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Electro-optical and laser spectrofluorimetry study of coumarins 7 and 30: evidence for the existence of the close-lying electronic states and conformers

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Abstract

Our experiments and calculations reveal a set of anomalous and interesting properties of coumarin 7 (CU7) and coumarin 30 (CU30) in solution. The spectral dependence of electro-optical coefficients and, consequently, dipole moments indicates that the absorption band is a superposition of several (at least two) electronic transitions. Probably, there are two close-lying π,π^* singlet electronic excited states which contribute to the first absorption band. The calculations using the MM2 program show that both dyes in the ground state have two stable plane anti conformers. From time-resolved spectrofluorimetric measurements we obtained evidence for the existence of conformers in paraffin oil solutions of CU30. © 1997 Published by Elsevier Science S.A.

Keywords: Coumarin 7; Coumarin 30; Absorption; Fluorescence; Dipole moment; Electro-optical method; Conformer

1. Introduction

Coumarins 7 and 30 (CU7 and CU30) were synthesized at the research laboratories of Eastman Kodak Company as efficient laser dyes in the blue–green region of the visible spectrum [1]. It is well known that the fluorescence band of the 7-aminocoumarins may be treated as an intramolecular charge-transfer transition from a π^* orbital associated with the benzo-ring 1 and the nitrogen atom to a π orbital of the benzo-ring 2 and the carbonyl group [2,3]. Hence, substituents that raise the orbital of ring 1 or lower that of ring 2 will generally result in a long wavelength shift of the fluorescence spectra. The substitution of a benzimidazolyl (CU7) or an *N*-methylbenzimidazolyl (CU30) group in position 3 of 7-diethylaminocoumarin leads to essential deformation of a π orbital of the coumarin moiety. As a result, the positions of the absorption and emission spectra are red shifted by about 30–40 nm as compared to other 7-aminocoumarins. In addition, dyes like CU7 and CU30 with heterocyclic substituents in the 3d position show excellent photostabilities in comparison with another 7-aminocoumarins [3].

Intramolecular charge redistribution after transition of molecules to another electronic state is a fundamental process in chemistry. A very fruitful and widely used method to study this process is the determination of electric dipole moments in different electronic states. A number of papers have been published concerning the spectra, efficiency and stability of CU7 and CU30 as active media of dye lasers in solution [1–10] and in the vapour state [11,12]. However, no experimental ground and first excited singlet-state dipole moments of CU7 and CU30 seem to have been reported. Only calculated dipole moments of CU30 has been published by McCarthy and Blanchard [13].

In this paper we describe an investigation by electro-optical absorption and emission methods of the equilibrated ground, excited Franck–Condon and equilibrated excited state dipole moments of CU7 and CU30. The results of electro-optical experiments are combined with time-resolved characteristics obtained by subnanosecond laser spectrofluorimetry. We conclude that for both compounds we have studied, there are at least two excited electronic states which contribute to the first absorption band. Additionally, our time-resolved experiments show that in viscous solutions of CU30 in paraffin

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Abbreviations: Coumarin 7 (CU7); Coumarin 30 (CU30); Electro-optical absorption measurements (EOAM); Integrated electro-optical emission measurements (IEOEM); Molecular mechanics method (MM2)

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oil, conformers exist with different spectral luminescent properties.

2. Electro-optical methods

The determination of ground and excited state dipole moments from electro-optical measurements has been fully described in previous papers [14,15]. Hence, for convenience only the basic principles and main equations are summarized. Using Liptay's formalism [16] the effect of an external electric field E_f on the molar absorption coefficient $\kappa(\nu)$ can be described by a quantity L, which is defined by

$$L=L(\nu,\chi)=[\kappa^{E}(\nu,\chi)-\kappa(\nu)]/\kappa(\nu)E_{f}^{2} \tag{1}$$

where κ^{E} is the molar absorption coefficient in the presence of an applied electric field and χ is the angle between the direction of E_f and the electric field vector of the incident light. For a homogeneously broadened absorption band L is given by the following equation [16].

