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Picosecond Absorption Spectroscopy of Polymethine Cis-Trans Isomerization

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Results are presented of time resolved fluorescence and absorption investigations of DDEOCI (3,3'-diethyl-6,6'-diphenyl-9-ethyl-oxacarbocyanine iodide) in solvents which differ in polarity and viscosity. The measured picosecond absorption and fluorescence kinetics probed at various wavelengths of the polymethine dye studied can be fitted to a double exponential decay with a minor fast component of lifetime τ_1 and a major slower component of lifetime τ_2 . Furthermore, probing in the $S_1 \leftarrow S_0$ absorption region and in the fluorescence region results in a residual with a lifetime of some ns and belonging to the detected red-shifted photoisomer with a low quantum yield ($\phi < 10\%$). The lifetime and the preexponential factors of the two components are in methanolic solution unaffected by changes of the anion.

The detected two picosecond lifetime components are supposed to belong to two isomeric species (all-trans and mono-cis isomer) with strongly overlapping absorption spectra.

KEY WORDS: Picosecond; absorption spectroscopy; cis-trans isomerization; polymethine.

INTRODUCTION

The trans-cis isomerization is a reversible process involving a photochemical induced excited state process of changing the dihedral angle

between different parts of a molecule around a double bond, deactivation of the excited state species to the ground state isomer forms followed by a thermal back reaction to the trans isomer (or reverse). The activation energy for the thermal reverse reaction is strongly dependent on the rigidity of the molecule and the bond order involved in the ground state showing energies from a few kT (polymethines) to more than 200 kJ/mol (stilbene). A model for the isomerization mechanism was proposed by Orlandi and Siebrand¹ as well as by Rulliere,² who started for analysis of experimental results.

The molecule is excited by light absorption to the spectroscopic minimum of the first excited singlet state (see Figure 1). The trans S_1 -state and a near 90° twisted conformation of motion of large molecular fragments are separated by a potential barrier E_0 with an activation energy of 20 kJ/mole or less. The molecule very quickly overcomes the barrier and a potential minimum near the 90° twisting angle of the molecular fragments in the excited state is attained, indicated in Figure 1 by the rate constant k_1 . In case of the cis-trans isomerization of stilbene Hochstrasser *et al.*³ measured this step to be 1.4 ps. This minimum is the starting point for effective non-radiative deactivation k_2 (through a "funnel," Smedartshina⁴) to the ground state potential energy surface. Though theoretically possible there is

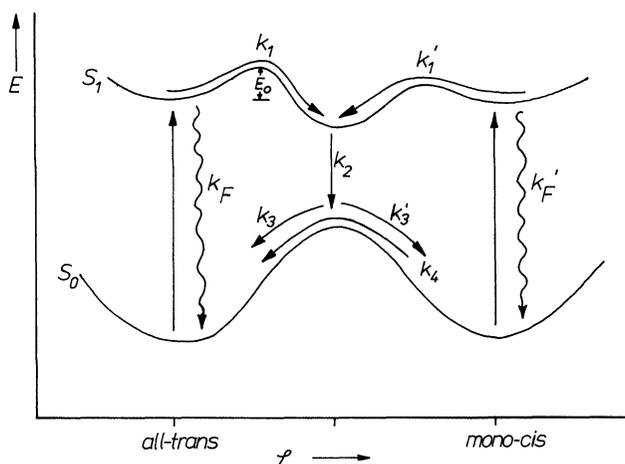


Figure 1 Excited state potential energy surface model for the interpretation of polymethine photoisomerization.

only scarce⁵ experimental evidence that stable ground state species of 90° twisting angle of the molecular fragments do exist. Probably, the twisted molecules in the excited state immediately relax to either trans or cis ground state conformation k_3 and k_3' , respectively. The shape of the ground state potential curve is responsible for the pathway of the thermal back reaction k_4 . In the case of isomerization of cyanine dyes the reaction pathway to the trans isomer is connected with a smaller barrier than the pathway to the cis isomer, for steric reasons.⁶ Therefore, the thermally induced ground state back reaction k_4 is favoured in the direction towards the trans isomer.⁷⁻⁹

For the cis isomer an absorption band is observed which is generally red-shifted with respect to the trans isomer but also the reverse situation has been found experimentally.^{8,9} Experimentally intense light absorption of the photoisomer was observed, which is of the same order of magnitude as for the trans isomer.¹⁰ The photoisomerization of cyanine dyes is a typical example for molecules the electronic relaxation mechanism of which involves internal large amplitude motion. The rate of large amplitude motion depends critically on the kind of frictional forces exerted by the solvent molecules on the rotating group. Size and shape of the relaxing group, as well as nature of the solvent are determining the friction.

