ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 89 (1995) 31-36

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Molecular engineering of cyanine-type fluorescent and laser dyes

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Received 24 October 1994; accepted 6 December 1994

Abstract

The absorption and emission characteristics of several bis(dialkylamino)benzopyrylium dyes are compared, and their very different fluorescence quantum yields are correlated with the calculated energies of the lowest excited states of twisted cyanine dyes. The latter are models for selectively bridged compounds.

The laser performance of the dyes is described and compared with well-known laser dyes. The 4-(2-carboxyphenyl)-substituted pyrylium salts are considerably more stable than the unsubstituted compounds.

Keywords: Cyanine dyes; Fluorescence properties; Lasing efficiency

1. Introduction

Benzopyrylium dyes with different substitution patterns have recently been studied to determine their fluorescence behaviour [1–3]. Particular emphasis has been focused on the non-radiative decay channels. By comparing chemically bridged model compounds with flexible compounds and with derivatives containing donor substituents of varying strength, it has been shown [2,3] that these channels are linked to the twisting of bonds and the electron donor–acceptor properties of the conjugated moieties on either side of the twisted bonds. This can be described using the model of twisted intramolecular charge transfer (TICT) states or its generalizations [4–6]. The predictability of the non-radiative properties of dyes opens up various application purposes, such as fluorescent probes for ion detection [7], improved dyes for solar collectors [8] or more efficient and versatile laser dyes [9].

Benzopyrylium dyes substituted with two amino groups can be regarded as bridged cyanine dyes. This is illustrated in Fig. 1 for dye **I**, which has been studied previously [3] and shows a very poor fluorescence quantum yield in polar solvents (e.g. $\phi_f = 0.02$ in acetonitrile) due to a strong non-radiative TICT-type channel, and for dye **II** which is the subject of the present study. The latter dyes show sizeable fluorescence quantum yields and even laser properties [10]. With derivatives **III** and **IV**, a possible method of improving both the thermal stability and photostability can be demonstrated. It is our aim to establish the photophysical data of the pair of dyes **III** and **IV** and to try to understand these properties within a theoretical framework with reference to the corresponding cyanine structure (Cy(15)). Comparison with the derivatives **V** and **VI** belonging to dye type **I** is also made.

The possible decay channels of cyanines have recently been studied quantum chemically for the shorter chain cyanine Cy(5) [11], and it was concluded that the centre bonds (2–3 and 3–4) are more reactive with respect to twisting/non-radiative decay than the outer ones (1–2 and 4–5). Although a generalization of these theoretical findings for longer chain length cyanines has not yet been attempted, dyes **I** and **II** lend themselves to an experimental comparison because they leave only three rotation possibilities open. These dyes can therefore serve as valuable model compounds for the understanding of the reactivity of the various cyanine bonds. While the outer twisting possibilities are similar for the two dyes, the inner flexible bond differs by the number of π atoms on either side (8 and 5 for **I**; 8 and 7 for **II**), and the two systems differ by the total number of π atoms.

