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Excited State Dynamics of a Julolidino Analogue of Crystal Violet: A Relaxation Path through a Conical Intersection?

Martin Jurczok,[†] Pascal Plaza,[‡] Monique M. Martin,*,[‡] and Wolfgang Rettig[†]

Laboratoire de Photophysique Moléculaire du CNRS (UPR 3361), Bât. 210, Université de Paris-Sud, 91405 Orsay, France, and Institut für Chemie, Fachinstitut für Physikalische und Theoretische Chemie, Humboldt-Universität zu Berlin, Bunsenstrasse 1, D-10117 Berlin, Germany

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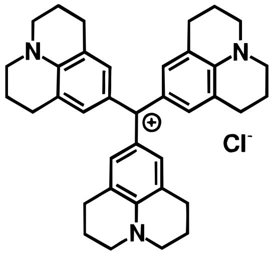
Transient absorption spectroscopy with subpicosecond time resolution was applied to the study of the excited-state dynamics of an analogue of crystal violet with julolidino-substituted phenyl rings in ethanol, propanol, and butanol at room temperature. Experiments were also carried out with crystal violet for comparison. The time-resolved spectra are interpreted by a barrierless adiabatic photoreaction, leading to the formation of a dark transient excited state involving the torsion of one of the substituted phenyl rings connected with the charge shift from the nitrogen of the amino substituent to the central carbon of the triphenylmethane structure. The effects of solvent viscosity, size, and electron donor−acceptor character of the substituted phenyl rings on the transient kinetics are examined. The relaxation of the transient excited state back to the equilibrium ground state is shown to be sensitive to the solvent viscosity but less than its formation reaction. A relaxation model via a conical intersection between the S_1 and S_0 potential surfaces, involving torsional motion of two of the phenyl rings, is postulated for the back charge-shift reaction.

1. Introduction

The triphenylmethane dyes have received much attention in physical chemistry from both fundamental and applied research.[1] The questions that were raised concern their stereochemistry,[2] ground-state geometry, symmetry and optical spectroscopy,[3] the hyperpolarizability properties from their octupolar nature,[4] their photostability as dyes for the textile industry and, thus, as water pollutants, their ability to be chemically converted,[1] their strongly solvent-dependent fluorescent properties,[5,6] and their specific behavior for converting efficiently light into large internal motion in fluid solvents.[7−26] In the present paper, we report a study of the excited-state dynamics of a triphenylmethane dye with three julolidino-substituted phenyl rings (CVJ) by picosecond transient absorption spectroscopy. This compound is an analogue of crystal violet (CV) and ethyl violet (EV), which have three dimethylamino and three diethylamino-substituted phenyl rings, respectively (see Scheme 1). Although a large number of pico- or femtosecond spectroscopy studies were already devoted to CV,[7−9,11−13,15−18,27,28] we also carried out measurements with this dye under the same conditions for direct comparison with CVJ.

SCHEME 1



CVJ

Oster and Nishijima[5] and Förster and Hoffmann[6] reported that the fluorescence yield (ϕ_{Fl}) of the di- and triphenylmethane dyes is determined by the environment rigidity and follows a sublinear increase with the solvent viscosity in solution. These authors suggested that a nonradiative process involving the rotational diffusion of the phenyl rings occurs in their excited state along a barrierless potential. For CV and CVJ, Vogel and Rettig[14] reported that the variation of ϕ_{Fl} versus viscosity does not strictly show a power law in the whole range of viscosity between 1 and 250 P, using glycerol as the solvent and varying the temperature to vary the viscosity. A sublinear increase of $\phi_{Fl} \propto \eta^{0.82}$ was, nevertheless, found for $\eta < 100$ P for both compounds, with a higher yield for CVJ under similar conditions. In glycerol at room temperature, the fluorescence yield of CVJ was found to be 3.4 times that of CV. In various alcohols at low temperature and at constant viscosity (32 P), the nonradiative deactivation rate was found to be about twice as large for CV than that for CVJ. Vogel and Rettig attributed this difference to the difference in the volume of the rotating substituted phenyl ring, which was estimated to be 33% larger for the julolidino derivative.[19]

The dynamics of the photoinduced barrierless single bond twisting in triphenylmethane dyes was theoretically treated by Bagchi, Fleming, and Oxtoby (BFO).[10,22] They assumed that the excited-state population diffuses along the torsional potential and relaxes to the ground state with a coordinate-independent radiative decay. Their model predicts nonexponential excited population decays that were reported in a number of experimental studies and viscosity effects that depend on the shape of the sink function used for the nonradiative decay rate. The excited-state dynamics of triphenylmethane dyes was investigated extensively by time-resolved fluorescence spectroscopy and by single-wavelength-probe or continuum-probe transient

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* To whom correspondence should be addressed.

