Spectrophotometric evidence for the existence of rotamers in solutions of some ketocyanine dyes

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Abstract

The existence of rotational conformers in solutions of 1,5-bis[dialkylaminophenyl]-1,4-pentadien-3-one (**I**) was investigated by infrared, absorption and fluorescence spectroscopy. Comparison was made with 2,5-bis{4-(dialkylamino)phenyl]-methylene}-cyclopentanone (**II**) and 2,6-bis{[4-(dialkylamino)phenyl]-methylene}-cyclohexanone (**III**) which may be considered as rigidified analogues of **I**. The study in organic solvents revealed that two different conformers coexisted in solutions of **I**. They differ by rotation about the carbonyl-carbon quasi-single bond and, according to spectroscopic data and AM1 calculations, could be *cis, cis* and *cis, trans* isomers, the latter being found in much larger proportions. ©2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Ketocyanine dyes derived from bis-amino-dibenzylidene-acetone display very attractive spectroscopic properties. They have been introduced as polarity probes [1,2] to evaluate the microenvironmental characteristics of biochemical and biological systems. Some of them are used as laser dyes or photosensitizers [3], and have found several industrial applications in photopolymer imaging systems [4,5]. Moreover, we have recently shown that a crown-ether-substituted derivative (**Ib**, Scheme 1) is an efficient fluoroionophore for alkaline and alkaline-earth cation recognition [6]. The same behaviour can be expected for the rigidified analogues, 2,5-bis{[4-(dialkylamino)phenyl]-methylene}-cyclopentanone (**IIb**) and 2,6-bis{[4-(dialkylamino)phenyl]-methylene}-cyclohexanone (**IIIb**) which are presently under study.

The photophysical properties of the basic dye, bis(*p-N,N*-dimethylamino)benzylidene acetone, were investigated by Eisenhart and Ellis [7] and De Voe et al [8]. However, no attention has been paid, until now, to the existence of different conformers which may be present in the ground and the excited Franck–Condon states, yet torsion might take place at different sites of the molecule. In particular, due to the existence of two degrees of rotational freedom imparted by the two single bonds between the olefin and carbonyl groups, three planar isomers might be expected to exist, that is the *cis, cis*, the *cis, trans* and the *trans, trans* conformers (Scheme 2). This is the case for parent compound dibenzylideneacetone (DBA), which exists in several isomeric forms and which has been investigated by many workers [9–14], although the nature and the relative proportions of the conformers in solution remain very controversial.

This prompted us to study the occurrence of such conformers in a solution of **Ib** and of the diethylamino parent compound, **Ia** (Scheme 1). Comparison was made with the blocked analogues of series **II** and **III**. The dyes were studied by infrared, UV–Vis and fluorescence spectroscopy, firstly in acetonitrile and then in five other organic solvents. AM1 calculations were used to provide additional information.
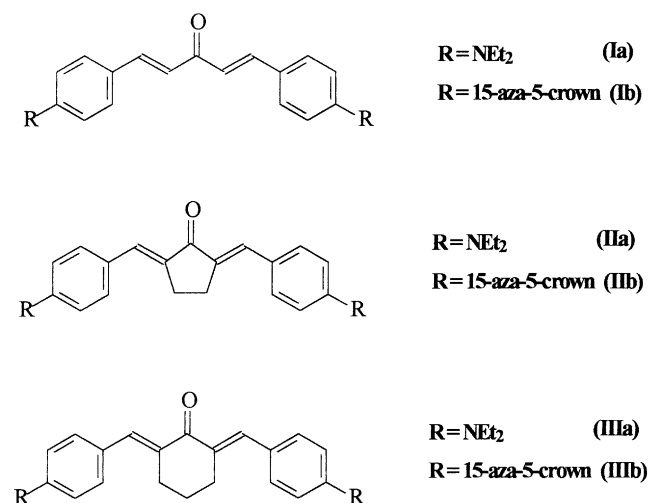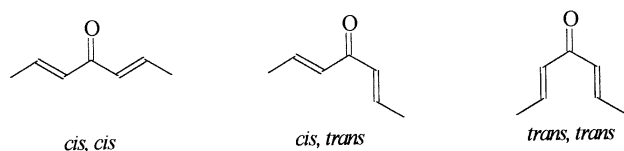
2. Experimental details

