

## An investigation into multiple photoisomerization processes of polymethine cyanines

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**Abstract.** Eight cyanine dyes including *bis*-pyrrolidinylpentamethinecyanineperchlorate (BPC), *bis*-dimethylamino-heptamethine cyanine perchlorate (BMC), 3,3'-diethyloxadicarbocyanine iodide (DODCI) and 6 differently substituted 3,3'-diethyloxadicarbocyanines have been investigated by means of conventional flash photolysis absorption and emission spectroscopy. Two photoisomers were detected with all dyes except DODCI (only one) and BMC (three isomers).

**Keywords.** Photoisomerization; polymethines; cyanines; flash photolysis.

### 1. Introduction

The most stable form in solution of open chain polymethine dyes is the all-*trans* configuration as long as there are no sterical constraints by bulky substituents. It has been well known that different *EZ*-isomers may coexist in thermal equilibrium with substituted cyanines, the most stable configuration being determined by the space requirement of the substituents (West *et al* 1967; Allman *et al* 1983).

Photoisomerization of polymethine cyanines has also been known for decades (Scheibe *et al* 1966). However, to the best of our knowledge it has never been observed hitherto that more than one photoisomer is generated upon light absorption.

It is the purpose of this preliminary communication to report that the occurrence of more than one photoisomer with polymethine cyanines of a proper chain length is not exceptional.

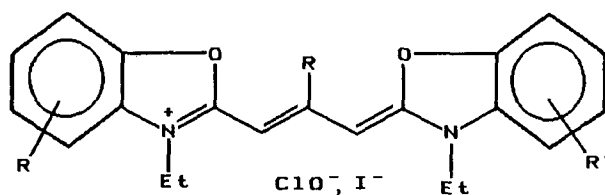
### 2. Experimental details

#### 2.1 Materials

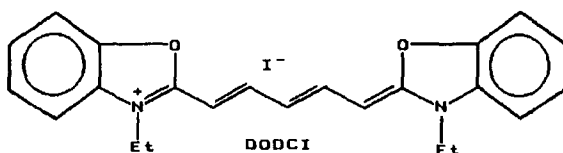
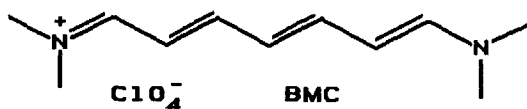
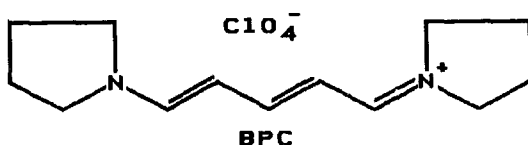
The oxacarbocyanines I...VI have been provided by Filmfabrik ORWO Wolfen. BPC and BMC have been kindly provided by Prof Dähne and Dr Freyer of the Academy of Sciences in Berlin. DODCI was synthesized by Dr Czerney in our laboratory.

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I	II	III	IV	V	VI
H	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
H	H	H	6,6'-di-C <sub>6</sub> H <sub>5</sub>	6,6'-di-C <sub>6</sub> H <sub>5</sub>	5-Cl



Ethanol was used as a solvent for all experiments UVASOL, Merck or "For UV spectroscopy" Jenapharm, Jena).

For the flash experiments, the sample concentrations were adjusted to give an optical density of about 0.15 for spectral measurements including the normal absorption region and  $0.6 < \text{OD} < 0.9$  for kinetic measurements outside that region. Solutions were repeatedly flashed after having proved that exactly reproducible results could be obtained and irreversible photodegradation was negligible. Air-saturated solutions were used since oxygen was shown not to affect the results. Transient difference spectra were recorded by point measurements of kinetic curves with a spectral resolution of 5 nm.

## 2.2 Apparatus

Fluorescence spectra were recorded with the help of a FICA 55 spectrofluorimeter.

