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Dual excited states in 4-dimethylamino 4′-cyanostilbene (DCS) revealed by sub-picosecond transient absorption and Kerr ellipsometry [1]

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Abstract

4-dimethylamino 4′-cyanostilbene (DCS) and p-dimethylamino, p′-cyano, 1-1′-bi-indanylidene (substituted "stiff stilbene" DCS-B24) are investigated using sub-picosecond time-resolved absorption and Kerr ellipsometry experiments. The latter technique makes it possible to work at low excitation energy and low concentration, thereby avoiding intensity and concentration effects which exist in DCS derivatives. Using this technique, in non-polar solvent (cyclohexane), only the presence of a single excited state is observed for the two studied compounds. In polar solvents, DCS-B24 derivative where twisting of the anilino moiety is prevented but double-bond twisting is allowed also reveals the presence of only one excited state. On the other hand, in polar solvents, for the DCS a precursor–successor relationship is clearly observed between two different excited states. These results can be understood within a four excited states model derived from a previously suggested diagram: the delocalized excited (DE) state, the internal charge transfer (ICT) state (highly polar, nearly planar configuration, formed quasi instantaneously from the DE state by electronic reorganization), the conformational relaxed ICT (CRICT) state (highly polar and fluorescent, involves conformational geometric changes such as twisting of the anilino group which enhances charge transfer) and the "phantom" state P* on the trans ⇄ cis isomerization pathway (twisted double bond, lowly polar, non-fluorescent). © 1997 Elsevier Science S.A.

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1. Introduction

In molecules formed by electron donor and acceptor groups linked by a single bond, dual luminescence, associated with the existence of two different singlet excited states, has been observed in polar solvents [1–3], a striking example being DMABN (4-*N*,*N*-dimethylamino-benzonitrile). The origin of this dual luminescence has been much debated but is now attributed to the formation of twisted intramolecular charge transfer (TICT) excited states [2–4]. After excitation of the nearly planar molecule (into the so-called delocalized excited (DE) state [5]), which emits the first band, a twisting of near 90° occurs around the bond linking the electron donor group (dimethylamino) to the electron acceptor group (benzonitrile) because of an energy minimum in the perpendicular conformation (TICT state), which emits the second band. Such TICT states have a large dipole moment and are therefore strongly stabilized in polar solvents. Solvent stabilization allows the TICT state to be populated from the DE excited state and makes it possible to observe its emission which is red-shifted relative to the DE excited state emission. In steady-state conditions, dual luminescence can be observed when an equilibrium exists between the DE and the TICT state populations, or if the TICT rate formation is not too fast, compared to the radiative deactivation rate of the DE excited state to the ground state. When the TICT formation rate is too fast only its emission can be observed. In such a situation, time-resolved spectroscopy generally allows observation of the dual luminescence, the sole requirement being that the time resolution of the experimental set-up should be smaller than the TICT formation rate.

The presence in "push–pull" stilbenes of four single bonds linking electron donor (dimethylamino) and electron acceptor (benzonitrile) groups makes TICT state formation theoretically possible. However, the central double bond can also lead to trans ⇄ cis isomerization which can compete with the TICT state formation and this adds a relaxation channel which complicates the photophysics of these compounds. The pres-

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ence of TICT states in DCS and derivatives has been under debate in recent years. First, Gruen and Görner [6] and Safarzadeh-Amiri [7] concluded that only one excited state exists in this compound and that twisting around a single bond, involving TICT state formation by twisting around the amino group, is not relevant. More recently, the fluorescence behavior of different "push–pull" stilbenes has been investigated and can be summarized as follows [8–10].