2.1. Materials

Spectroscopic grade solvents (Merck and SDS) were used for absorption and fluorescence measurements. Dyes **Ia**, **Ib** and **IIa** were prepared as previously described [6] according

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R=NEt₂ **(Ia)**

R=15-aza-5-crown **(Ib)**

R=NEt₂ **(IIa)**

R=15-aza-5-crown **(IIb)**

R=NEt₂ **(IIIa)**

R=15-aza-5-crown **(IIIb)**

Scheme 1.

cis, cis   *cis, trans*   *trans, trans*

Scheme 2.

to the general procedure of Olomucki and Le Gall [15]. Extensive purification was achieved by recrystallizing **Ia** and **IIa** in carbon tetrachloride. Dye **Ib** was purified on silica plates. Dyes **IIb** and **IIIb** were a gift from Dr. V.P. Pivovarenko, Kiev University. Purity was checked by TLC and elemental analysis.

2.2. Measurements

Infrared spectroscopy was performed with a Perkin Elmer 1760-X Infrared Fourier Transform spectrometer using CaF₂ cells of 100 μm path-length. Absorbance spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer. Steady-state fluorescence work was performed on a Photon Technology International (PTI) Quanta Master 1 spectrofluorometer. All fluorescence spectra were corrected. The fluorescence quantum yields were determined using coumarin 6 in ethanol as standard ($\Phi = 0.78$) [16]. They were calculated using the standard formula: $\Phi_x = (A_s/F_s) \times (F_x/A_x) \times (n_x/n_s)^2\ \Phi_s$ where Φ is the quantum yield, A is the absorbance at the excitation wavelength, F is the area under the corrected emission curve and n is the refractive index of the solvents used. Subscripts s and x refer to the standard and to the unknown, respectively. The measurements were made at 25°C in a thermostatted cell.

3. Results and discussion

We have shown in a previous work [6] that, in this series, substitution by crowns does not affect the photophysical properties compared with diethyl or dimethyl derivatives. So, there is nothing to prevent direct comparison of **Ia** with the crown compounds **IIb** and **IIIb**, as long as the photophysical behaviour is investigated. However, the presence of the crowns leads to minor wavelength shifts in the absorption and emission spectra, and marked differences in the molar absorption coefficient may appear. So, in order to make a rigorous comparison of the spectral characteristics, the crown cyclopentanone and cyclohexanone derivatives (**IIb** and **IIIb**) were studied side by side with **Ib**.

3.1. AM1 calculations

AM1 calculation was performed on molecule **Ia** to determine the optimal conformation of the possible isomers. The torsion angle between the carbonyl and the ethylene groups was allowed to vary by increments of 10° for the two chromophore arms. Therefore, all the possible conformations were considered. Three minima were detected, corresponding to three rotamers. The two lower minima correspond to the *cis, cis* ($\Delta H_f = 170.6\,\mathrm{kJ\,mol^{-1}}$) and *cis, trans* ($\Delta H_f = 175.8\,\mathrm{kJ\,mol^{-1}}$) conformers. The third one corresponds to the *trans, trans* conformer and lies slightly higher ($\Delta H_f = 181.6\,\mathrm{kJ\,mol^{-1}}$). Note that these conformers are almost isoenergetic, as it must be the case for rotational isomerism to be observed ([17–23] and references therein). However, the *trans, trans* conformer is unlikely to be found in solution, not only because it is the most thermodynamically disfavoured, but also due to the high energy barrier which separates it from the others. Additional information about the geometry were also provided by the calculation. The *cis, cis* conformer was more stable when the whole conjugated system was planar. In contrast, the *cis, trans* conformer was more stable when the trans-moiety was twisted by 30° with respect to the plane of the molecule (Scheme 3, a). As expected, the *cis, trans* conformer was more polar than the *cis, cis* one, since the dipole moments were calculated to be $\mu = 5.3$ and 4.2 D, respectively, assuming that the nitrogen free electron pairs were involved in conjugation.