Flash experiments were performed with the help of a home-made conventional apparatus. A cylindrical cell of 10 cm length and 10 mm diameter was used in a double elliptical reflector with two flashlamps. A double-walled quartz cell thermostated by

a water thermostat or a methanol cryostat was used for the temperature dependent measurements above and below room temperature, respectively. Cut-off filters were used to avoid UV-excitation. The electrical energy of the flashes amounts to 900 J at a duration of 14  $\mu$ s. An 8 bit 10 MHz ADC (NEO 205 KFKI Hungary) connected to an AT computer was used for data acquisition and evaluations. Kinetic data analysis was performed by nonlinear regression using the ALAU program (Schuetz *et al* 1984) in a modified PASCAL version.

### 3. Results

#### 3.1 Fluorescence

Fluorescence excitation spectra of dyes I to III do not reveal any differences in the absorption spectra if the fluorescence is taken from the emission maximum. However, if the excitation spectra are recorded for the fluorescence at the long wavelength tail then the existence of two emitting species becomes obvious from both the fluorescence and the excitation spectra as shown in figures 1 and 2.

Unfortunately we failed to measure these spectra at lower temperatures. Because of increased scattered light due to the additional quartz windows in the low temperature cell both fluorescence spectra were no longer resolvable. However, we can definitely state that the relative intensity of the long wavelength fluorescence does not increase with decreasing temperature. Thus we can rule out aggregation as the origin of the weak long wavelength emission.

#### 3.2 Flash photolysis

Figure 3 shows a set of transient difference spectra of I recorded at room temperature. The rank of the corresponding  $\Delta A$  matrix is unity, (Grummt and Paetzold 1982), as indicated by the isobestic point at  $\Delta A = 0$  and  $\lambda_{\text{max}} = 490$  nm. The decay follows

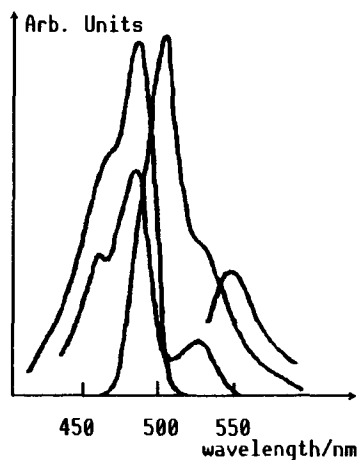


Figure 1. Fluorescence and excitation spectra of dye I. Excitation of fluorescence spectra at 480 and 520 nm; fluorescence for excitation spectra taken at 498 and 570 nm.

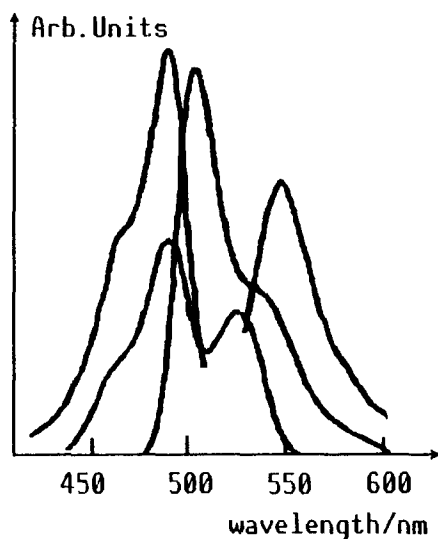


Figure 2. Fluorescence and excitation spectra of dye III. Excitation of fluorescence spectra at 465 and 516 nm; fluorescence for excitation spectra taken at 520 and 570 nm.