1. A large Stokes shift of fluorescence was observed in polar solvents revealing a large dipole moment of the emitting state.
2. Under normal conditions of excitation (low concentration and weak excitation), dual luminescence or the indication of a precursor–successor relationship between two excited states was not observed until very recently [11]. Time-resolved experiments revealed only a dynamic solvatochromism compatible with solvent relaxation around a giant dipole moment.
3. Bridging the DCS compound at different positions preventing twisting around the single and double bonds was investigated. When the benzonitrile and the dimethylanilino groups were prevented from twisting by bridging the single bonds (compound DCS-B24 in Ref. [10]), a strong increase of the non-radiative transitions was observed.
4. The fluorescence decay time in polar solvents does not increase monotonically when the temperature is lowered, but passes through a maximum near the solvent freezing point (≈ 160 K in ethanol) and then decreases below this point [10,12]. This behavior is observed only if the rotation of the dimethylanilino moiety is possible.
5. Moreover, we have also observed concentration and excitation intensity effects in such stilbene derivatives [9,13] and in other polyenic derivatives [14]. When the concentration is increased ($c > 10^{-3}$ mol l^{-1}) and at the same time the excitation intensity is strong (> 30 μJ pulse^{-1}; focalization area, 10^{-2} mm^2), a new emission band appeared on the red side. A dual luminescence was then observed with a precursor–successor relationship between the blue and the red part of the spectra. The intensity of the red band varies in relation to the square of the excitation intensity. Such a behavior was observed in all bridged compounds studied except the DCS-B24 and only in polar solvents. It was proposed that the new emitting species was formed by the association of two electronically excited molecules and was called "bicimer" [9,13]. This was observed at high concentration and high excitation intensity conditions, for those compounds able to form TICT states. This indicated that the species emitting the new band included at least one molecule with the TICT geometry. Let us note that similar intermolecular interactions between excited molecules have already been observed in other compounds [15,16]. However, after these studies with stilbene derivatives, two points remained unclear. (1) We were not able to time resolve the transformation of the DE state to the TICT state population in such derivatives (no dual luminescence behavior). (2) As a consequence, it was difficult to precisely determine the formation pathway of the bicimer.

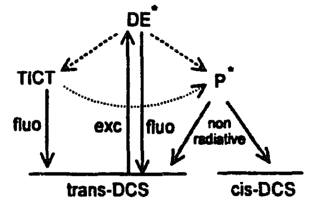
All these results have been discussed [10,17] within the model first proposed by Rettig and Majenz [12] and described below as Scheme 1.

In weakly or strongly polar solvents, the Franck–Condon excited state (DE state) relaxes rapidly, through twisting of the ethylene–anilino single bond towards a TICT state which is strongly luminescent (excepted in nitro derivatives [18] and ionic systems [19]). This process competes efficiently with non-radiative deactivation through double bond twisting, which leads to trans $\rightleftarrows$ cis isomerization [10,12,17]. In the case of high concentration and high excitation intensity, we proposed a mechanism involving two excited molecules (a bicimer), where at least one of the molecules is in the TICT state, which is stabilized by solvent interaction [13]. Nevertheless, these very specific conditions are far from ideal to prove or not the existence of TICT states and their formation in DCS derivatives. The main problem is that all these studies are based on luminescence, which supposes that the states involved are sufficiently luminescent to be detected, taking into account the sensitivity of the methods and the time resolution.

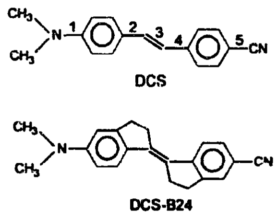
Very recently, using femtosecond time resolution, Eilers-König et al. [11] were able to note a dual luminescence in DCS in two polar solvents (acetonitrile and methanol) and directly observed for the first time the DE → CT transition. These experiments were performed under low concentration (3×10^{-5} mol l^{-1}) and low excitation (15 μJ pulse^{-1}), thus ruling out a possible bicimer formation which may obscure the initial step of the DCS photophysics. However, in this study, an important question was not addressed: is there necessarily a conformational geometric change (such as twisting) taking place on the formation route to the CT state stabilization? In this paper we propose to answer this question by observing if, after excitation of DCS in polar solvents, the TICT state (i.e. conformation changes of the molecule by twisting around a single bond) may be involved in the CT stabilization process.

To address this question, we compare the photophysical behavior of DCS with the photophysical behavior of the model compound (DCS-B24) described in Scheme 2.