[†] Humboldt-Universität zu Berlin.

[‡] Université de Paris-Sud.

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absorption spectroscopy. Although it is generally admitted that the first-excited-state relaxation process involves the rotational diffusion of the substituted phenyl rings, various interpretations of the experimental observation were given.[1,7−9,11−21,23−28] The interpretation of the present authors is in favor of a barrierless relaxation mechanism of the emissive locally excited (LE) state into a dark twisted conformer in the excited state, with a charge-shifted electronic configuration[14,19−21,23−26] according to Scheme 2

SCHEME 2

$$S_0(\text{eq}) \xrightarrow[\text{abs}]{} S_1(\text{LE}) \xrightarrow[k_1]{} S_1(\text{BCT}) \xrightarrow[k_x]{} S_0(\text{eq})$$

Vogel and Rettig proposed that in the twisted conformer, one of the phenyl rings lies perpendicularly to a plane containing the two others and that the twisted donor (aniline) group bears a full positive charge (radical cation), whereas the rest of the molecule is a neutral radical, hence the terminology “biradicaloid-charge-transfer” (BCT) state for the transient state.[14] For the relaxation mechanism of the transient state down to the equilibrium ground state S_0(eq), Martin et al. suggested that it involves coupled intramolecular high-frequency modes in addition to the phenyl ring motion.[26]

In the present paper, we report a comparative study of the excited-state dynamics of crystal violet (CV) and its julolidino analogue (CVJ), which aims in the first place at confirming and characterizing the presence of a BCT state in these two compounds by transient absorption spectroscopy. Previous fluorescence decay measurements on CVJ were obtained at low temperature[19] and the reaction kinetics are measured herein at room temperature. We focus our interest on the role of the size of the rotating group and of the electron donor−acceptor character of the substituted rings on the formation rate of the transient dark excited state as well as on its deactivation process. Particular attention is paid to the deactivation process, and we propose a new mechanism involving a conical intersection between the excited- and ground-state potential surfaces.

2. Experimental Section

2.1. Pump−Probe Setup. Time-resolved transient absorption and gain spectra were measured by applying the pump-continuum probe technique. The subpicosecond laser source is a non-mode-locked dye laser system developed at Orsay and described elsewhere.[29] Starting from a 6 ns single-seeded Q-switched Nd:YAG laser (10 Hz), the system produces 500 fs pulses (400 μJ/pulse) around 610 nm. A few microjoules (15−17 μJ) of the 610 nm beam was used to excite the sample and a few hundreds to generate the continuum probe after passing through a variable optical delay line. The probe beam was split in two beams, one was directed through the sample, whereas the other was used as a reference. Then, the two were focused on the entrance slit of a polychromator (Jobin-Yvon Spex 270M, entrance slit 64 μm) through optical fibers (600 μm diameter) and simultaneously analyzed with a computer-controlled double-diode array detector (Princeton Instruments, Inc.). The polarization of the pump light was set at the magic angle relative to the polarization of the probe light. Data were accumulated over 500 or 1000 laser shots. The measurements were carried out at room temperature. The time-resolved spectra were corrected in order to take into account the chirp of the probe pulse.

2.2. Samples. Crystal violet (CV) was purchased from Aldrich (A.C.S. Reagent, Cat. #22,928-8) and used without further purification. The analogue CVJ, with julolidino-substituted rings instead of dimethylamino-substituted rings, was prepared in Berlin.[14] The solutions were prepared in *n*-alcohols of increasing viscosity: UV spectroscopy grade ethanol (Uvasol Merck, $\eta = 1.12$ cP), 1-propanol (LiChrosolv Merck, $\eta = 2.2$ cP), and 1-butanol (Uvasol Merck, $\eta = 2.9$ cP). Because of the small quantity of CVJ available, only a few milliliters of solution were prepared and used in a 1 mm non-recirculating cell for the pump−probe experiments. The concentration was fixed to have an optical density between 0.3 and 1 at the excitation wavelength. Solutions of CVJ could not be prepared in solvents more viscous than butanol because of its low solubility. CV samples were studied under the same conditions. The sample absorption spectrum was checked during and after the experiment.