AM1 calculations were also carried out on structures **IIa** and **IIIa**. The whole conjugated system of **IIa** was found to be practically planar. In contrast, for **IIIa**, the propylene bridge induced steric hindrance such that both phenyl groups

(a)   (b)
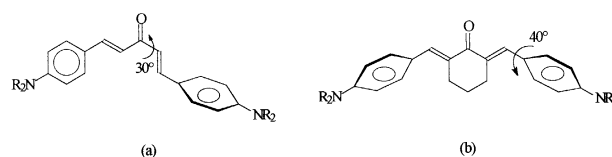
Scheme 3.

displayed an angle of 40° with respect to the core of the molecule (Scheme 3, b).

3.2. Infrared spectroscopy

The infrared spectrum of **Ib**, **IIb** and **IIIb** in solution were recorded in acetonitrile. Dyes **IIb** and **IIIb** displayed only one C=O band at 1679 and 1654 cm^{-1}, respectively, corresponding to only one species in each solution. In contrast, the spectrum of **Ib** exhibited doublet C=O bands at 1660 and 1641 cm^{-1}, the relative proportions of which, calculated from the areas after deconvolution, were 11 and 89%, respectively. These two C=O bands provide evidence for the existence of at least two distinct species in solution for **Ib**. Their frequency and intensity were affected by the nature of the solvent. In the spectrum of **Ib** in toluene, the two bands appeared at 1664 and 1645 cm^{-1}. Their relative proportions were 23 and 77%, respectively. This change in the relative intensity of the bands shows that the corresponding species are in equilibrium. Very similar results were obtained with the diethylamino analogue **Ia** (Fig. 1).

The main difference between all the compounds is that rotation is allowed about the carbonyl-carbon quasi-single bond in loose analogues **I**, whereas such a rotation is prevented in the blocked compounds **II** and **III**. The most reasonable working hypothesis seems to be that the species detected in solutions in series **I** are rotational conformers which differ in conformation about this bond.

In fact, in their study of DBA and of many α,β-unsaturated ketones, Venkateshwarlu and Subrahmanyam have proven the existence of such conformers by the splitting of the C=O band in the IR spectrum [12,13]. They have found that *trans* conjugation produced a lowering of the C=O frequency by 21 cm^{-1} in CCl$_4$ [13]. A very close value was found here for **Ib**, since the difference between frequencies of the two bands was 19 cm^{-1}. The weak band at 1660 cm^{-1} can be attributed to the *cis, cis* conformer, and the intense band appearing at 1641 cm^{-1} can thus be assigned to the *cis, trans* one, i.e. the

two species most likely to be encountered, according to AM1 calculation. Since the relative proportions of the conformers can be determined from the band intensities, the *cis, trans* conformer is seen to strongly predominate in solutions of **I**.

The band assignments ares in total accordance with two observations: firstly, the bands found for the blocked *cis, cis* analogues, **IIb** and **IIIb**, also appeared at high frequency. Secondly, for **I**, the *cis, cis* conformer is twice as abundant in toluene than in acetonitrile, due to the fact that, being less polar than the *cis, trans* form, it is more stabilized by a non-polar solvent.

3.3. UV–Vis absorption study

It is now interesting to see whether the existence of the two conformers in solutions of **I** has an influence upon the UV–Vis absorption properties. The absorption spectrum of every compound exhibited an intense long-wavelength band which corresponding to intramolecular charge transfer from the electron-donor amino substituent to the carbonyl group acting as electron acceptor [1] (Fig. 2). At low wavelengths, it displayed distinct bands which have been assigned by Khalaf et al [1] to π–π* transitions of the benzenoid and conjugate systems and to the weak n–π* transition masked underneath.