Moreover, the large amplitude motion can be viewed as a translational or rotational motion, or a mixture of both. Which one is active in the relaxation process is probably important for the interaction between the moving group and the solvent molecules. In the light of these considerations it is interesting to investigate the influence of various solvent parameters on the lifetime of the excited S_1 -state of such molecules. In all cases the interaction with the solvent determines the rate constants of such deactivation processes.^{11,12} Usually the attempts to describe the solvent dependence of the deactivation of the S_1 -state correlate the viscosity within a homologous series of alcohols with the deactivation rates from the S_1 -state.¹³⁻¹⁵ Isoviscosity investigations¹⁶ as well as investigations in less polar solvents¹⁷ have shown that the polarity of the solvent essentially affects the deactivation behaviour of polymethines. For this reason we have included less polar solvents in our investigations of the isomerization process of a polymethine dye.

In some cases mixtures of different isomers with overlapping absorption spectra do already exist in the ground state^{18,19} as it is the

case in rotations around single bonds. Such a behaviour is expected if the ground state is by sterically reasons nonplanar and so various ground state conformations are favoured. Then excitation of different isomers to the common twisted 90° S_1 state leads to a more complicated picture. Instead of single exponential deactivation decay which is normally observed for isomerization reactions, then appear multiexponential decays. The lifetime of the photoisomer having values usually in the nanosecond to microsecond region is drastically shortened.^{18,20,21}

2. EXPERIMENTAL

The dye 3,3'-diethyl-6,6'-diphenyl-9-ethyl-oxacarbocyanine iodide (abbr. DDEOCI) was purified several times by column chromatography and by recrystallization from methanolic solution. The experiments were made with a pump-and-probe pulse spectrometer which has been described in detail elsewhere.²² The samples were excited by 490 nm pump pulses and probed at different wavelength regions (ground state recovery $\lambda_{\text{probe}} = 508$ nm, $S_1 \rightarrow S_n$ absorption $\lambda_{\text{probe}} = 426$ nm, probe pulse amplification by fluorescence $\lambda_{\text{probe}} = 549$ nm) (see Figure 2).

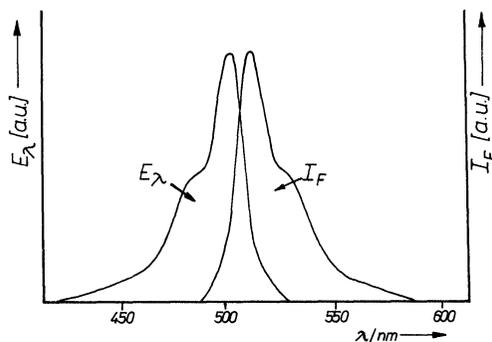


Figure 2 Absorption and fluorescence spectra of DDEOCI in methanolic solution ($c = 5 \cdot 10^{-7}$ mol/l).

The absence of an excitation energy dependence was proved by measurement at different excitation energies. No evidence was found for excitation energy dependent lifetime components or spectral

changes. Aggregation effects were excluded by using very low concentrations (10^{-6} molar) as well as test measurements at different concentrations.

The fitting procedure of the lifetime components to the experimental curves were done with the help of the ALAU-program.²³

3. RESULTS AND DISCUSSION

The results of the absorption investigations are shown in Figures 3 and 4 and summarized in Table I and Table II.