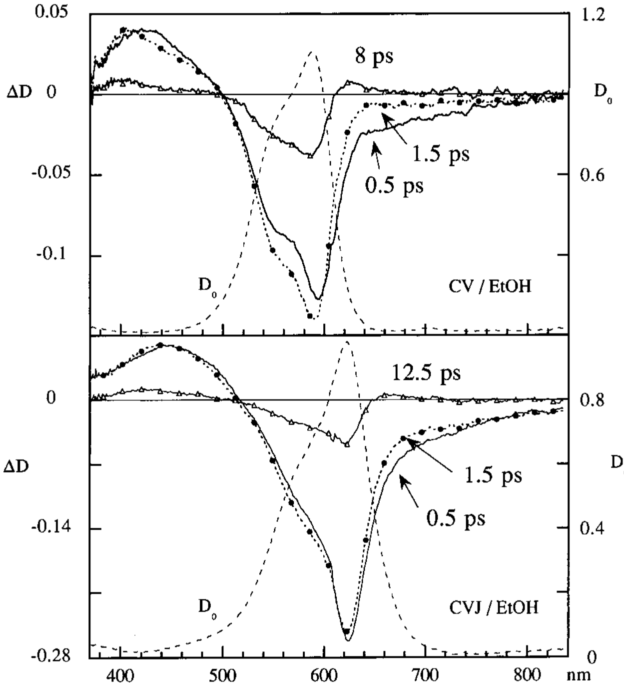

Figure 1. Time-resolved differential absorption spectra ($\Delta D(t)$, left scale) of crystal violet (CV, up) and its julolidino analogue (CVJ, down) in ethanol under subpicosecond excitation at 610 nm. Unexcited sample absorption (D_0, dotted line, right scale).

3. Results

3.1. Time-Resolved Absorption Spectra. Figure 1 shows the time-resolved differential absorption spectra $\Delta D(t)$ for crystal violet (CV) and its julolidino derivative (CVJ) in ethanol, between 370 and 840 nm. The ground-state absorption spectra are given in the figures in order to situate the three regions, where either transient absorption ($\Delta D > 0$), bleaching or gain ($\Delta D < 0$) is dominant. Since the ground-state absorption peak of CVJ is red-shifted from that of CV by about 30 nm, the regions, where gain is dominant ($\Delta D < 0$ and no ground-state absorption) are observed for wavelengths longer than 700 and 640 nm, respectively. A transient absorption band is observed below 500 nm for both compounds. After the initial growth from the pumping (not given in the figure), the time-resolved spectra show a fast decrease of the gain band together with an increase of $|\Delta D|$ both in the blue edge of the bleaching band and in the blue edge of the transient absorption band. Afterward, the whole ΔD spectrum decays, except in the red edge of the ground-state absorption spectrum where a weak transient absorption replaces the gain signal and then vanishes. This trend is observed for both CV and CVJ; nevertheless, the early spectral changes in the transient absorption and bleaching bands are less