Concerning the position of the spectra, dyes **Ib** and **IIIb** absorbed at very similar wavelengths, while the absorption of **IIb** was red-shifted by 30 nm (Table 1).

It can be verified using the recent data from Barnabas et al [3] that the absorption maximum of **IIa** was also strongly red-shifted compared to that of **Ia** in the six solvents investigated (Table 2). This indicates that electron delocalization was indeed far better in the case of **IIa**, and agrees with the fact that the latter compound is planar, whereas **III** and the major isomer of **I** are twisted structures.

Regarding the shape, the absorption spectrum of **Ib** was obviously more complicated than those of **IIb** and **IIIb**. It also was the widest, as shown by the full width at half max-
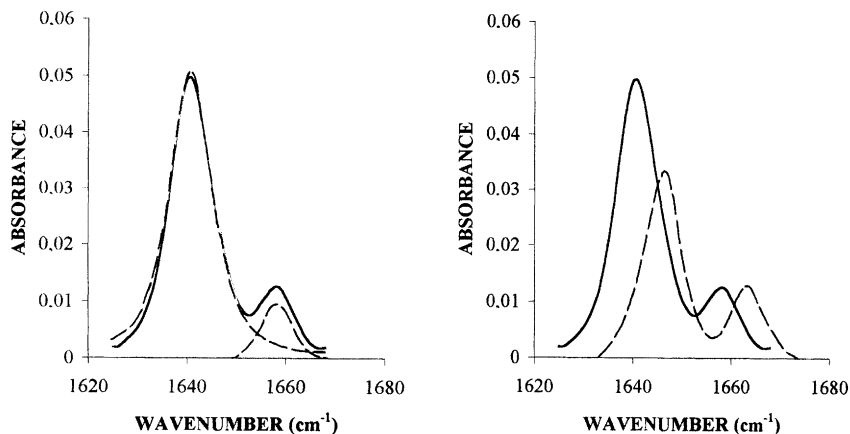

Fig. 1. Left: rough (full line) and deconvoluted (broken line) infrared spectrum of **Ia** in acetonitrile. right: infrared spectrum of **Ia** in acetonitrile (full line) and toluene (broken line).

Table 1

Spectral characteristics in acetonitrile. Maximum absorption wavelength λ_{abs}, full width at half maximum for the absorption (FWHM$_{abs}$) and emission (FWHM$_{em}$) spectra, molar absorption coefficient e, maximum excitation wavelength λ_{ex}, maximum emission wavelength λ_{em}, fluorescence quantum yield Φ, Stokes shift $= \nu_{ex} - \nu_{em}$

	λ_{abs} (nm)	FWHM$_{abs}$ (cm^{-1})	ε (l mol^{-1} cm^{-1})	λ_{ex} (nm)	λ_{em} (nm)	FWHM$_{em}$ (cm^{-1})	Stokes shift (cm^{-1})	Φ
Ib	438[a]	5150	28000[a]	446	566[a]	3060	4754	0.16[a]
IIb	464	3510	68000	464	556	2790	3566	0.14
IIIb	434	4880	52500	434	564	3940	5311	0.017

[a] From ref. [6].
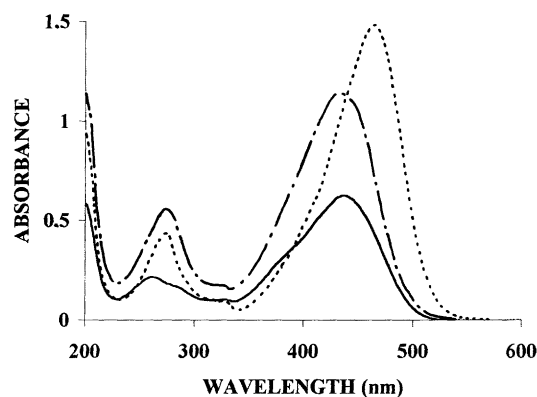

Fig. 2. Absorption spectra of **Ib** (full line), **IIb** (dotted line) and **IIIb** (broken line). Dye concentration 2.2×10^{-5} M in acetonitrile.