DCS-B24 (substituted "stiff stilbene": p-dimethylamino, p′-cyano, 1-1′-bi-indanylidene) was selected because the bridging around the single bonds prevents the twisting of these bonds, and therefore the formation of a possible TICT



Scheme 1. Conventional three-state kinetic scheme from Ref. [12] used as a basis for the interpretation of the photophysical behavior of donor–acceptor stilbenes.



Scheme 2. Molecular structure of derivatives studied.

state. In this compound, we should only observe the double bond isomerization channel relaxation via the phantom state P* (Scheme 1).

Apart from time-resolved luminescence techniques, another method to observe an intermediate state is transient absorption studies, since if a state is not luminescent it can nevertheless absorb light and be observed through its absorption spectrum. However, the sensitivity of this method is limited and generally requires several microjoules of excitation energy and high concentration to observe sufficient optical density changes, particularly if the laser system works at a low repetition rate. Since the photophysical behavior of DCS is very sensitive to excitation energy and concentration [9,13], this technique is far from ideal. In the present experiments we have observed, for example, that above 15 μJ pulse^{-1} (< 1 ps) the photophysical behavior of the compounds begins to depend on the excitation intensity, therefore making the results questionable. However, another method may be used to detect a transient state: Kerr ellipsometry. As has been proved [20], this method may make it possible to detect transient dichroism spectra, which are related to the transient absorption spectra, with lower excitation energy than transient absorption. The evolution of transient species can thus be measured using the Kerr ellipsometry experiment at low concentration and excitation conditions. It is mainly this method that we used in this paper to elucidate the photophysics of DCS and its derivative.

The paper is organized as follows. Section 2 describes briefly the experimental conditions. Section 3 presents experimental results on the two derivatives studied in polar and non-polar solvents. Section 4 discusses these results and compares them with the model developed in Scheme 1. Conclusions are then drawn.

2. Experimental

2.1. Compounds and solvents studied

The trans-isomer of DCS was prepared and purified as described in the literature [7] while we have reported elsewhere the preparation and purification of the bridged compound DCS-B24 [10]. Cyclohexane (CH) and methanol (MeOH) were of spectroscopic grade from Aldrich Chem. For the preparation of the solutions, great care was taken to avoid trans ⇄ cis isomerization of DCS derivatives by preventing any direct illumination of the samples. Moreover, no transient absorption was observed [21] for pure cis isomer in the visible spectral region on a nanosecond timescale.

2.2. Laser sources, pump–probe experiments and streak camera measurements

Our laser set-up and the pump–probe experiments have been described in detail elsewhere [22]. They are based on a hybridly mode-locked dye laser (Coherent 702) associated with an actively mode-locked cw-pumped Nd^{3+}:YAG laser (Coherent Antares-76), a dye amplifier (Continuum PTA 60) and a regenerative amplifier (Continuum RGA 10). This system generates 500 fs pulses (1.5 mJ, 10 Hz repetition rate) at 600 nm.

The parameter of interest, obtained from pump–probe experiments, is the optical density (OD) of the excited part of the sample at wavelength ω_c and time Δt after excitation:

$$\mathrm{OD}(\omega_c,\Delta t)=\log\left[\frac{I_0(\omega_c)}{I(\omega_c,\Delta t)}\right]=\sum_i \epsilon_i(\omega_c).N_i(\Delta t)d \qquad (1)$$

where $I(\omega_c, \Delta t)$ and $I_0(\omega_c)$ are respectively the transmitted intensity of the probe beam with and without excitation. The quantity $\epsilon_i(\omega_c)$ is the absorption spectrum of a transient species whose population at time Δt is $N_i(\Delta t)$, d being the length of the excited part of the sample crossed by the probe beam. To ensure rotational reorientation effect-free kinetics, the angle between the linearly polarized pump and probe beams was set to the magic angle 54.7° [23].

For fluorescence studies we used a 15 ps resolution streak camera (Hamamatsu streakscope C4334). Owing to the time resolution it was not possible to observe the first excited state modifications of the compounds occurring on a picosecond time scale, but we were able to measure their fluorescence decays even at low concentration and low excitation energy. To measure longer excited state lifetimes (> 15 ps) we used the streak camera instead of the classical pump–probe experiment because of the better accuracy. Moreover, the evolution of the maximum of the fluorescence spectra gives information on the interaction between the solute and the solvent through Stokes shift measurements, for example.