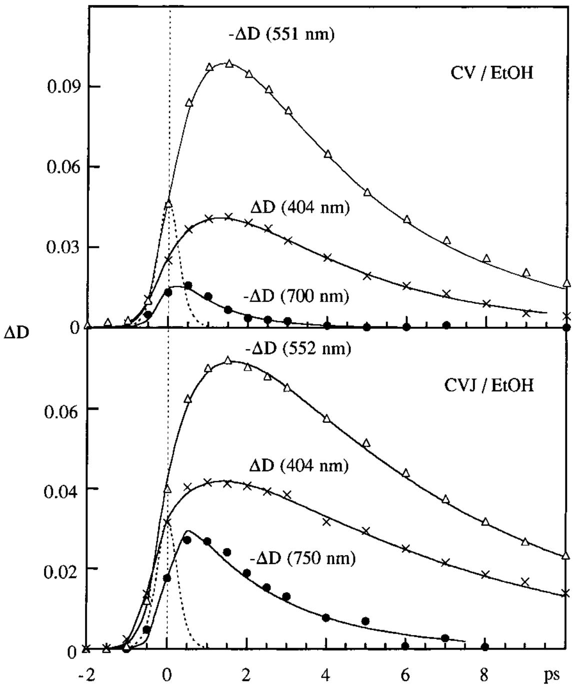

Figure 2. Experimental (●, △, ×) and fitted (curves) kinetics of the time-resolved differential absorption ($\Delta D(t)$) observed at selected wavelengths for crystal violet (CV, up) and its julolidino analogue (CVJ, down) in ethanol after subpicosecond excitation at 610 nm. The pump−probe cross-correlation function is given in the dotted line.

pronounced for the julolidino derivative. The transient absorption band that appears at long delays on the red edge of the ground-state absorption spectrum is also weaker for CVJ. In 1-propanol and 1-butanol, similar changes are observed at a slower rate. The final red-edge band is not clearly seen for CVJ in 1-butanol.

3.2. Kinetics at Selected Wavelengths. Figure 2 shows the time-resolved differential absorption $\Delta D(t)$ measured at selected wavelengths for CV and CVJ solutions in ethanol. The wavelengths were chosen in the gain band, in the blue side of the transient absorption band, and in the blue side of the bleaching band in order to emphasize the spectral changes described previously. The short-time decays were fitted with exponential functions reconvoluted with the pump-probe cross-correlation function shown in a dotted line in the figures. The cross-correlation function was derived from the initial rise of the signal around 450 nm for CVJ in butanol, where almost no spectral change is observed in the first picoseconds; it was fitted by a hyperbolic square secant with a full width at half maximum (fwhm) of about 600 fs. For long-time decays, the fits were completed with commercial software (Kaleidagraph) without reconvolution of the instrument response. In the net gain band (700−750 nm), the decays can be fitted with a one-exponential decay, whereas the difference of two exponential functions are needed at the other two wavelengths (404−424 nm, depending upon the solvent and around 550 nm), except for CVJ in butanol where a single exponential decay can reasonably be used to describe the change in $\Delta D(t)$ in the blue edge of the bleaching band. The parameters of the best fits of the $\Delta D(t)$ curves are given in Table 1 for CV and CVJ in ethanol, propanol, and butanol.

4. Discussion

4.1. Time-Resolved Spectra and Molecular Mechanism: Internal Rotation with Charge Shift. The spectral changes observed at both short and long times for CV and CVJ are very similar to those we previously reported for ethyl violet[21,23−26] and amino−rhodamine[25,26,30] (a crystal violet analogue where two of the three dimethylamino-substituted phenyl rings are bonded with an oxygen atom to form a xanthenic chromophore,[31] the third substituted-phenyl ring being free to rotate like in CV). The fast decay of the gain signal followed by a residual transient absorption in the red edge of the ground-state absorption was reported previously in single-wavelength probe studies.[9,13,32] The fast decay of the gain signal indicates the fast depopulation of the initially excited state. The apparently delayed bleaching in the short wavelength edge of the ground-state absorption was first reported, with different kinetics, for ethyl violet[21] as well as the fast change in shape of the transient absorption bands, with a delayed increase of the blue edge of the band.[21,23,24] The apparent "delayed bleaching" signal at short pump−probe delays was attributed to the decay of the initially excited-state population, the absorption of which overlaps that of the ground state.[21] Both the rising signal in the blue edge of the transient absorption band and the weak residual transient absorption in the red edge of the ground state were attributed previously to a dark photoproduct in experiments carried out with ethyl violet and amino−rhodamine.[21,23−26,30] From the present time-resolved absorption spectra, one may conclude that a similar fast nonradiative process occurs in CV and CVJ, leading to the formation of a transient dark state. For ethyl violet, the absorption cross sections of the initially excited state (LE state) and of the transient dark state were extracted tentatively from the time-resolved differential absorption spectra.[24] The spectrum of the transient state was found to be roughly similar to the absorption spectrum of the LE state, with two bands between 380 and 700 nm, but shifted to higher energies. Such a similarity and blue shift were taken as an indication that the transient state was a distorted excited state (Scheme 2), with a strongly reduced radiative rate, rather than a distorted ground state, as was suggested in another study.[9] A transient ground state with a distorted geometry would not be expected to absorb in the red side of the stable ground state that has a nearly flat propeller geometry, since a blue shift is expected when one reduces the π-electron delocalization length of a conjugated system. It cannot be ruled out completely that this twisted ground state is excited vibrationally, thus explaining the red absorption, but a similar hypothesis involving a nontwisted ground state [32] was discarded previously since the vibrational cooling time is not expected to depend on the solvent viscosity.[24] The viscosity and rotor size effects that we are observing in the present study and will discuss in details in the next sections are strong indications that the internal twisting dynamics dominates not only the formation but also the decay of the transient-state kinetics. No evidence of a vibrational cooling was found in this latter process, neither as a temporally identifiable kinetics nor as a spectral shift. We will, thus, favor the transient excited state interpretation.