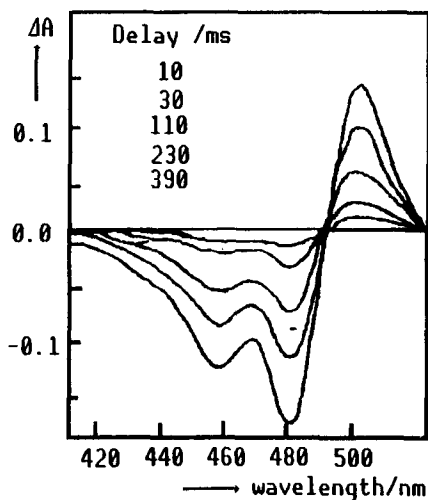


Figure 3. Transient absorbance difference spectra of I at room temperature.

strict first order kinetics independently of the recording wavelength. At  $-28^{\circ}\text{C}$  for example we observe a new shorter lived transient absorbing at  $\lambda_{\text{max}} = 520 \text{ nm}$ , figure 4. After about 3 ms the maximum of the difference spectrum has shifted to about 505 nm as observed at room temperature. The decay obeys a biexponential rate law. The rank of the  $\Delta A$  - matrix equals 2.

If there is a substituent  $\text{R} = \text{Me}$  or  $\text{R} = \text{Et}$  at the meso-position (compounds II...IV) a transient absorption is no longer observed at room temperature in  $\mu\text{s}$  to ms time scale. Merely a weak transient depletion occurs, the spectral distribution of which

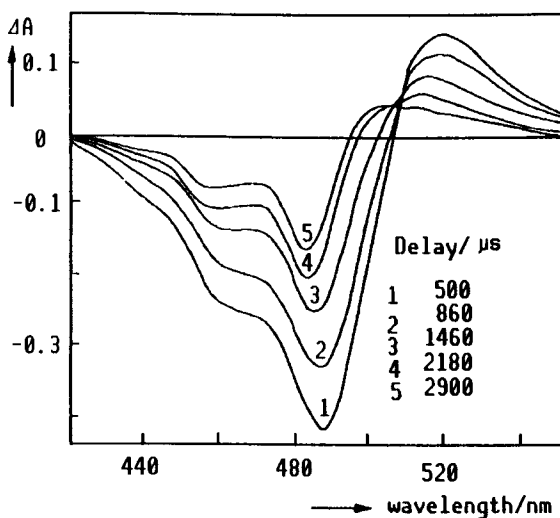


Figure 4. Transient absorbance difference spectra of I at  $-28^\circ\text{C}$ .

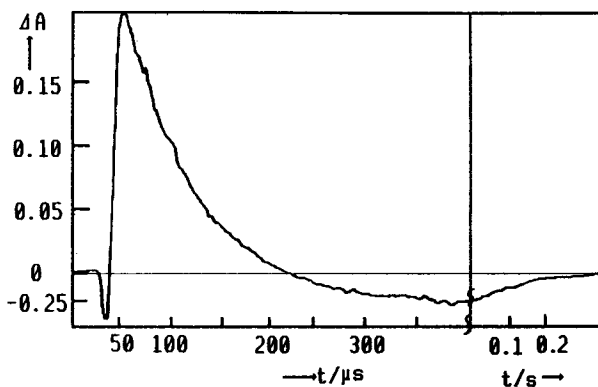


Figure 5. Kinetic curve of IV at  $-48^\circ\text{C}$  (switched timebase).

closely resembles that of the normal absorption with the opposite sign. Upon cooling to  $-15\dots-60^\circ\text{C}$  a transient absorption becomes observable. Figure 5 shows a kinetic curve as an example. The decay does not immediately restore the normal equilibrated state. Again the rank is two and biexponential behavior is observed. By contrast with the chain-unsubstituted oxacarbocyanine I the slow component is observed as a depletion rather than an absorption signal.

The spectroscopic and kinetic behavior of BPC and BMC qualitatively resembles that of dye I. As shown in figures 6 and 7, additional transients are detected upon lowering the temperature. The short-lived transient absorption difference in the right part of figures 6 and 7 relate to the absorbance after the decay of the short-lived transients, that is a quasi photostationary state with respect to the long-lived transient and most stable isomer. The decay of the long-lived transients is negligible on the time scale of the short-lived ones.