1010-6030/95/$09.50
SSDI 1010-6030(94)04018-4

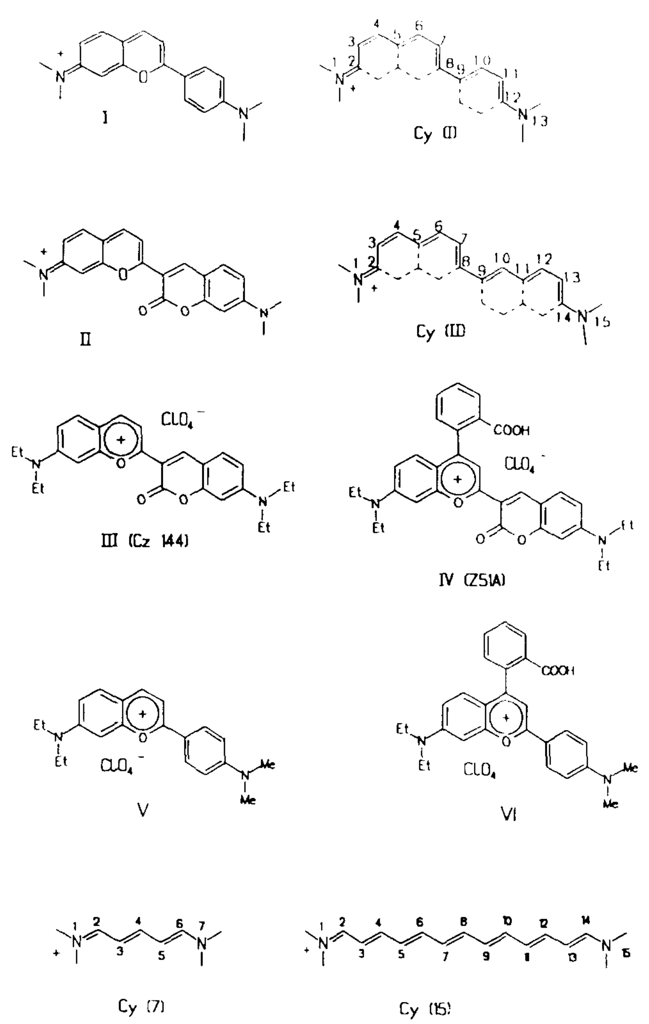

Fig. 1. Structures of molecules I–VI and of the related cyanine model compounds.

2. Experimental details

The formulae of the compounds are given in Fig. 1. The synthesis of **III** (Cz144) has been reported in Ref. [12] and those of **IV** (Z51A) and **VI** are given below. **V** was synthesized according to Ref. [13].

The solvents used were of spectrograde purity. The compounds dissolved in acetonitrile were stabilized by the addition of small amounts of 0.1% perchloric acid.

The absorption and fluorescence spectra were measured on Perkin–Elmer spectrometers (Lambda 16 and LS-50). The LS-50 was equipped with a red-sensitive photomultiplier (R928, Hamamatsu), and the emission correction was performed with a tungsten calibration curve.

The fluorescence quantum yields were determined relative to rhodamine 101 in ethanol ($\phi_f = 1.0$) as standard and with refractive index correction. To avoid errors due to uncertainties in the excitation correction above 600 nm, all samples were excited at the maximum of the rhodamine 101 absorption band at 565 nm.

Due to the strongly red-shifted absorption spectra and their large overlap with the fluorescence of the investigated compounds, there are potential error sources. Measurements of solutions with the commonly used absorbance of 0.05 at the excitation wavelength (i.e. absorbance up to 0.5 at the maximum) would lead to large re-absorption effects at the maximum, whereas measurements of solutions with an absorbance of 0.05 at the maximum (i.e. absorbance much less than 0.015 at the excitation wavelength) would lead to a large error in the determination of the absorbed light intensity. To overcome these problems, we used the following procedure. For each compound, we prepared and measured solutions with an absorbance of 0.05 at the excitation wavelength (dilute solution) and of 0.05 at the absorption maximum (very dilute solution). The fluorescence spectra of the very dilute solutions were normalized to the spectra of the dilute solutions at a wavelength outside the re-absorption region, and the quantum yields were thus determined using spectra which had been corrected both for system sensitivity and re-absorption effects.

Fluorescence lifetime measurements were carried out using a sampling technique (nitrogen laser apparatus LIF 200, ZWG Berlin) or by single photon counting (SPC) using synchrotron radiation from BESSY (single bunch mode) as excitation source (see Ref. [14]).

The measurements for the determination of the lasing characteristics were performed using the cavity of a dye laser (Fabry–Perot-type with holographic grating as dispersive element). At 500 nm, the dispersion efficiency was 20%, and the reflectivity of the output mirror was 0.66.

The laser dyes were pumped with a 4 ns pulse from a nitrogen laser at 337.1 nm, with an energy of 4.3 mJ per pulse. The pumping pulse was focused to a narrow line in the laser dye cell in a transverse geometry. The laser dye cell had an optical path length of 1.2 cm, with a slightly rhombic geometry of 4° angular deviation to prevent optical feedback from the windows. The dye concentration was around 10^{-3} M.

The photostability was studied by irradiation with the unfiltered light of a mercury lamp (200 W).

The lasing efficiency is defined as the ratio "lasing output/pumping input". In a different way, the lasing efficiency can be described by the threshold value at the beginning of the laser activity with the minimum of pumping input [15].