2.3. Kerr ellipsometry

The experimental basis, the principle and the performances of this set-up are described in detail elsewhere [24].

Using a procedure developed in Ref. [20], we were able with this set-up to deduce the imaginary part (dichroism $\Delta\phi''(\omega_d, \Delta t)$) of the third-order Kerr-type non-linear optical susceptibility and their spectral dependence, as demonstrated by Charra et al. [20].

The correspondence of dichroism and absorption spectra measured can be found by comparison of theoretical developments of Refs. [20,25]:

$$\Delta\phi''(\omega_c,\Delta t)=\frac{1}{2}\sum_i \epsilon_i(\omega_c)N_i(\Delta t)r_i(\Delta t)d \qquad (2)$$

The difference between Eq. (2) and Eq. (1) is only the reorientational factor $r_i(\Delta t)$ [26] which does not change the excited state spectrum shape. It can only modify the dichroism kinetics as compared with transient absorption. The dynamic response of the Kerr signal is controlled by the reorientation time τ_{or} of the molecules inside the solvent [27,28]. The reorientation is long enough (>30 ps in DCS) to observe excited state transformations occurring during the first picoseconds after excitation, but does not allow measurements of lifetimes which are longer than τ_{or}.

As described in Section 1, there are concentration and excitation effects in DCS derivatives modifying the transient absorption spectra and the lifetime measurements. The formation of new excited species such as the bicimer was proposed [9,13] to describe this behavior. To avoid these effects which make it difficult to study monomolecular processes, it is necessary to work with low concentration solutions ($<10^{-4}$ mol l^{-1}) excited with less than a 15 μJ pulse. However, under these experimental conditions, the amplitude of transient absorption spectra is noisy, which complicates interpretation of the excited behavior of DCS derivatives. Yet, in Kerr ellipsometry experiments, the dichroism amplitude depends only on the non-linear optical properties of the studied compounds. Owing to the high optical non-linearity values of DCS derivatives [29,30], it is then possible to obtain excited state spectra with a better resolution than with pump–probe experiments to elucidate the photophysics of DCS at low concentrations and low excitation energy. An illustration is given in Fig. 1 which compares the two methods under the same experimental conditions. The similarity between the spectra obtained with the two methods is striking, but the Kerr ellipsometry shows a better sensitivity for the determination of the transient excited spectra. The dichroism spectrum in Fig. 1(b) appears as a smoothing of the optical density spectrum (Fig. 1(a)), thereby making it possible to resolve properly the gain band at 560 nm and the component at 440 nm inside the main absorption band centered at 490 nm.

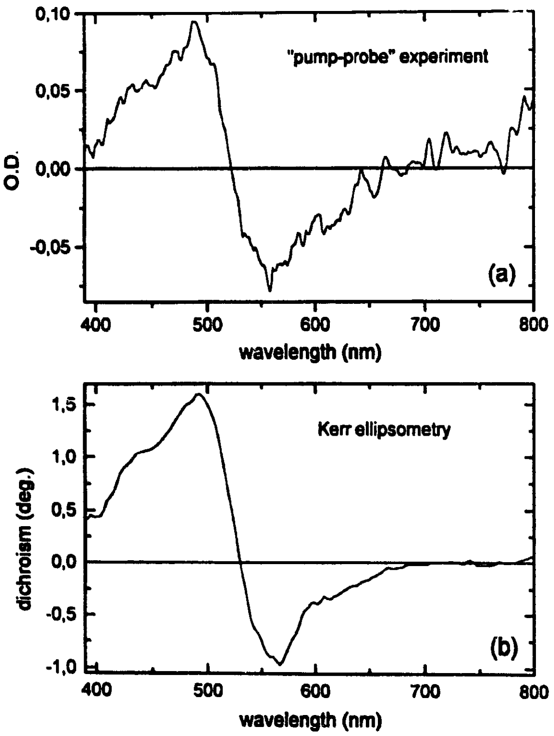


Fig. 1. Comparison between pump–probe (a) and Kerr ellipsometry (b) experiments. The excited spectra are obtained with the same sample (DCS in acetonitrile), in the same conditions (low concentration, 10^{-4} mol l^{-1}; weak excitation, 3 μJ pulse^{-1}).