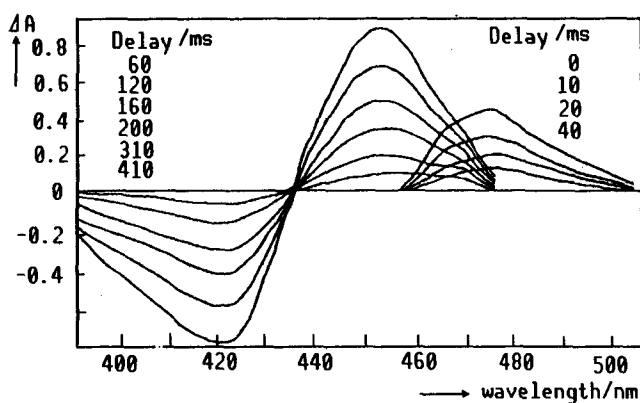


Figure 6. Transient absorbance difference spectra of BPC at room temperature and at  $-26^{\circ}\text{C}$ .

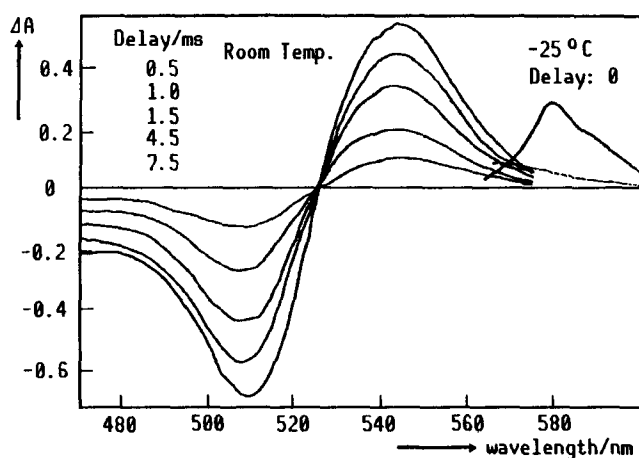


Figure 7. Transient absorbance difference spectra of BMC at room temperature and at  $-25^{\circ}\text{C}$ .

Table 1. Arrhenius parameters and absorption maxima of the dyes and their transients.

Wavelengths are given in nm, activation energies in kcal/mol.

	Long-lived transients				Short-lived transients		
	$\lambda_e$	$\lambda_t$	$\lg A$	$E_a$	$\lambda_t$	$\lg A$	$E_a$
I	485	500	$12.5 \pm 0.1$	$66.7 \pm 0.7$	525	$12.1 \pm 0.1$	$44.4 \pm 0.5$
II	491	505*	$12.7 \pm 0.3$	$58.7 \pm 1.6$	515	$10.8 \pm 0.2$	$32.6 \pm 0.8$
III	493	505*	$13.3 \pm 0.3$	$62.5 \pm 1.4$	515	$12.1 \pm 0.1$	$38.5 \pm 0.8$
IV	497	515*	$12.8 \pm 0.2$	$59.5 \pm 0.9$	525	$12.1 \pm 0.1$	$38.6 \pm 0.5$
V	499	520*	$12.6 \pm 0.7$	$58.3 \pm 0.7$	530	$12.3 \pm 0.8$	$39.6 \pm 0.8$
VI	496	515*	$13.4 \pm 0.8$	$60.6 \pm 3.9$	525	$11.8 \pm 0.4$	$35.5 \pm 1.8$
BPC	424	455	$13.8 \pm 0.1$	$57.8 \pm 0.2$	475	$13.3 \pm 0.1$	$30.6 \pm 0.1$
BMC	512	545	$13.1 \pm 0.2$	$60.9 \pm 0.5$	580	$12.9 \pm 0.9$	$45.0 \pm 4.0$
						$9.2 \pm 0.6$	$23.4 \pm 2.6$
DODCI	582	620	$12.7 \pm 0.1$	$57.5 \pm 0.5$			

\*Depletion,  $\lambda_e$  and  $\lambda_t$  refer to equilibrated solution and transient, respectively.