Quantum chemical calculations were carried out using the AM1 method [16] for the ground state energies. The energy gaps between the ground and excited states were calculated by the CNDO/S method of Del Bene and Jaffé [17] using the QCPE program 333 with the original parameters, but modified to cope with larger molecules and to calculate excited state dipole moments and charge distributions Configuration interaction between 40–50 singly excited configurations was included. In view of the qualitative nature of the conclusions to be derived, geometry optimization procedures were avoided, and the definition of the molecular geometry was kept as simple as possible. Standard geometries were used (bond lengths R(C–C), R(C=C) and R(C–N) = 1.40 Å; R(C–H) = 1.08 Å; angles, 120° except for the tetrahedral methyl groups). For geometries with twisted bonds, the remainder of the molecule was kept rigid.

The synthesis of 2-(4-dimethylaminophenyl)- and 2-(7-diethylamino-2-oxo-2H-1-benzopyran-3-yl)-4-(2-carboxyphenyl)-7-diethylamino-1-benzopyrylium perchlorate (**VI** and **IV**) was carried out by heating a solution of 3.13 g (0.01 mol) of 2-(4-diethylamino-2-hydroxybenzoyl)-benzoic acid (gift from BASF) and 0.01 mol of the appropriate aryl- or coumar-3-yl-methylketone in 30 ml of concentrated sulphuric acid on a boiling water bath for 6 h. The reaction mixture was then poured onto 200 g of ice, and 4 ml of perchloric acid (70%) was added. The precipitate was separated and recrystallized from acetic acid. The dark blue crystals were recrystallized a second time from acetonitrile. Satisfactory elemental and nuclear magnetic resonance (NMR) analyses were obtained. **IV**: yield, 3.37 g (53%); m.p. 328–330 °C. **VI**: yield, 3.46 g (64%); m.p. 208 °C.

3. Results

3.1. Absorption and emission spectra

The absorption and emission spectra of **III** (Cz144) and **IV** (Z51A) differ only marginally (Fig. 2). They are similar to those of **V** and **VI** with somewhat blue-shifted spectral features. The relevant data including the quantum yields and lifetimes are summarized in Table 1.

The fluorescence quantum yields for **III** and **IV** are unusually large compared with related unbridged cyanine dyes with the same length of the chromophoric system. The present data confirm the large quantum yields measured for **III** in a previous study [18]. This strong increase in the fluorescence quantum yield is usually traced to the bridging of the chromophoric backbone (see Fig. 1). Z51A has parts of the cyanine chromophore bridged, and other parts (the middle bond (8–9) and the bonds connecting the amino groups) remain unbridged. We can therefore conclude that, in order to obtain a large increase in the fluorescence quantum yield, it is sufficient to bridge only some of the bonds (the photochemically "active" ones) while others (the "inactive" ones) can be left unbridged.

In order to gain some insight into which of the bonds may be photochemically active and which inactive, we conducted quantum chemical calculations on a semi-empirical level, using AM1 for the relative energies of the ground state species and CNDO/S-CI for the energy differences to the excited states. The results for various twisted bonds of the cyanine model system Cy(15), possessing the same length of the chromophore chain as **III** and **IV**, are collected in Table 2 and summarized in Fig. 3.