3. Experimental results

3.1. *In non-polar solvent (cyclohexane)*

Typical transient dichroism spectra of DCS in CH are shown in Fig. 2(a) as well as the associated kinetics (Fig. 2(b)). The spectra are formed by a main absorption band peaking near 550 nm and a structured gain band peaking at 420 and 440 nm, corresponding to the spontaneous emission of DCS in this solvent. These two bands evolve in parallel with an instantaneous rise time limited by the pulse duration. The decay is linked to the reorientation time τ_{or} of the solute inside the solvent (see Table 1 for spectral and time characteristics). Time-resolved emission, using the streak camera, gives a monoexponential decay at any wavelengths without any particular behavior (lifetime, $\tau_f = 85$ ps).

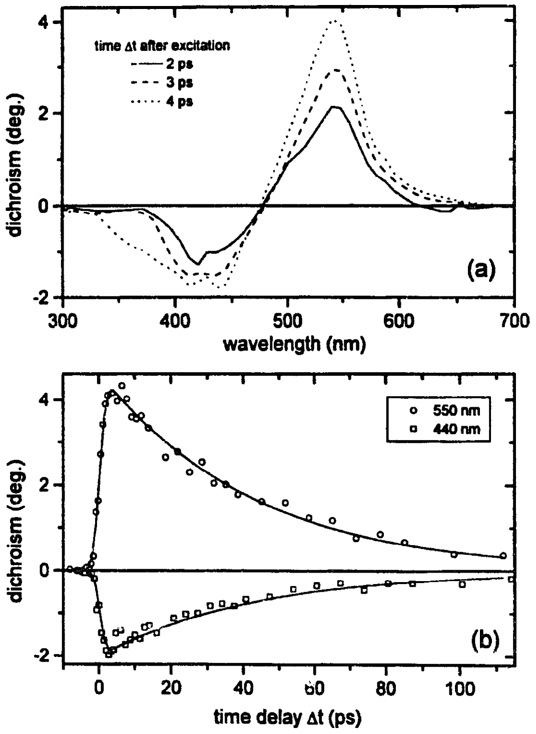


Fig. 2. DCS in cyclohexane: (a) Dichroism for different delays Δt after excitation at 300 nm; (b) kinetics of the dichroism at 550 nm (absorption band) and between 420 and 440 nm (gain band) as a function of excitation pulse delay Δt. The long decay time corresponds to a convolution between the excited state lifetime and the reorientation time of DCS in CH.

Table 1
Results obtained for DCS and DCS-B24 in the different solvents studied. Solvent characteristics: dielectric constant ϵ and viscosity η (in cp)

Solvent		Solute	1st excited state			2nd excited state			λ^{max}_{fluor} (nm)	Characteristic times (ps)		
			λ^{max} (weight)		τ_1 (ps)	λ^{max} (weight)		τ_2 (ps)		τ_f	τ_{rise}	τ_{or}
CH		DCS	550(1)	420, 440(−0.3)	85				420, 440	85		75
$\epsilon=2$	$\eta=1$	DCS-B24	545(1)	440(≈0)	7.5				440	7.5		
MeOH		DCS	505(1)		4	505(0.8)	560(−0.7)	460	520	460	4	100
$\epsilon=33.5$	$\eta=0.59$	DCS-B24	460(1)		25				510	25		

For each excited state, we present the fit of results derived from Eq. (3) (see also text in Section 3.2): λ^{max} represents the maximum wavelength (nm) of the band studied and the number in parenthesis is the weight of the band (weight > 0 means absorption band, < 0 means gain band) in the excited state spectrum. The time τ_1 is the lifetime of the first excited state (ICT state) and τ_2 the lifetime of the second excited state if it exists (CRICT state for DCS in polar solvents). λ^{max}_{fluo} (nm) corresponds to the maximum of the fluorescence spectra obtained with the streak camera.