$$L=Dr+[1/6]Es+Frt+Gst+Hru+Isu \tag{2}$$

where the parameters r and s are determined by the angle χ, and the quantities t and u depend on the first and second derivatives of the absorption spectrum:

$$r=(2-\cos^{2}\chi)/5 \tag{3}$$

$$s=(3\cos^{2}\chi-1)/5 \tag{4}$$

$$t=(1/hc)(k/\nu)^{-1}\mathrm{d}(k/\nu)/\mathrm{d}\nu \tag{5}$$

$$u=(1/2h^{2}c^{2})(k/\nu)^{-1}\mathrm{d}^{2}(k/\nu)/\mathrm{d}\nu^{2} \tag{6}$$

The coefficients D, E, F, G, H and I are connected with intrinsic properties of the solute molecules and within some assumptions may be written in the form:

$$D=(f_{e}^{2}/kT)\boldsymbol{R}^{(1)}\boldsymbol{\mu}_{g} \tag{7}$$

$$E=(f_{e}/kT)^{2}[3(\boldsymbol{m}_{a}\boldsymbol{\mu}_{g})-\boldsymbol{\mu}_{g}^{2}]+(f_{e}^{2}/kT)(3\boldsymbol{R}^{(2)}-2\boldsymbol{R}^{(1)})\boldsymbol{\mu}_{g} \tag{8}$$

$$F=(f_{e}^{2}/kT)(\boldsymbol{\mu}_{g}\Delta^{a}\boldsymbol{\mu})+f_{e}^{2}\boldsymbol{R}^{(1)}\Delta^{a}\boldsymbol{\mu} \tag{9}$$

$$\mathrm{G}=(f_{e}^{2}/kT)(\boldsymbol{m}_{a}\boldsymbol{\mu}_{g})(\boldsymbol{m}_{a}\Delta^{a}\boldsymbol{\mu})+(f_{e}^{2}/2)\boldsymbol{R}^{(2)}\Delta^{a}\boldsymbol{\mu} \tag{10}$$

$$H=f_{e}^{2}(\Delta^{a}\boldsymbol{\mu})^{2} \tag{11}$$

$$I=f_{e}^{2}(\boldsymbol{m}_{a}\Delta^{a}\boldsymbol{\mu})^{2} \tag{12}$$

where k is the Boltzmann constant, T is the temperature, $\boldsymbol{m}_a$ is the unit vector in the direction of the transition moment for absorption, $\boldsymbol{\mu}_g$ is the equilibrated ground state dipole moment vector, $\Delta^{a}\boldsymbol{\mu}$ is the change of the dipole moment vector upon excitation to the Franck–Condon excited state considered. The vectors $\boldsymbol{R}^{(1)}$ and $\boldsymbol{R}^{(2)}$ are related to the transition polarizability of the considered transition and describe the effects due to the electric field dependence of the transition moment [16]. The cavity field correction f_e is defined according to Onsager's model [17].

The experimental set-up for electro-optical absorption measurements (EOAM) has been described in detail previously [14,15]. The quantity $L(\nu,\chi)$ in the present work was determined for two values of the angle χ ($\chi=0$ and $\chi=\pi/2$) and for a set of wavenumbers within the first absorption band. Then the coefficients in Eqs. (7)–(12) and their standard deviations were obtained by multiple linear regression. For correct statistical weighting reasons the multiple linear regression was performed with the quantity LK/ν, where K is the absorption coefficient.