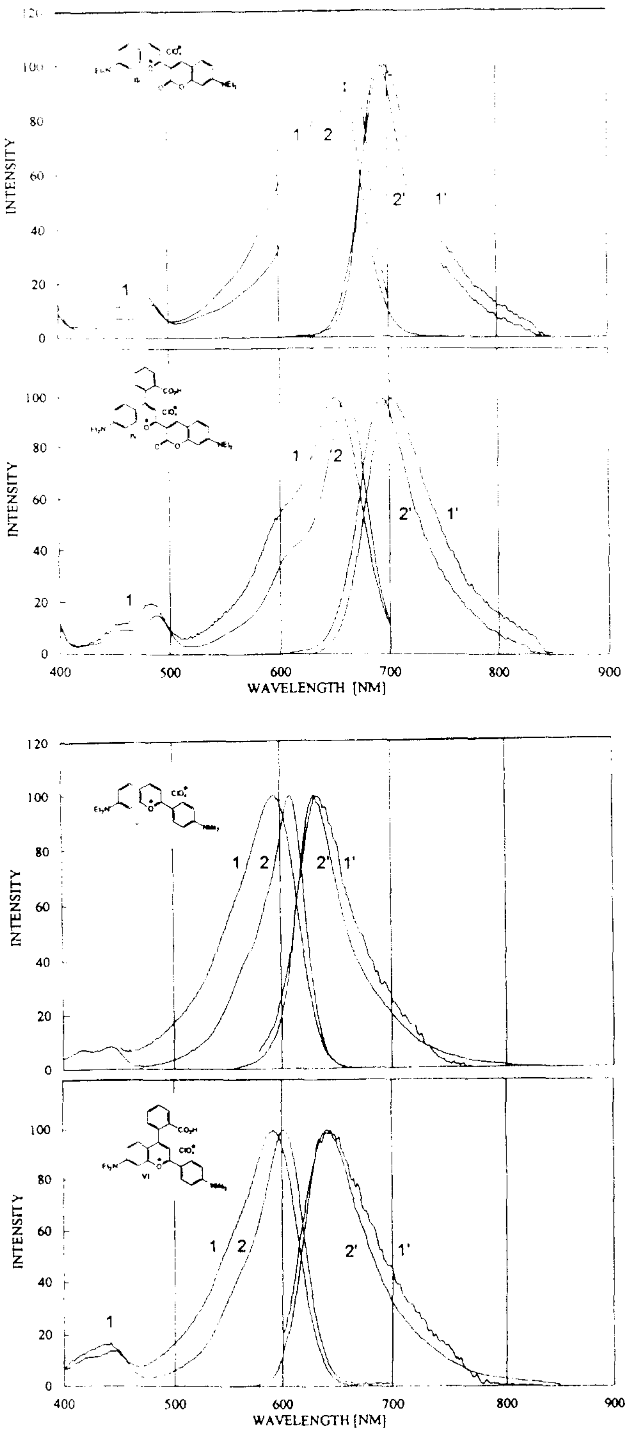

Fig. 2. Absorption and corrected fluorescence spectra of compounds III–VI in acetonitrile (1,1′) and dichloromethane (2,2′) at room temperature.

Table 1
Absorption and fluorescence spectral data, fluorescence quantum yields and lifetimes of **III** and **IV** in dichloromethane and acetonitrile (ACN) at room temperature

Compound	Solvent	λ_{abs} (nm)	λ_{fl} (nm)	$\Delta\nu_{st}$ (cm^{-1})	τ_f (ns)	ϕ_f
III (Cz144)	CH_2Cl_2	670	692	480	3.8	0.6
III (Cz144)	ACN	653	698	990	2.4	0.34
IV (Z51A)	CH_2Cl_2	662	695	720	3.3	0.84
IV (Z51A)	ACN	651	703	1140	2.2	0.30
V	CH_2Cl_2	609	631	572	–	0.79
V	ACN	594	637	1136	–	0.023
VI	CH_2Cl_2	602	642	1035	–	0.76
VI	ACN	592	646	1412	–	0.023

Table 2
Calculated ground and excited state energies and oscillator strengths of the planar and twisted conformations of the cyanine Cy(15)

Bond twisted	$E(S_0)$ (eV)	$\Delta E(S_1\text{–}S_0)$ (eV)	f^a	$\Delta E(S_2\text{–}S_0)$ (eV)	f^a
All planar	0	2.135	1.48	3.705	0
1–2	0.50	2.54	1.49	3.68	0
2–3	0.77	1.29	0	2.28	1.36
3–4	0.56	2.28	1.34	2.66	0
4–5	1.0	1.27	0	2.61	1.27
5–6	0.61	2.04	0	2.56	1.21
6–7	0.85	1.46	0	2.95	1.25
7–8	0.71	1.61	0	2.88	1.32

[a] Oscillator strengths $f < 10^{-3}$ are given as zero and indicate TICT-type (twisted geometry) or n,π* (planar geometry) states.