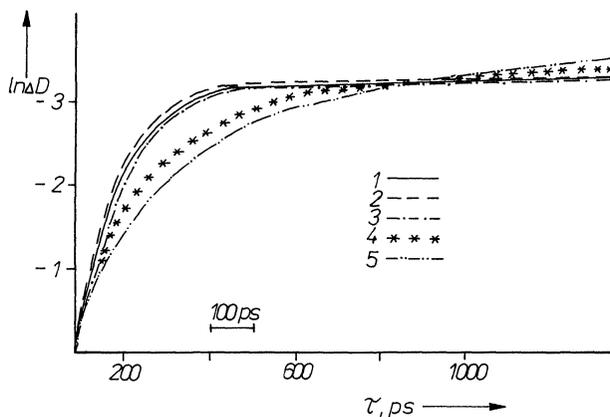


Figure 3 Absorption kinetics of DDEOCI in different solvents at probe wavelength 508 nm 1—acetone, 2—methanol, 3—acetonitrile, 4—ethanol, 5—dimethylsulfoxid (DMSO).

In Figure 3 the ground state recovery kinetics of DDEOCI in different solvents is depicted. Whereas the recovery kinetics in methanol, acetone and acetonitrile are very similar, the recovery kinetics in more viscous (ethanol) and less polar solvents (DMSO) become less steep.

The absorption kinetics in the $S_n \leftarrow S_1$ absorption region are double exponential with two picosecond components (see Table II).

The measured absorption kinetics of DDEOCI can in the absorption ($\lambda_{pr} = 508$ nm) (Figure 3) and fluorescence region ($\lambda_{pr} = 549$ nm) be fitted to a triple exponential decay with two time components having ps

decay times and a residual having nanosecond decay kinetics by means of the Eq. (1) (for DDEOCI in toluene see Figure 4).

$$D = A \exp(-t/\tau_1) + B \exp(-t/\tau_2) + C \exp(-t/\tau_3) \quad (1)$$

Whereas the residual belongs to a long-living photoisomer,^{24,25} the two ps components should be attributed to the existence of two ground state species having different relaxation rates. This is in accordance with the presumption of two different fluorescence states indicated by our streak-camera measurements.²⁶

Whereas in methanolic solution the effect of the anion on the two components is within the experimental error (see Table I), the detected lifetimes strongly depend on the solvent. The detected τ_2 -values in the fluorescence region ($\lambda_{\text{probe}} = 549 \text{ nm}$) as a function of the solvent agree very well with previous fluorescence lifetime investigations.^{26,17} Although the time resolution of the fluorescence measurements was not sufficient to detect both components it was however already obvious from this measurements that a second shorter component exists.

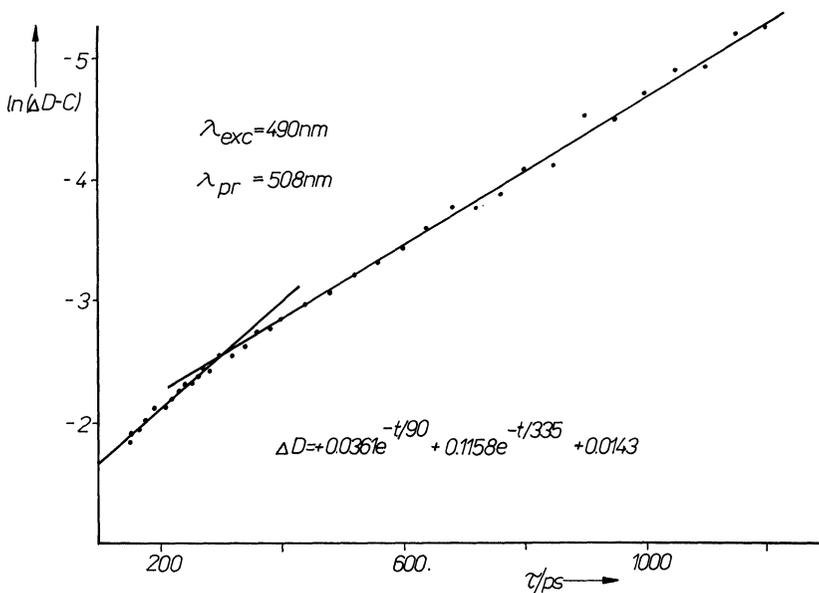


Figure 4 Absorption kinetics of DDEOCI in toluene $\lambda_{\text{pr}} = 508 \text{ nm}$.

Table I Results of ps absorption measurements of the investigated dye with different anions in methanol.