Previous fluorescence decay or quantum yield measurements of various bridged and unbridged TPM dyes[14,19,20] showed that a flexible substituted phenyl ring with a certain electron donor potential (in most cases, an anilino or dialkylanilino group) has to be present to observe the fluorescence quenching; its transformation into an anilinium or into a phenyl group takes away the possibility for the nonradiative process to occur. For bridged compounds where all aniline-type donors are held planar, the quenching is absent. For example, the bridged derivative of crystal violet CVB with one rotatable aniline group and two planar ones is weakly fluorescent, whereas the bridged derivative of malachite green MGB which has one rotatable

TABLE 1: Time Components (τ_1 and τ_2)[a] Obtained from the Fit, with a Monoexponential or a Two-Exponential Function, of the Time-Resolved Differential Absorption $\Delta D(t)$) Observed at Selected Wavelengths, for Crystal Violet (CV, up) and Its Julolidino Analogue (CVJ, down) in Solvents of Increasing Viscosity (η)

		ethanol (1.2 cP)				propanol (2.2 cP)				butanol (2.9 cP)			
		404 nm	552 nm	700 nm	$\langle\tau\rangle$	407 nm	550 nm	700 nm	$\langle\tau\rangle$	405 nm	550 nm	700 nm	$\langle\tau\rangle$
CV	τ_1 (ps)	$1.1^b \pm 0.2$	$0.9^b \pm 0.2$	1.2 ± 0.2	1.1	$1.2^b \pm 0.2$	$0.9^b \pm 0.2$	1.7 ± 0.2	1.3	$3.0^b \pm 0.5$	$2.0^b \pm 0.5$	3.9 ± 0.5	3.0
	τ_2 (ps)	3.5 ± 0.5	4.0 ± 0.5		3.7	7.2 ± 1.0	7.4 ± 1.0		7.3	7.0 ± 1.0	7.0 ± 1.0		7.0

		ethanol (1.2 cP)				propanol (2.2 cP)				butanol (2.9 cP)			
		404 nm	552 nm	700 nm	$\langle\tau\rangle$	424 nm	550 nm	700 nm	$\langle\tau\rangle$	423 nm	550 nm	700 nm	$\langle\tau\rangle$
CVJ	τ_1 (ps)	$1.2^b \pm 0.2$	$1.1^b \pm 0.2$	2.1 ± 0.2	1.5	$2.0^b \pm 0.4$	$1.5^b \pm 0.3$	4.0 ± 0.3	2.5	$5.0^b \pm 1.0$		$6.2^b \pm 1.0$	5.6
	τ_2 (ps)	6.5 ± 0.5	6.5 ± 0.5		6.5	13 ± 2	12.5 ± 2		13	14 ± 2	17 ± 2		16.5

[a] The average values of τ_1 and τ_2 in each solvent are given by $\langle\tau\rangle$. [b] Correspond to a rising exponential function.

unsubstituted phenyl group and two planar aniline groups is fluorescent. It was, thus, concluded that the nonradiative process is linked with the transfer of an electron from the anilino donor to the remaining moiety and with an internal twisting motion. The strong fluorescence quenching was explained by the fact that the twisting relaxation occurs from a near planar LE-type geometry toward a twisted geometry[14] with an intrinsically lower transition moment (but not necessarily completely nonfluorescent, as evidenced for the related charged molecules,[33,34] which further supports the idea that the transient state is electronically excited). On the other hand, protonation of the donor site in amino−rhodamine (which can be viewed as an oxygen-bridged derivative of CV) by hydrochloric acid was shown to increase drastically the fluorescence yield [30,31] and to block [25,26,30] the fast spectral changes shown in Figure 1. From the present study, one can, thus, conclude that an adiabatic reaction involving not only the rotation of the phenyl rings but also an intramolecular charge shift from the dimethylamino substituents to the central carbon (Scheme 2) occurs also in CV and in its julolidino derivative.