The characteristic times column is a summary of the different time results: τ_f is the fluorescence lifetime obtained with the streak camera or with "pump–probe" experiment: fluorescence from the ICT state (DCS-B24 in all solvents and DCS in cyclohexane) or from the CRICT state (DCS in polar solvents), rise time τ_{rise} is the formation time of the CRICT state, and τ_{or} is the reorientation time of molecules dissolved in the corresponding solvent obtained by Kerr ellipsometry.

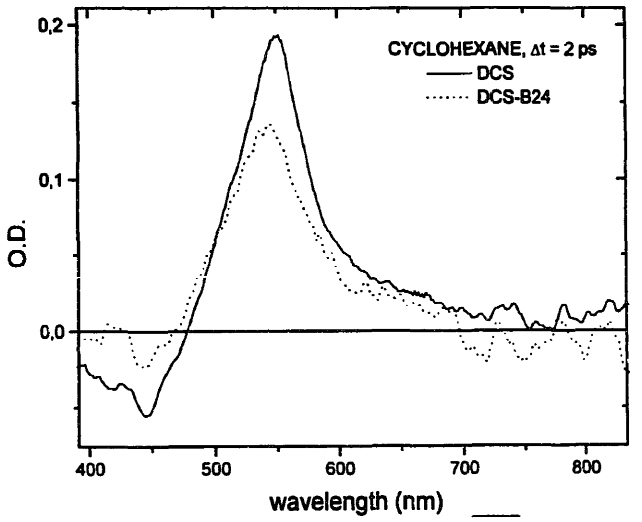


Fig. 3. Transient absorption spectra of the two derivatives in cyclohexane, obtained by pump–probe experiment for delay $\Delta t = 2$ ps after excitation.

As shown in Fig. 3, the same general behavior is observed for DCS-B24 with a less intense gain band and a shorter fluorescence lifetime. For the two compounds and at any wavelengths inside the dichroism spectra, the kinetic behavior may be simulated with only one excited state, formed instantaneously during pulse excitation and with a lifetime τ_f (see Table 1). So in non-polar solvents such as CH, no spectral difference can be observed between the two compounds and only one excited state is revealed within the time resolution. The situation is quite different in polar solvents.

3.2. In polar solvent (methanol)

Fig. 4 shows the behavior of DCS in MeOH, which can be summarized as follows. Just after excitation there is only one broad absorption band centered near 505 nm and appearing during the pulse excitation (Fig. 4(a)). However, as the time passes, strong spectral evolution occurs characterized by a gain band appearing near 560 nm. The formation of this gain band is delayed with respect to the pulse excitation with a clear rise time as shown in Fig. 4(b).

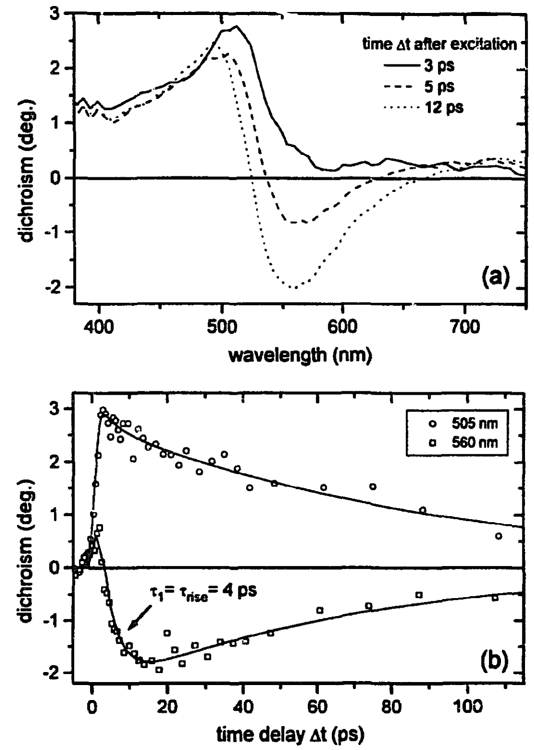


Fig. 4. DCS in methanol: (a) dichroism spectra at different delay times Δt after excitation; (b) kinetics of the dichroism at 505 nm (absorption band, 1st excited state) and at 560 nm (gain band, 2nd excited state). The data are fitted according to Eq. (3) (see Table 1).