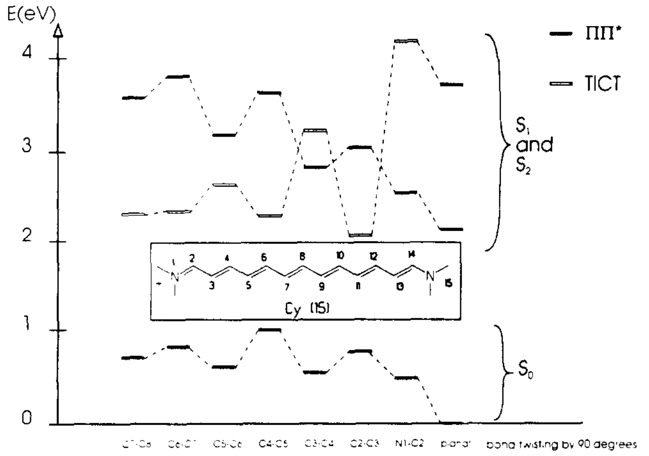

Fig. 3. Summary of the quantum chemical results for Cy(15). The excited state energies are constructed by adding the energy differences from CNDO/S to the respective ground state energies of the various twisted conformers. The perpendicularly twisted bond is indicated by the numbering of the carbon atoms. π,π* states with allowed character are indicated by filled bars, TICT-type states by open bars.

Twisting of bond 8–9 (the unbridged bond in Z51A) leads to a lowest forbidden state of TICT type which is not energetically favourable with respect to the energy of the S_1 excited state of the planar conformation. Twisting of this bond is therefore not expected and thus does not lead to fluorescence quenching. The same applies to twisting of the dimethylamino groups, where the lowest excited state is of π,π* type. Twisting of bond 2–3 or 13–14, on the other hand, leads to a lower lying TICT-type state, which could correspond to a photochemical funnel connected with fluorescence quenching, but these bonds are bridged in **III** and **IV**.

The relatively large fluorescence quantum yields of Cz144 and Z51A are sufficient for use as laser dyes. Fig. 4 shows the tuning curves as measured in acetonitrile, and a comparison with those observed for rhodamine 6G, dichloromethane (DCM) and pyridine-2. With respect to the obtainable lasing efficiency (Table 3), Z51A is only slightly superior to Cz144, but pyridine-2 represents a sizeably more efficient laser dye for this long-wavelength region around 750 nm. With respect to their photo- and thermal stability, both dyes are not ideal, but Z51A possesses much better values than Cz144, as shown in Table 4.

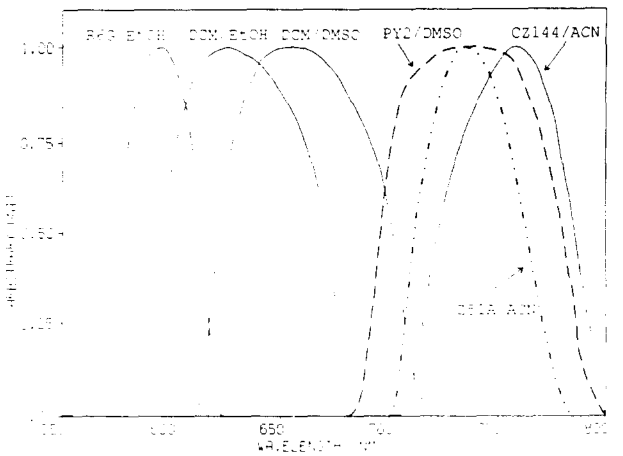

Fig. 4. Comparison of the normalized laser tuning curves of Cz144 and Z51A in acetonitrile, pyridine-2 and dichloromethane (DCM) in dimethylsulphoxide (DMSO) and DCM and rhodamine 6G in ethanol.

Table 3
Tuning maxima and range of Cz144, Z51A and several other laser dyes, together with their lasing efficiency η

Dye and solvent	λ_{max} (nm)	Tuning range (nm)	η (%)
R6G/EtOH	595	562–620	14.5
DCM/EtOH	625	588–680	11.5
DCM/DMSO	656	615–712	13.8
Pyridine-2/DMSO	735	687–787	11.0
Cz144/CH_3CN	761	712–795	7.4
Cz144/CH_2Cl_2	760	713–795	7.7
Z51A/CH_3CN	735	704–778	8.1

R6G, rhodamine 6G; EtOH, ethanol; DCM, DMSO, dimethylsulphoxide.