4.2. Formation Rate of the Transient Dark State: Solvent-Viscosity, Rotor Size, and Substituent Effects. *(a) Photoinduced Reaction Kinetics.* Assuming that a dark state is formed directly from the initially excited fluorescent state, the reaction rate may be probed either from the decay of the gain signal or from the rise time of the dark state absorption band (blue edge of the transient absorption band). It can also be given by the delayed rise time of the bleaching in the blue edge of the ground-state absorption. In Figure 2 and in Table 1, it is seen that the reaction kinetics can be described approximately by a single-exponential function with a time constant ranging from 1.1 to 3.0 ps, depending on the solvent, for CV and from 1.5 to 5.6 ps for CVJ. Similar results were reported in early transient absorption measurements of CV,[13,15] except for the rising differential absorption in the blue edge of the transient absorption band, which was not observed because the transient absorption band at wavelengths below 500 nm was assumed to be due to a single species. This assumption led the authors to consider the photoinduced process as a barrierless internal twisting along a single excited electronic state potential.[13,15−17] In previous studies reported by some of the present authors, exponential kinetics could also reasonably fit the transient absorption data at selected wavelengths for ethyl violet and amino−rhodamine in low viscosity solvents, whereas nonexponential fluorescence and gain decays were observed for these two compounds in decanol[21,23,25,30] in agreement with the predictions of the theoretical models for photoinduced barrierless reactions.[10,22]

In the present study, the apparent monoexponential reaction kinetics does not preclude the existence of subpicosecond components that cannot be resolved by the experimental setup. However, it must be noted that for both CV and CVJ the rise time of the delayed bleaching signal is found to be slightly shorter than that of the blue edge of the transient absorption band, which is itself shorter than the gain decay time. In most cases, the discrepancy between the time components falls roughly within the experimental error, but for CVJ in ethanol and in propanol the gain decay time is found to be about twice as long as for the corresponding rise time in the blue edge of the transient absorption band. The reason for these differences remains unclear to us. Furthermore (not indicated in the table), the gain decay time was found to increase slightly with the observation wavelength. For wavelengths above 720 nm, the fits might, nevertheless, not be reliable because of the weakness of the signal. Such a wavelength-dependent gain decay time is expected for a barrierless reaction[35] since a given wavelength probes the motion of the excited-state population along the potential surface through a narrow observation window. This was indeed observed in a recent femtosecond fluorescence up-conversion study of the diphenylmethane dye auramine,[36] which is thought to undergo similar photoinduced processes.

(b) Solvent Viscosity Effect. From Table 1, it can be seen that for both CV and CVJ, the gain decay time and the transient-state rise time increase nonlinearly with the viscosity. Taking the average value $\langle\tau\rangle$ given in the table, the variation of the fluorescent excited-state lifetime in the 1−3 cP (narrow) range of solvent viscosity cannot be fit accurately with a power function but a very rough tentative fit leads to an exponent larger than 1. Furthermore, one observes a steeper initial increase for CVJ than for CV. These observations were not previously reported.

(c) Rotor Size and Substituent Effects. The fact that the reaction is slower in the julolidino derivative in all solvents is in agreement with previous fluorescence yield determinations[14] and fluorescence decay measurements at low temperature.[19] The average excited-state reaction time ($\langle\tau\rangle$) is 1.4 times larger for CVJ than that for CV in ethanol, which is roughly equal to the estimated increase of the volume of the rotating substituted phenyl,[19] as expected by a simple friction effect. In propanol and in butanol, the increase of the reaction time reaches a factor of 1.9. This could be accounted for, following the BFO model,[10,22] by the shape of the reaction potential. Since a lower torsional frequency, and, thus, a flatter torsional potential is expected for CVJ than for CV, one may expect a slower spreading of the excited-state population on the excited-state potential. The same arguments hold to explain the slower reaction rate[23,25,26] (4 ps) of EV in ethanol. Furthermore, if the reaction path results from the adiabatic electronic coupling of a locally excited fluorescent state and a dark twisted charge-transfer state, the shape of the potential depends also on the