Anion	$\lambda_{\text{probe}} = 426 \text{ nm}$		$\lambda_{\text{probe}} = 508 \text{ nm}$		$\lambda_{\text{probe}} = 549 \text{ nm}$	
	τ_1 (ps)	τ_2 (ps)	τ_1 (ps)	τ_2 (ps)	τ_1 (ps)	τ^2 (ps)
I ⁻	14	50	17	51	16	50
Br ⁻	15	48	14	49	12	49
Cl ⁻	12	50	13	48	15	48
C ₂ H ₅ SO ₄ ⁻	21	48	13	49	18	50
SCN ⁻	16	49	18	50	13	48
TPB ⁻	18	49	14	51	12	50
ClO ₄ ⁻	11	52	16	49	16	52

$$\bar{\tau}_1 = 16 \pm 5 \text{ ps} \quad \bar{\tau}_2 = 50 \pm 4 \text{ ps}$$

The solvent dependence of the calculated components agrees with the previous discussed influence of solvent parameters upon the deactivation of polymethines.¹⁷ Within the experimental error no significant difference in the solvent dependence between the τ_1 and τ_2 values was found (see Table II).

In our experiment the τ_3 -values could only be estimated within the order of magnitude because the upper limit for the delay times was about 1.5 ns (given by the decreasing signal/noise ratio). The rate $C/(A + B + C)$ was in all cases less than 0.1. In polar low viscous solvents the third component was estimated to be 2.5 ns and it is higher in less polar solvents (DMSO, toluene).

The origin of the two detected fluorescent species is supposed to represent two isomer states of the investigated polymethine dye existing already in the ground state. Polymethine dyes are normally planar existing in the all-trans conformation. Substitution of the

Table II Results of ps absorption investigations of DDEOCI at different probe wavelengths ($\lambda_{\text{pump}} = 490 \text{ nm}$).

Solvent	$\lambda_{\text{probe}} = 426 \text{ nm}$		$\lambda_{\text{probe}} = 508 \text{ nm}$		$\lambda_{\text{probe}} = 549 \text{ nm}$	
	τ_1 (ps)	τ_2 (ps)	τ_1 (ps)	τ_2 (ps)	τ_1 (ps)	τ_2 (ps)
Methanol	14	50	17	51	16	50
Ethanol	30	87	32	86	34	88
Acetone	15	40	17	43	16	42
Acetonitrile	15	44	15	48	15	52
DMSO	47	192	43	192	44	193
Toluene	60	340	50	335	62	340

hydrogen atom for methyl or ethyl groups within the polymethine chain leads to sterical hindrance of the heterocyclic rings resulting in an out-of-plane twisting of the linking polymethine chain. In this case the thermodynamical preference of the all-trans configuration is lost.²⁷ Knudtson and Eyring¹⁹ have shown that sterically hindered polymethines exist in at least two isomer states in the ground state with more or less overlapping spectra. The existence of two ground state isomers is confirmed by low temperature absorption measurements.²⁸ From theoretical calculations as well as experimental results^{16,29} the second ground state isomer is supposed to be a mono-cis isomer (Figure 5).

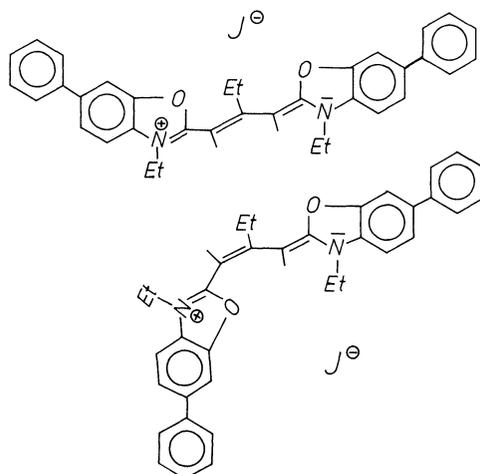


Figure 5 Supposed isomer conformation in DDEOCl.

The results are interpreted in an excited state potential surface model based on the Rulliere model² depicted in Figure 1.

In this model both isomers are excited to their S_1 -state and relax to an intermediate state at an intermediate twisting angle between the two isomers through a large amplitude motion. In our case the S_1 potential energy surface has different barrier heights between the various isomer conformations.¹⁷ The different deactivation rate of the two components are the reason for the assumption of different barrier heights between the two excited states. The excited state barrier height E_0 of the nonradiative deactivation pathway via k_1 of the slow component was calculated to 16.2 kJ/mole from other experiments.¹⁷ The

faster S_1 state deactivation of the mono-cis isomer leads to the assumption of lower excited state barrier height for this reaction pathway k_1' as indicated in Figure 1.