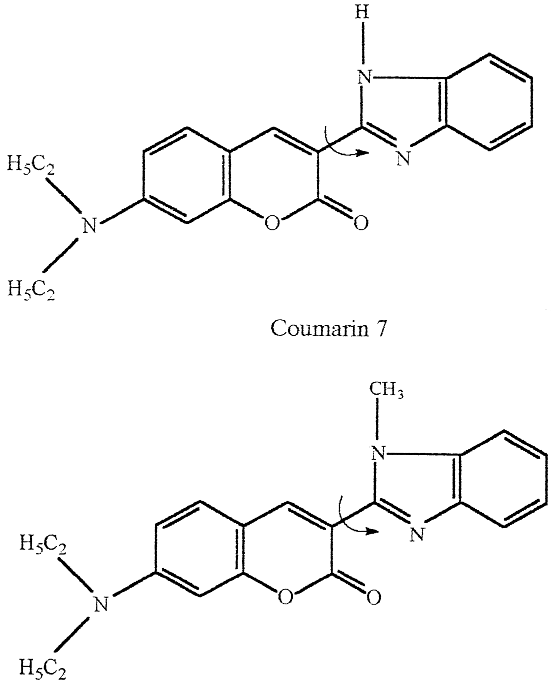
In this work the equilibrated electric dipole moment μ_e in the excited state has been determined by integral electro-optical emission measurements (IEOEM) in the manner described in [18,19]. The experimental set-up for IEOEM is described in [14].

3. Laser spectrofluorimeter and materials

The time-resolved fluorescence characteristics were measured by an automated laser spectrofluorimeter described in detail in [20]. The excitation of this set-up includes an atmospheric pressure nitrogen laser (pulse half-width 0.35 ns, peak power 350 kW) and a distributed-feedback dye laser (tuning range 400–750 nm, spectral width 0.1–0.6 nm). After the polarizer (Glan prism) the exciting radiation is directed on the sample, which is placed in front of an analysing polarizer (Glan prism). The recording part of the apparatus includes a double diffraction monochromator (1200 lines per mm replica, 0.6 nm per mm dispersion). An FEU-164 photomultiplier (1.8 ns temporal resolution) records the optical radiation in a selected spectral range. The output signal of the photomultiplier is fed into a B4-24 Boxcarintegrator (1.0 GHz transmission band). The registered signal is normalized on the reference signal from the photodiode. The data are input into an IBM PC/AT-386. The laser spectrofluorimeter is fully automated, all optical and electronic systems are controlled by computer. The coefficients for correction of the spectral sensitivity of the detection system were determined by a conventional method using a tungsten band lamp. The use of the deconvolution procedure allows improvement of the temporal resolution up to 50 ps for single-exponential fluorescence lifetime measurements and up to 200 ps for the registration of time-resolved spectra. The steady-state fluorescence spectra were registered by a spectrofluorimeter SFL-112A.

The deconvolution procedure is based on the method of modulating functions [21] combined with truncated singular value decomposition [22], thus resembling the implementation of Striker [23], though with slight differences. The fitting procedure is a nonlinear minimisation reconvolution routine based on a combination of the Nelder–Mead simplex method [24] and the ''switching method'' [25].

Fig. 1 presents the molecules CU7 and CU30 studied in this work. Both compounds were purified by repeated liquid chromatography and recrystallization. The purity of CU7 and



Coumarin 7

Coumarin 30

Fig. 1. Coumarin 7 and 30 studied in this work.

CU30 was checked by thin layer chromatography. The solvents used in this work (cyclohexane, dioxane and paraffin oil) were purified by methods described in [26]. The purified solvents were dried prior to use in electro-optical measurements by distillation under reflux condition over sodium/potassium alloy employing an argon atmosphere. The purity of all solvents was checked by UV absorption measurements (1 cm cell; reference air).

4. Experimental results and discussion

4.1. Electro-optical measurements

The optical absorption spectra of CU7 and CU30 in cyclohexane and dioxane are displayed in Figs. 2 and 3, where the open and dark bars indicate the wavenumber range of the electro-optical measurements. The analyses of the data by partial regression analyses revealed the existence of two different spectral regions corresponding to pure transitions, one at the red edge and one at the blue edge of the spectrum. This was found for both compounds and in both solvents.