free energy of the transient-state formation reaction (ΔG). In a crude comparison, considering that the julolidino-substituent is the best electron donor among the three amino substituents, one might expect a larger $|\Delta G|$, i.e., a faster reaction for CVJ. The reaction is indeed about 3 times faster for CVJ than that for EV, which is expected to have the smaller $|\Delta G|$ in addition to the larger rotor. The reaction is even slightly faster for CV than for CVJ despite a smaller $|\Delta G|$, but CV has a smaller rotor than CVJ. These results strongly suggest that both the internal twisting motion and the donor−acceptor properties of the substituents determine the reaction but that the twisting motion dominates the kinetics, in agreement with previous conclusions from fluorescence lifetime studies[14,19,20] of the sequence of TPM compounds $C^+(Ar)_3$ with Ar = aniline (pararosaniline) showing the fastest reaction, and Ar = dimethylaniline (CV) and julolidine (CVJ) being subsequently slower. If $|\Delta G|$ were the key parameter, as in the Marcus-type forward electron transfer, the order should be the reverse because aniline is a weaker donor than dimethylaniline and julolidine.

4.3. Deactivation Process of the Transient Dark State, Internal Conversion, Back Charge Transfer, and Phenyl Ring Rotation. In Table 1, it is seen that the same long-time component (τ_2) is found for the decay of the differential absorption when probing both in the transient absorption band and in the bleaching band. τ_2 is attributed to the decay of the transient state back to the ground state. The values found for CV are in good agreement with previously published data.[13,15] The increase of τ_2 with the solvent viscosity is slightly sublinear for CV and roughly linear for CVJ. A sublinear increase of the nonradiative relaxation rate with the solvent viscosity was reported by Sundström and Gillbro[11] for CV and EV in a viscosity range reaching 30 cP, from ground-state absorption recovery measurements. Assuming that the transient absorption below 500 nm is due to a single species, Ben-Amotz et al.[17] reported a linear increase of the excited-state decay rate of CV with the viscosity up to 500 cP and used the prediction of several models of diffusive large amplitude motion to explain their observation. According to our own relaxation model, one can think that the viscosity effect found in these studies applies to the dark transient-state relaxation and not to the decay of the initially excited state. The decay rate of the dark twisted transient state is less sensitive to the solvent viscosity than its formation rate as already noted for ethyl violet [21] and auramine.[36] The increase of the transient-state decay time, with both increasing solvent viscosity and increasing rotor size, indicate a further large-amplitude motion for the transition to the ground state. One could argue that this might be the donor motion in the S_1(BCT) state away from perpendicularity but, first, this motion would be thermodynamically unfavorable since S_1(BCT) is supposed to be a local minimum, and second, a barrier crossing to the ground state, in the Marcus inverted region without tunneling through coupled internal modes, is unlikely to lead to very fast nonradiative decays. Actually, Martin et al. previously proposed[26] a molecular relaxation scheme, where the decay of the charge-transfer state back to the ground state involves internal conversion via intramolecular high-frequency modes, in addition to the phenyl-ring torsional motion. As a matter of fact, in ethanol, the decay rate of the twisted charge-transfer state was found to decrease exponentially when the free energy change of the back reaction increases, from EV (∼7 ps) to amino−rhodamine (∼13 ps) and auramine (∼30 ps), as in the case of electron-transfer reactions in the Marcus inverted regime.[26,37,38] If the observed relationship were not accidental, then it would mean that the internal conversion process would be the rate-limiting step of the ground-state repopulation process. One of the drawbacks of this explanation is that it seems limited to fluid solvents and fails in simply describing the strong viscosity effect found on the back reaction. A second difficulty arises when examining the behavior of EV, CV, and CVJ in ethanol within this context. If the $|\Delta G|$ of the CT state formation reaction is assumed to increase from EV to CV and to CVJ because of the increase in the donor character of the substituent, the CT-state energy should decrease and, according to a nonradiative transition like energy gap law, the CT state decay should be faster and faster. This is indeed true when going from EV (7 ps) to CV (3.7 ps) in ethanol but not for CVJ (6.5 ps), which exhibits a deactivation rate close to that in EV. As an alternative to this picture, it may be convenient to postulate a unique point on a multidimensional reaction hypersurface, leading to a surface touching of the S_0 and S_1 adiabatic states, namely, a conical intersection (C.I.). Many well known photochemical reactions follow pathways necessitating several large-amplitude coordinates typically connected with C.I.s. As an example, the C.I. for butadiene may be cited, which is well-characterized by large-scale ab initio calculations:[39,40] the geometry of the C.I. (the “photochemical funnel”[41−43]) involves not one but three twisted bonds, resulting in four uncoupled orbitals (or radical sites). C.I.s have been shown to be able to provide the mechanism for internal conversion processes on the femtosecond time scale.[44] They have been suggested to be at the basis of many ultrafast excited-state decay processes, such as isomerization of polyenes, polyenals, and their Schiff bases (including the visual process),[39,40,45,46] and they have been used for a mechanistic explanation of fast internal conversion processes. In this model, internal conversion is not the nonradiative S_1-S_0 decay of a rigid conformation but the photochemistry along various intramolecular dimensions, allowing a continuous transition from S_1 to S_0 without energy gap.[47] In light of this model, we propose a C.I. for the TPM dyes, as indicated in Scheme 3, involving the rotation around a further flexible bond.