Table 4
Comparison of the thermal stability and photostability of Cz144 and Z51A: (a) thermal decay of the long-wavelength absorption band of the dyes in phosphate buffer (pH 7.4) at 310 K; (b) decrease in the lasing efficiency on irradiation with a mercury lamp

(a) Thermal stability

	Relative intensity (%)			
	$t=0$ h	$t=3$ h	$t=5.7$ h	$t=4$ days
Cz144	100	53	37	10
Z51A	100	100	100	83

(b) Photostability

	Relative intensity (%)		
	$t=0$ min	$t=15$ min	$t=30$ min
Cz144	100	76	36
Z51A	100	–	85

4. Discussion

4.1. Photophysics as controlled by adiabatic photochemistry

The fluorescence properties of dyes, and therefore their applicability as laser dyes, are often dictated by the possibility of relaxation to non-emissive states by rotation of one (or several) flexible bonds. If the triplet manifold is not populated, but the fluorescence quantum yield is low, these non-radiative loss processes in the singlet state are often called "internal conversion", e.g. in the poorly fluorescing triphenylmethane (TPM) dyes, but their understanding as adiabatic photochemical channels opens up the possibility of predicting and controlling their presence and thus the performance of fluorescent dyes [9,19,20]. In cyanine dyes (TPM dyes also belong to this class), the TICT nature of the lowest excited state of the twisted geometry, connected with charge and orbital localization, has been confirmed by several theoretical results [21,22]. These states correspond to the excitation of an electron from the highest occupied molecular orbital (HOMO), localized on the subchromophore with an odd number of π atoms, to the lowest unoccupied molecular orbital (LUMO), localized on the other subchromophore with an even number of π atoms [21].

The present results demonstrate that not all the bonds in an unbridged cyanine dye lead to such a low-lying TICT state by twisting, but that some are more and others less reactive. In particular, it can be concluded from the results in Fig. 3 that the central bonds need not be the most "TICT reactive". Interestingly, the most reactive bond in this study is bond 2–3, and the adjacent bonds 1–2 and 3–4 are predicted to be inactive; in contrast, in the study of pentamethine cyanine (Cy(7) with seven π atoms, Fig. 1) [21], bond 3–4 was more reactive than bond 2–3. Clearly, the reactivity pattern seems to depend sensitively on the cyanine length. If highly fluorescent cyanines are desired for application purposes, it is sufficient to bridge these reactive bonds, as demonstrated above for dyes **III** and **IV**.

4.2. Applicational aspects of Z51A

As demonstrated by the lasing action curves in Fig. 4 and the lasing efficiencies reported in Table 3, both dyes **III** and **IV** exhibit lasing properties in the long-wavelength range around 750 nm, similar to pyridine-2. The efficiency, however, is somewhat reduced with respect to this dye, and sizeably smaller than for the well-known laser dyes DCM and rhodamine 6G. On the other hand, the result is significant because it demonstrates that cyanine dyes, often very weakly luminescent due to their adiabatic photochemical activity, can be developed into laser dyes by suitable bridging. It must be emphasized that the stability properties of Cz144 and Z51A prevent the use of these dyes as suitable new laser dyes. However, a structure–reactivity comparison of these two compounds allows the following conclusions to be drawn.

(1) The photophysical properties (spectra, quantum yields, lasing efficiencies) are roughly comparable for the two compounds.

(2) The photochemical stability is sizeably increased for Z51A.

(3) The thermal stability is very much better for Z51A than for Cz144.

(4) The increased thermal and photochemical stability of the 4-(2-carboxyphenyl)-substituted benzopyrylium dyes is similar to the increased stability of rhodamine laser dyes with respect to the unsubstituted pyronine dyes.

Thus a comparison of the stability properties of the two dyes leads to a clear structure–reactivity pattern which can be applied in the development of further laser dyes of related structure.

Acknowledgments

This work was performed with the support of the Deutsche Forschungsgemeinschaft. For the experiments at BESSY, support by the Bundesministerium für Forschung und Technologie (project 05 414 FAB 1) is gratefully acknowledged.

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