An apparent blue-shift of the absorption band may be observed as a function of time, but this can be explained by competition between the absorption and gain bands which develop. Simulation of the kinetics requires more than one excited state in this solvent, with a precursor–successor relationship between these two excited states. The first excited state is characterized by the 505 nm absorption band, whereas the second excited state is characterized by an overlap between the same absorption band and a new gain band at 560 nm. To determine the evolution of the kinetics for a given wavelength, e.g. to describe the excited state populations, the following two-level rate equations have been used:

$$\begin{cases} \dfrac{dN_1}{dt} = I(t,\Delta\tau) - \dfrac{1}{\tau_1}N_1(t) \\ \dfrac{dN_2}{dt} = \dfrac{1}{\tau_1}N_1(t) - \dfrac{1}{\tau_2}N_2(t) \end{cases} \qquad (3)$$

where N_i is the population of the excited state i ($i = 1,2$), $I(t,\tau)$ is the gaussian profile (FWHM $= \Delta\tau$) of the pump pulse which excites the sample at $t = 0$ and τ_i is the lifetime of state i. Resolving the system, we used $N_1(t)$ and $N_2(t)$, with appropriate weights, to fit the kinetics of the different excited species for a given wavelength. The results of the simulations are given in Table 1. For each excited state, we noticed the spectral region of interest (absorption or gain band) with the appropriate weights necessary to fit the experimental kinetics. In the case of DCS in MeOH, the rise time τ_1 is evaluated at 4 ps and is the result of the formation of the second excited species.

It is interesting to compare the behavior of the two compounds in this same solvent as shown in Fig. 5. DCS-B24 has a completely different behavior. No gain appears at any time after excitation. Only a strong absorption band exists, similar to the absorption band observed in DCS just after excitation. This band is formed instantaneously during the pulse duration, and the kinetics may be simulated well only by one excited species formed during excitation. As described below, the same behavior was observed for DCS and DCS-B24 in other polar solvents such as dimethyl-sulfoxide (DMSO) and acetonitrile (ACN) [24].

From these studies two main conclusions may be reached.

1. In DCS in polar solvents we clearly observed the presence of two excited states linked by a precursor–successor relationship, while in non-polar solvents only one species is formed.
2. Bridging the single bonds on both sides of the central ethylene bond in DCS-B24 prevents the formation of the second excited species. Let us now discuss these results in the light of the model proposed in Scheme 1.

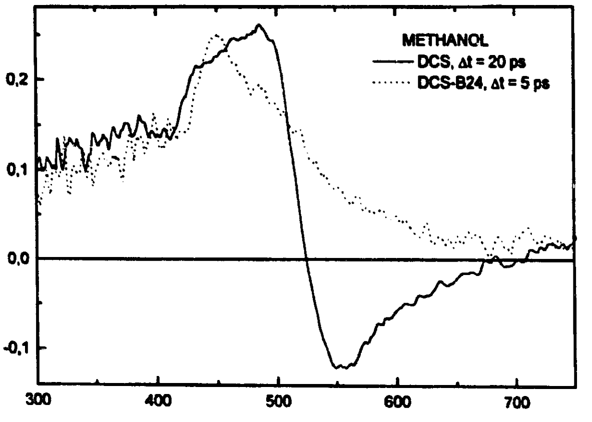
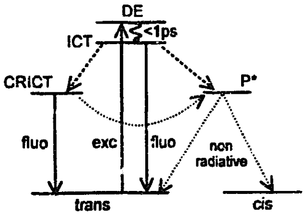


Fig. 5. Transient absorption spectra of the two derivatives in methanol, obtained by pump–probe experiment for different delays Δ*t*.