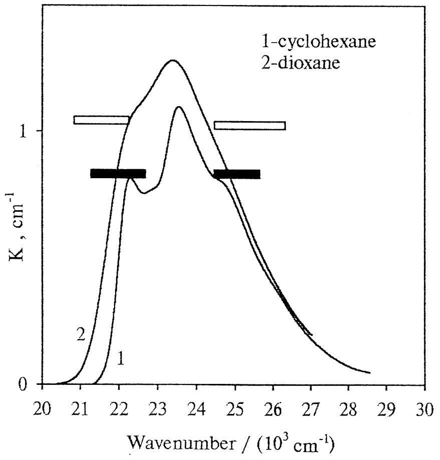


Fig. 2. Absorption spectra of CU7 in cyclohexane (curve 1) and dioxane (curve 2). The open and closed bars indicate the spectral range of EOAM in dioxane and cyclohexane, respectively.

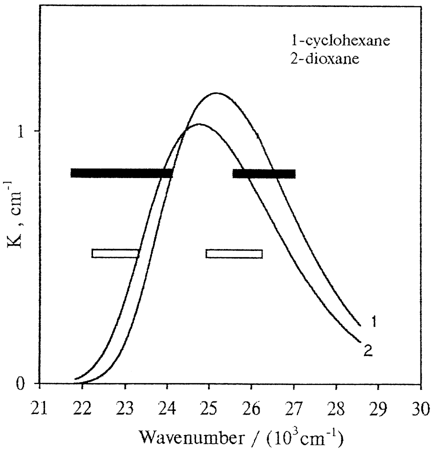


Fig. 3. Absorption spectra of CU30 in cyclohexane (curve 1) and dioxane (curve 2). The open and closed bars indicate the spectral range of EOAM in dioxane and cyclohexane, respectively.

In Table 1 the electro-optical coefficients *D*, *E*, *F* and *G* obtained by a regression analysis according to Eq. (2) at different slopes of the absorption spectrum of CU7 in cyclohexane are presented. Regrettably, for CU7 and CU30, as sometimes for other derivatives, the coefficients *H* and *I* cannot be determined with sufficient accuracy and they were omitted in the subsequent regressions. As follows from Table 1 the coefficients *F* and *G* obtained at the red slope of the absorption spectrum are smaller (about two times) that the same coefficients measured at the blue slope of the absorption spectrum. Hence, at least two different electronic transitions must contribute to the absorption within the wavenumber interval of the electro-optical measurements.

In Table 2, the values μ_g, $\Delta^a\mu$, μ_e^{FC} and μ_e calculated from the EOAM and IEOEM are presented. The dipole moments of the solute molecules were derived as follows. First, the dipole moments μ_g and $\Delta^a\mu$ were found from [27]

$$\mu_g = (kT/f_e)\left(\frac{E-6D}{2}\right)^{1/2} \tag{13}$$

$$\Delta^a\mu = (kT/f_e^2)(F+G)/2\mu_g \tag{14}$$

which are valid for CU7 and CU30 with sufficient approximation, because for both compounds in cyclohexane and dioxane F≅G within experimental error. The last condition means that $\boldsymbol{m}_a \| \mu_g \| \Delta^a\mu$.

The dipole moment in the excited Franck–Condon state (μ_e^{FC}) was determined by the formula

$$\Delta^a\boldsymbol{\mu} = (\boldsymbol{\mu}_e^{FC} - \boldsymbol{\mu}_g) \tag{15}$$

which is sufficiently valid for non-polar solvents.

It is seen from Table 2 that for both dyes in cyclohexane and dioxane the values of the dipole moment μ_g determined

Table 1
Results from electro-optical absorption measurements at different edges of the absorption spectrum of CU7 in cyclohexane solution at $T = 298$ K [a]

Coefficient	Spectral region of EOAM	
	21 277–22 676 cm^{-1} (red edge)	24 450–25 641 cm^{-1} (blue edge)
D $(V^{-2}\,m^2)/10^{-20}$	402 ± 10	-17 ± 10
E $(V^{-2}\,m^2)/10^{-20}$	$11\,733 \pm 62$	9110 ± 61
F $(CV^{-1}\,m^2)/10^{-40}$	649 ± 17	1162 ± 47
G $(CV^{-1}\,m^2)/10^{-40}$	625 ± 17	1127 ± 47

[a] The accuracy of the wavenumber settings is ± 10 cm^{-1}.

