ground state configuration and finally to the cis and trans configurations with an equal chance.³¹ An important difference between the Dauen–Salem–Turro picture³² and the Orlandi and Siebrand model is the occurrence of the nonradiative deactivation pathway at a rotation angle smaller than 90° in the former, lowering thereby the efficiency of the conformational change to the perpendicular configuration.³² The solvent effect has also been taken into account by Dietz et al.³³ in the photoisomerization of streptocyanines but the radiationless deactivation takes place from the perpendicular state which has the properties of a funnel,^{33–35} leading to a vibrationally excited ground state from which the cis and trans

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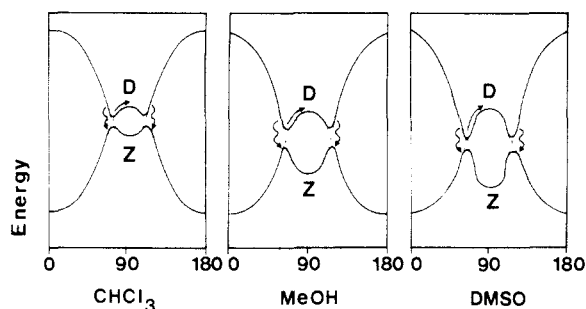


Figure 11. Schematic diagrams of the potential energy surfaces of the excited and ground states of DCM in chloroform, methanol, and DMSO according to the Salem's picture of olefin isomerization.

isomers can be reached as in the Orlandi-Siebrand model. A tentative description of the DCM photoisomerization process is made possible by a careful examination of the trans-isomer S_1 fluorescence lifetime and photoisomerization normalized quantum yield in various solvents (Table I). While the rates of the S_1 nonradiative decay and photoisomerization of DODCI in low viscosity solvents behave in the same way,^{36,37} a short fluorescence lifetime of DCM does not necessarily correspond to a high photoisomerization efficiency. For a 1.3–1.4-ns fluorescence lifetime measured in methanol and chloroform, the photoisomerization quantum yield is 14 times greater in chloroform. Moreover, more similar photoisomerization efficiencies are met in methanol and dimethyl sulfoxide despite a much longer DCM fluorescence lifetime and higher viscosity in dimethyl sulfoxide. A nonradiative deactivation process thus appears independent of the twisting process leading to the isomerization, and the common idea proposed for the visual rhodopsin³⁸ that a high S_1 – S_0 jump probability in the twisted form is related to an efficient photoisomerization can be rejected for DCM.

The longer fluorescence lifetime and low photoisomerization of DCM in dimethyl sulfoxide explain the more efficient laser action in this solvent. The surprising absence of photoisomerization of the IR-140 laser dye in dimethyl sulfoxide again has been noticed by Fouassier et al.³⁹ and attributed to the heightening of the energy barrier and a specific solvent effect. However the energy barrier decreases generally with increasing solvent polarity as observed in the photoisomerization of 4,4'-diaminostilbene⁴⁰ and substituted styrenes.⁹ More experimental data are needed

to separate the effects of solvent viscosity and polarity and deduce the intrinsic molecular barrier height to DCM photoisomerization. The activation energy of the DCM photoisomerization thus includes an important contribution ΔE solvent due to solute-solvent interactions resulting from molecular properties as dipole moment and polarizability.⁴¹ In the present case, the low polar chloroform induces an enormous "specific" effect since the photoisomerization quantum yield is increased by 1 order of magnitude with respect to methanol of similar viscosity. In chloroform which exhibits specific interactions through H-bond formation,¹⁷ an additional charge displacement might occur as reflected by the absorption energy E_A , reducing thereby the double bond character.

The rotation angle of the DCM configuration playing the role of a funnel toward the S_1 nonradiative deactivation cannot be actually predicted. We feel however that in methanol and dimethyl sulfoxide this angle could be smaller than 90° (Dauben-Salem-Turro diagram)³² decreasing thereby the photoisomerization efficiency. On the other hand in the less polar chloroform, it could be closer to 90° enabling a more efficient photoisomerization. In this picture, the lowering of the orthogonal zwitterionic singlet (Z) in polar solvents causes an avoided crossing of the potential surfaces at an angle smaller than 90° and a higher energy barrier to isomerization as depicted in the schematic diagrams proposed in Figure 11 for DCM in chloroform, methanol, and dimethyl sulfoxide. The nonradiative $S_1 \rightarrow S_0$ internal conversion and trans-cis isomerization processes might thus compete under the influence of the solvent polarity.

In conclusion, we have characterized the solvent effect on the absorption and fluorescence spectra of the DCM pure trans isomer, i.e. both the electronic and orientation polarizabilities of the solvent molecules. The large dipole moment increase experienced by DCM in the first excited singlet state ($\mu_e - \mu_g = 20.2$ D) indicates an important charge transfer from the dimethylamino-donor group to the dicyanomethylene acceptor group. We have demonstrated that intersystem crossing to the triplet state is inefficient. Our results indicate that the excited-state decay is controlled by the competition between the radiative process and the nonradiative $S_1 \rightarrow S_0$ deactivation and trans-cis isomerization processes. The $S_1 \rightarrow S_0$ jump probability in a twisted form and the isomerization are influenced differently by the solvent polarity.

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Registry No. trans-DCM, 96042-30-7; cis-DCM, 96042-31-8; acetonitrile, 75-05-8; tetrahydrofuran, 109-99-9; chloroform, 67-66-3; methanol, 67-56-1; dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5.

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