4. Discussion

In DCS-B24 we observe directly the excited state formed during excitation. This state has a similar absorption spectrum as the first excited state formed in DCS. We may note that this state has a polar character as shown by the fluorescence spectra of DCS-B24 obtained with the streak camera: the maximum of the fluorescence spectra is red-shifted from 440 nm (CH) to 530 nm (DMSO) when increasing solvent polarity [24]. We can then assign this excited state to an intramolecular charge transfer state (ICT) formed during a time shorter than the pulse duration (< 1 ps) after vertical transition to the DE state. From this state, according to Scheme 1, isomerization can occur in all solvents by population of the P* state with non-radiative transition. We have observed [24] that the formation rate of the P* state increases with the solvent. This means only that the P* state is less polar than the ICT state, as previously suggested [10,17,31,32]. Increasing solvent polarity stabilizes the ICT state (lower energy minimum) without changing the P* state configuration. Thus, the energy barrier ICT → P* increases with solvent polarity. The same behavior occurs in DCS in non-polar solvents, but the formation rate of the P* state (80 ps^{-1} in CH) is 10 times faster in DCS-B24 (7.5 ps^{-1} in CH). This has previously been observed for these compounds [10] and also for stilbene derivatives [33] but no clear explanation was proposed. This point shows the importance of single-bond rotations for the double-bond twisting process: single-bond rotations seems to strongly modify the activation barrier from the ICT state to P*. A possible explanation [10] should be a more complex reaction pathway involving an intermediate state reached from the ICT state by barrierless relaxation through single bond twisting.

In DCS in polar solvents, the ICT state is populated as in DCS-B24 during the excitation process, as shown by the fluorescence measurements. However, single bonds can twist in DCS. So, from this ICT state, a conformational relaxed ICT (CRICT) state is formed fast involving rotation around single bonds and strong interaction with the solvent which stabilizes the CRICT polar state. In this paper we prefer to use the term CRICT rather than the term TICT, because it is not sure (like in the standard model DMABN) that the twist is complete and goes to 90°. Moreover in an ideal TICT configuration, the molecules should possess a forbidden fluorescent nature which is not observed here [5]. We suggest rather that some twisting angle exists which increases the dipole moment and the polarity of this state more than the ICT state. We recently observed [24] that the formation rate of this CRICT state is controlled by the solvent viscosity, but it is also controlled by solvent polarity which dramatically changes the barrier crossing owing to the dipole moment of the CRICT state. Since the relaxation channel from ICT to



Scheme 3. Updated model for the interpretation of DCS photophysics, derived from the conventional three-state kinetic scheme (Scheme 1).

CRICT state (measured by the rise time $\tau_{\rm rise}$ in Table 1) is very fast compared to the relaxation channel between ICT and P* state (evaluated from the lifetime τ_f of DCS-B24), the route for isomerization is practically hindered in polar solvents, as observed experimentally [10]. In this case the development of the second excited state observed in our experiments can be assigned to the formation of the CRICT state, since the isomerization channel is quenched. So the CRICT state relaxes with nanosecond decay and with high fluorescence quantum yield [10].

To summarize all these results, we propose an updated model (Scheme 3), derived from that in Scheme 1, which takes into account our present observations and those of Eilers-König et al. [11].

5. Conclusion

From this study we propose the following photophysical steps to explain the behavior of DCS. Just after excitation, by vertical transition into the DE state, a fast internal charge transfer state (ICT; formation time, < 1 ps [11]) is formed. This is more or less stabilized depending on the solvent properties. In a rigidified compound or in non-polar solvents, this state decays to the P* state on the trans ⇄ cis isomerization pathway. However, in polar solvents, when geometry changes are possible (twisting of single bonds), the charge transfer character may be increased, thus leading to a more stabilized ICT state called CRICT (conformational relaxed ICT) state.

Therefore, these results show that Kerr ellipsometry can be an interesting alternative tool to classical pump–probe experiments, particularly when the molecules studied possess high optical non-linearity properties but are associated with weak transient absorption spectra of the excited state species.

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