Table 2
Dipole moments μ_g, $\Delta^a\mu$, μ_e^{FC} of CU7 and CU30 determined from EOAM at different slopes of absorption spectrum and dipole moment μ_e determined from IEOEM at $T = 298$ K [a]

Molecule	Solvent	Spectral region of EOAM/cm^{-1}	$\mu_g/(10^{-30}$ C m)	$\Delta^a\mu/(10^{-30}$ C m)	$\mu_e^{FC}/(10^{-30}$ C m)	$\mu_e/(10^{-30}$C m)
CU7	Cyclohexane	21 277–22 676	23.4 ± 0.2	7.9 ± 0.3	31.3 ± 0.5	32 ± 0.2
		24 450–25 641	23.3 ± 1	14.0 ± 0.6	37.3 ± 0.7	
	Dioxane	20 833–22 523	24.7 ± 0.2	14.3 ± 0.1	39.0 ± 0.3	36.4 ± 0.5
		24 450–26 316	24.5 ± 0.4	28.4 ± 0.7	52.9 ± 1.1	
CU30	Cyclohexane	21 739–24 096	17.7 ± 0.3	7.8 ± 0.6	25.5 ± 0.9	28.9 ± 0.5
		25 575–27 027	17.9 ± 0.1	18.9 ± 0.9	36.8 ± 1.1	
	Dioxane	22 222–23 310	22.6 ± 0.2	15.5 ± 0.4	38.1 ± 0.6	34.7 ± 0.4
		24 938–26 247	22.2 ± 0.1	28.6 ± 0.9	50.8 ± 1.0	

[a] The accuracy of wavenumber settings is ± 10 cm^{-1}. μ_g is the value of the electric dipole moment in the equilibrated ground state. $\Delta^a\mu$ is the change in the electric dipole moment on optical excitation. μ_e^{FC} is the value of the electric dipole moment in the excited Franck–Condon state; μ_e is the value of the electric dipole moment in the equilibrated excited state.

at the blue and red edges of the absorption spectrum are equal within experimental error. On the contrary, the values of $\Delta^a\mu$ and μ_e^{FC} measured in the same spectral intervals are essentially different. These results are evidence for the existence of several transitions in the first absorption band of CU7 and CU30.

It seems likely that CU7 and CU30 have two close-lying π,π^* singlet electronic states S_1 and S_2 with different charge distribution and dipole moments. The existence of (n,π^*) and (π,π^*) states simultaneously is less probable because usually for dyes an (n,π^*) absorption band is less intensive that a (π,π^*) band. However, in our case, as seen from Figs. 2 and 3, the absorption coefficients at the different edges of the spectrum are comparable. The above conclusion is also confirmed by $\boldsymbol{m}_a \| \boldsymbol{\mu}_g$ throughout the first absorption band. This would be surprising if the absorption band is a superposition of (n,π^*) and (π,π^*) transitions, because for an (n,π^*) state the transition dipole moment is usually perpendicular to the plane of the molecule, but for a (π,π^*) state it lies in the plane of the molecule.

As follows from Table 2 the values of the dipole moment μ_e in the equilibrated excited state determined from IEOEM (last column) is similar to the values of the dipole moment μ_e^{FC} in the excited Franck–Condon state at the red edge of the absorption spectrum. This indicates that the close-lying excited state (probably S_2) is non-fluorescent.

Another explanation of the electro-optical results obtained in this work is the possible existence of several conformers for CU7 and CU30 due to the rotation of benzimidazolyl (CU7) and *N*-methylbenzimidazolyl (CU30) groups around the C–C bond with respect to the coumarin moiety (shown in Fig. 1 by arrows). If the conformers have different electronic spectra, the results of EOAM depend on the spectral region of the measurements. Our analysis of the conformational states for CU7 and CU30 performed using the Molecular Mechanics Method (MM2) [28] shows that both dyes have two stable planar anti conformers in the ground state with a dihedral angle near zero and a significant barrier to rotation. Additionally, CU30 has one gauche conformer with an angle between the planes of the coumarin moiety and the *N*-methylbenzimidazolyl group of about 150°.