SCHEME 3

$$S_0(\text{eq}) \xrightarrow[\text{abs}]{} S_1(\text{LE}) \xrightarrow[k_1]{} S_1(\text{BCT}) \xrightarrow[k_x]{} \text{C.I.(BCT)}/S_0(\text{FC}) \xrightarrow[k_0]{} S_0(\text{eq})$$

Given the bridged amino groups in CVJ, this can only be the rotation of one of the two flexible julolidino groups in the acceptor neutral radical moiety of this compound, leading to a second twisted bond: whether the C.I. really looks like that will be the subject of further mechanistic studies of both experimental and theoretical nature. This scheme presents the advantage of satisfactorily describing the viscosity behavior of the transient-state decay and its remarkable high speed. Furthermore, it has an important corollary: S_1(BCT) does not decay directly to the ground state but through an intermediate (C.I.), and the ground-state reached (S_0(FC)) is far away from the equilibrium-ground-state conformation. Given that there is no experimental evidence that the ground-state recovery is slower than the decay of S_1(BCT), we, therefore, have to assume that the ensuing ground-state relaxation (rate constant k_0) is much faster than k_x. This is consistent with an energetic model, where S_1(FC), S_1(BCT), and C.I. are not far energetically, and most of the energy changes occur in the ground state.[13] The question of whether this model accounts correctly for the energy gap law found in ethanol still remains to be clarified.

5. Conclusion

The transient absorption and gain spectra measured in alcoholic solutions of crystal violet and its julolidino derivative exhibit time-resolved changes that are interpreted by a photoinduced process, involving both phenyl-ring torsional motion and charge shift from the amino-group of the phenyl substituent to the central carbon. The rate of the photoinduced process is lower in the julolidino derivative and, for both compounds, decreases when the solvent viscosity increases. The kinetics and the solvent viscosity effect are discussed by assuming a barrierless adiabatic photoreaction, resulting from the electronic coupling between the fluorescent locally excited state and a dark twisted charge-transfer state and by considering a potential shape that depends both on the phenyl-ring torsional frequency and on the free energy of the charge-shift reaction, i.e., the electron donor−acceptor character of the substituted phenyl rings. The analysis of the data allowed us to conclude that the twisting motion dominates the kinetics. On the other hand, the relaxation of the transient state back to the equilibrium ground state is also found to be slowed when the solvent viscosity increases, but this viscosity effect is smaller than that on its formation rate. Moreover, this relaxation is slower for the compound with the larger rotating groups (CVJ). These observations are considered as an indication of a further large-amplitude motion on the excited-state potential. A relaxation mechanism via a conical intersection between the S_1 and S_0 potential surfaces, involving torsional motion of two of the phenyl rings, is proposed.

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