**Table 2.** MM-energy [kcal/mol] from molecular mechanics calculations.

	I	II	III	BPC	BMC
All- <i>trans</i>	57.2	61.5	63.0	29.8	10.5
2,3- <i>cis</i>	62.6	65.7	67.5	34.7	14.6
3,4- <i>cis</i>	59.3	58.9	59.8	31.3	11.0
2,3,3,4-di- <i>cis</i>	68.8	61.4	63.6	36.3	16.9

By contrast with BPC the decay of the short-lived transient absorption cannot properly be described by first-order kinetics. An additional exponential is used to fit the kinetic curves. The dashed line in figure 7 shows the amplitudes of that exponential.

The only dye investigated here which shows only one transient in the temperature region of  $-60^{\circ}\text{C}$  to  $70^{\circ}\text{C}$  is DODCI (Rentsch *et al* 1987). The same applies to the thia-analogue (Bilmes *et al* 1989).

Activation parameters for the decay of all transients are presented in table 1.

In order to assist the assignment of the transients to particular isomers we have performed molecular mechanics calculations with the help of the PC-MODEL program package. The results are given in table 2. The all-*trans* form is the most stable one only if there are no chain substituents. Chain substitution (II...IV) lowers the energy of the 3,4-*cis* form with respect to the all-*trans* isomer. The 2,3-*cis* isomer is the species of the highest energy among the singly isomerized dyes.

#### 4. Discussion

Principal component analysis (Brueckner *et al* 1990) of the series of absorption spectra recorded in the temperature region from  $-60^{\circ}\text{C}$  to room temperature reveal three components with II to VI. One component is always due to the band narrowing caused by temperature lowering. With dye I only one chemical species is detectable from absorption measurements. However it becomes obvious from the fluorescence spectra (figure 1) that even a chain-unsubstituted oxacarbocyanine may exist as an equilibrium between two isomers.

The problem is to assign the transient absorptions to particular species and to design a mechanistic scheme which includes all photochemical and thermal reactions.

From a recent study by Lau *et al* (1990) we adopt the assignment of the long-lived transient to the 2,3-*cis* isomer. This is in accord with theoretical results by Momicchioli *et al* (1988) which predict a lower barrier for the 3,4-*cis* to all-*trans* than for the 2,3-*cis* to all-*trans* isomerization. We assume by analogy that the same assignment also applies to the other dyes investigated.

The species in thermal equilibrium with the all-*trans* form should be assigned to the 3,4-*cis* isomer. This conclusion is supported by the MM-calculations, table 2. The 3,4-*cis* isomer is probably identical with the short-lived photoisomer. However, we cannot rule out the occurrence of transient species rotated about more than one bond. If we do not take into consideration di- and tri-*cis* configurations then the third isomer of BMC should be assigned to the 4,5-*cis* isomer.

There is one observation in favour of a di-*cis* isomer to be assigned to the short-lived isomers: With decreasing temperature the relative yield of the short-lived transient

increases at the expense of the long-lived isomer. This effect is greatly diminished if the intensity of the analyzing light beam is reduced by suitable interference filters. Intense analysing light produces a photostationary state which contains non-negligible amounts of the 2,3-isomer at lower temperature which in turn may be the source of the short-lived transient.

Why do we not observe a transient absorption due to the long-lived 2,3-isomer of the chain-substituted oxacarbocyanines II... VI? Whether a particular one in a system of several species in an equilibrium mixture can be observed upon flashing as transient absorption or a transient bleaching depends on the absorptivities of all species, on the actual state of the equilibrium and on the relative quantum efficiencies of all photoreactions involved. We can conclude from the absorption and fluorescence spectra supported by the molecular mechanics calculations that the 3,4-isomer is present to a considerably larger extent with the chain-substituted dyes than with I. Rotation around two bonds would be necessary to generate the long-lived 2,3-*cis* isomer from the 3,4-*cis* configuration which seems less probable. A detailed equilibrium study is under way.

The question about the mechanistic scheme cannot be definitely answered at the present stage of knowledge. Transient absorption and emission experiments with more selective laser pulses particularly with two-color excitation should be able to solve the problem.

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