There is also evidence in the literature for the existence of several conformers for CU7 and CU30 in frozen solutions [29] and in silica glass [30]. In order to obtain some information concerning the conformers we performed time-resolved spectroscopic experiments in cyclohexane and dioxane and in a viscous non-polar solvent, paraffin oil.

4.2. Time-resolved measurements

Fluorescence lifetimes are very sensitive observables regarding various processes in the excited state. We measured the fluorescence lifetime τ_{fl} using an automated laser spectrofluorimeter to check the homogeneity of the fluorescence bands of coumarins under consideration in different solvents. As an example the response function and the fluorescence

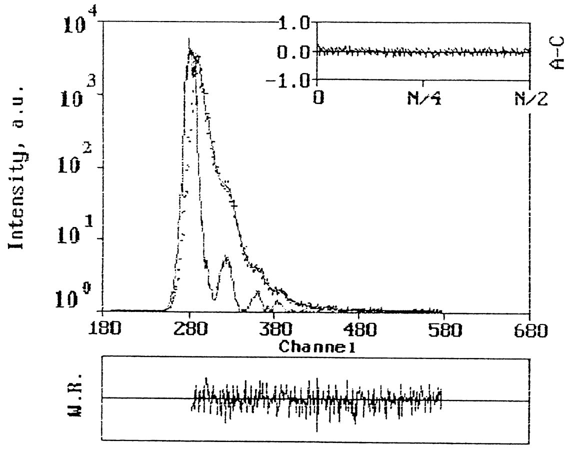


Fig. 4. Response function of the automated laser spectrofluorimeter and fluorescence decay of CU30 in paraffin oil. Immediately below and in the right top corner weighted residuals (W.R.) and autocorrelation function (A–C) are shown. Time resolution, 100 ps per channel.

Table 3
Fluorescence lifetimes (τ_{fl}) of CU7 and CU30 measured at different edges of the fluorescence spectrum [a]

Molecule	Solvent	τ_{fl}/ns	ν_{reg}/cm^{-1}
CU7	Paraffin oil	2.50 ± 0.1	$22\,220 \pm 10$
		2.47 ± 0.1	$18\,520 \pm 10$
	Cyclohexane	2.1 ± 0.1	$21\,740 \pm 10$
		2.7 ± 0.1	$20\,410 \pm 10$
	Dioxane	2.5 ± 0.1	$21\,740 \pm 10$
		2.5 ± 0.1	$19\,230 \pm 10$
CU30	Paraffin oil	2.3 ± 0.1	$22\,730 \pm 10$
		2.8 ± 0.1	$18\,520 \pm 10$
	Cyclohexane	2.7 ± 0.1	$22\,730 \pm 10$
		2.7 ± 0.1	$19\,610 \pm 10$
	Dioxane	2.7 ± 0.1	$22\,220 \pm 10$
		2.7 ± 0.1	$19\,610 \pm 10$

[a] The accuracy of the lifetime determination is ±0.1 ns following the deconvolution procedure.

[b] ν_{reg} is the registration wavenumber of the fluorescence lifetime measurements.

decay of CU30 in paraffin oil are shown in Fig. 4. The results of the fluorescence lifetime measurements are listed in Table 3. It is seen that for both compounds in cyclohexane and dioxane (and for CU7 also in paraffin oil) the values of the fluorescence lifetime measured at the blue and red edges of the fluorescence spectrum are equal within experimental error. This supports the fact that the fluorescence bands are homogeneously broadened in the subnanosecond time scale. If the existence of different conformers is assumed, the independence of τ_{fl} with respect to the detection wavelength in cyclohexane and dioxane may be explained by fast transformation of the conformational states on a time scale which is outside our time resolution.