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References

1. G. Orlandi and W. Siebrand, *Chem. Phys. Lett.* **30**, 352 (1975).
2. C. Rulliere, *Chem. Phys. Lett.* **43**, 303 (1976).
3. F. E. Doany, R. M. Hochstrasser, B. I. Greene and R. R. Millard, *Chem. Phys. Lett.* **118**, 1 (1985).
4. Z. Smedartchina, *Chem. Phys. Lett.* **113**, 307 (1985).
5. R. Bonneau, P. F. deViolet and J. Jousot-Dubien, *Nouv. J. Chem.* **1**, 31 (1977).
6. F. Dietz, W. Förster, C. Weiss, A. Tadjer and N. Tyutyulkov, *J. Signal AM.* **9**, 177 (1981).
7. D. N. Dempster, T. Morrow, R. Rankin and G. F. Thompson, *J. Chem. Soc. Faraday II* **68**, 1479 (1972).
8. M. Arvis and J. C. Mialocq, *J. Chem. Soc. Faraday II* **75**, 415 (1979).
9. Y. U. I. Lifanov, V. A. Kuzmin, A. K. Chibisov, I. J. Levkoev and A. V. Karjakin, *Z. Pr. Spekt.* **20**, 21 (1974).
10. S. Rentsch, R. Danelius and R. Gadonas, *J. Signal Rec. Mat.* **12**, 319 (1984).
11. K. Berndt, E. Klose, P. Schwarz, K.-H. Feller and D. Fassler, *Z. phys. Chemie (Leipzig)* **266**, 2 (1985).
12. J. Jaraudias, *J. Photochem.* **13**, 35 (1980).
13. S. P. Velsko and G. R. Fleming, *Chem. Phys.* **65**, 59 (1982).
14. B. Wilhelmi, *Chem. Phys.* **66**, 351 (1982).
15. M. Kaschke, J. Kleinschmidt and B. Wilhelmi, *Laser Chem.* **5**, 119 (1984).
16. V. Sundström and T. Gillbro, *J. Chem. Phys.* **81**, 3463 (1984).
17. K.-H. Feller, K. Berndt and H. Dürr, *Exp. Techn. Phys.* **35**, 57 (1987).
18. D. F. O'Brien, T. M. Kelly and L. F. Costa, *Photogr. Sci. Eng.* **18**, 76 (1974).
19. J. T. Knudtson and E. M. Eyring, *J. Phys. Chem.* **78**, 2355 (1974).
20. V. A. Kuzmin and A. P. Darmanyany, *Chem. Phys. Lett.* **54**, 159 (1978).
21. V. A. Kuzmin, A. P. Darmanyany and M. M. Kulchitzky, *Izv. Akad. Nauk SSSR, ser. khim.* **229**, 2392 (1976).
22. R. Gadonas, R. Danelius and A. Piskarskas, *Kvantovaya Elektron.* **8**, 669 (1981).
23. H. Schütz, E. Stutter, K. Geller and I. Petri, *studia biophysica* **104** (1984) 23.
24. K.-H. Feller, R. Gadonas and V. Krasauskas, *Z. phys. Chemie (Leipzig)* in press.
25. S. Rentsch, *Chem. Phys.* **69**, 81 (1982).
26. K.-H. Feller, J. Siegel, D. Fassler, H. Bergner and F. Kerstan, Proceedings of SOS-84, in: *Teubner Texte zur Physik*, **4**, ed. by D. Fassler, K.-H. Feller and B. Wilhelmi, (BSB B. G. Teubnerverlagsgesellschaft, Leipzig 1985), p. 216.
27. R. Allmann, H.-J. Anis, R. Benn, W. Grahn, S. Olejnek and A. Waskowska, *Angew. Chem. Suppl.* **1147** (1983).
28. K.-H. Feller, *Z. phys. Chemie (Leipzig)*, in press.
29. F. Dietz and S. Rentsch, *Chem. Phys.* **96**, 145 (1985).