The position of maxima, halfwidth and shape of the absorption and fluorescence spectra of CU7 and CU30 in paraffin oil are practically the same as in cyclohexane. However, the viscosity of paraffin oil (117.9×10^{-3} Pa s at $T = 295$ K) is much higher and the rotational diffusion of such groups as in position 3 of CU7 and CU30 may lie in the nanosecond time scale, i.e. inside the time resolution of the set-up used. Our measurements show that only for CU30 in paraffin oil the fluorescence lifetime depends on the detection wavelength (see Table 3). Instantaneous fluorescence spectra of CU30 in paraffin oil measured at 1 and 6 ns after the onset of the excitation pulse (Fig. 5) are quite different. The position and shape of the steady-state fluorescence spectrum also depend on the excitation frequency (Fig. 6). Paraffin oil is an aprotic solvent and hence there is no possibility for donor–acceptor interactions like hydrogen bonding for solute and solvent molecules which may also lead to a dependence of the fluorescence lifetime on the detection wavelength. Hence, the experimental results may be treated as evidence for the existence of different conformational states for CU30 in paraffin oil both in the ground and excited states. Nevertheless, it does not seems very probable that the conformers are responsible

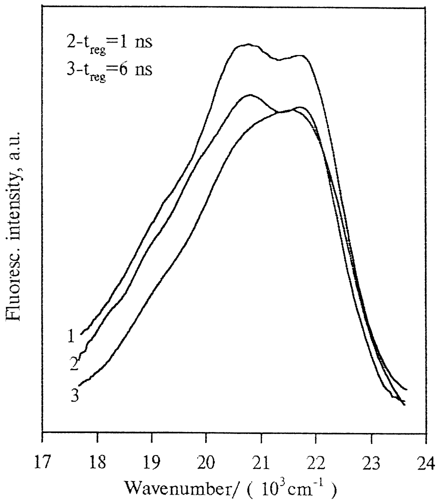


Fig. 5. Steady-state (curve 1) and instantaneous fluorescence spectra (curves 2 and 3) of CU30 in paraffin oil. The registration time is 1 ns (curve 2) and 6 ns (curve 3) after onset of the excitation pulse. Excitation wavelength $\nu_{ex} = 29\,639$ cm^{-1}.

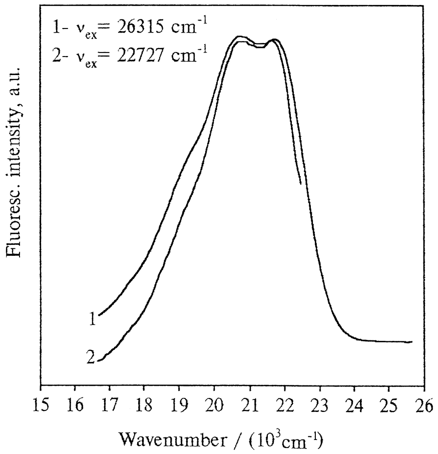


Fig. 6. Steady-state fluorescence spectra of CU30 in paraffin oil at different excitation wavelengths: $\nu_{ex} = 26\,315$ cm^{-1} (curve 1) and $22\,727$ cm^{-1} (curve 2).

for the electro-optical results discussed in this work. In fact, we have evidence for the existence of conformers only for CU30 in paraffin oil. However, spectroscopic effects even for CU30 in paraffin oil are not significant enough to explain the quite large differences in electro-optical coefficients determined at the red and blue edges of the absorption spectrum.

5. Conclusions

Our experiments and calculations reveal a set of anomalous and interesting properties of CU7 and CU30 in solution. The spectral dependence of the electro-optical coefficients and, consequently, dipole moments indicate that the absorption band is a superposition of several (at least two) electronic transitions. Probably there are two close-lying π,π^* singlet electronic states which contribute to the first absorption band. The state S_2 is non-fluorescent.

The calculations using the MM2 program show that both dyes have two stable planar anti conformers and, additionally, one gauche conformer in the case of CU30. From time-resolved spectrofluorimetric measurements we obtained evidence for the existence of conformers in paraffin oil solutions of CU30.

Nevertheless, the elucidation of the role of close-lying singlet electronic states or conformers in the absorption and fluorescence bands of CU7 and CU30 in liquid solutions needs special electro-optical and picosecond absorption and fluorescence experiments. We plan to perform such investigations in the future.

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