imum (FWHM) value, and displayed the lowest molar absorption coefficient (28 000 l mol^{-1} cm^{-1} for **Ib** instead of 68 000 and 52 500 l mol^{-1} cm^{-1} for **IIb** and **IIIb**, respectively). The discrepancies observed for **Ib** can partly originate from the fact that two species at least coexist in solution, the absorption spectrum of each species adding up to yield the spectrum of the solution. Based on the fact that a planar structure is more conjugated than a twisted one, the planar, well-conjugated *cis, cis* conformer of **I** may be expected to absorb in the red part of the spectrum, whereas the twisted *cis, trans* conformer should absorb at lower wavelengths. This assumption differs from that of Hoshi et al [9], who worked on DBA and who expected this conformer to absorb at higher wavelengths than the *cis, cis* one, on the basis of MINDO/2 calculations. However, it is possible that

results dealing with DBA are not directly transposable to our amino derivatives, where strong charge transfer takes place.

3.4. Fluorescence excitation spectra

The complexity of the absorption spectrum of **I** was stressed on comparison with the excitation spectrum. In every solvent investigated (Tables 1 and 2), the most striking feature in the behaviour of **Ia** and **Ib** was that the excitation spectra peaked at higher wavelengths than the absorption spectra (Fig. 3). In contrast, the absorption and excitation spectra of the blocked analogues **IIb** and **IIIb** were superimposable. The discrepancy observed for **I** indicates the presence in solution of two species with different emission properties. The *cis, cis* conformer which absorbs in the red part of the spectrum seems to exhibit the higher fluorescence efficiency.

3.5. Emission spectra

This hypothesis is confirmed by the observation of the emission spectrum of **I**. The quantum yield of **Ia** passed from 0.12 to 0.18 when the excitation wavelength varied from 360 to 470 nm. Therefore, emission was more intense when exciting the long-wavelength absorbing component, assumed to be *cis, cis*-like. No variation was detected for **IIb** in equivalent conditions.

However, no significant variation was observed in the spectrum shape by changing the excitation wavelength. Only one fluorescence lifetime, which was measured to be 800 ps,
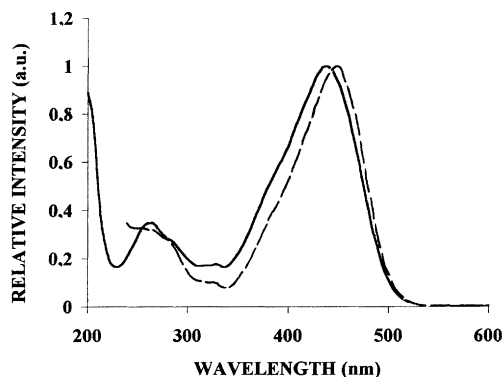
Table 2

Maximum absorption wavelength λ_{abs}, maximum excitation wavelength λ_{ex}, difference between the absorption and excitation wavelengths $\Delta\lambda$, maximum emission wavelength λ_{em}, fluorescence quantum yield Φ

Solvent	**Ia**					**IIa**[a]		
	λ_{abs}[b] (nm)	λ_{ex}[b] (nm)	$\Delta\lambda$ (nm)	λ_{em}[b] (nm)	Φ	λ_{abs} (nm)	λ_{em}(nm)	Φ
cyclohexane	414	430	16	453	0.0004[c]	445	453	0.005
toluene	434	438	4	485	0.051[c]	461	487	0.11
dichloromethane	454	456	2	557	0.16[c]	480	550	0.20
acetonitrile	444	454	10	572	0.15[b]	471	564	0.29
								0.16[b]
ethanol	466	476	10	620	0.27[b]	492	618	0.25
methanol	472	480	8	640	0.087[b]	496	635	0.07

[a] From ref. [3].
[b] This work.
[c] From ref. [6].

Fig. 3. Comparison of the absorption (full line) and excitation (broken line) spectra of **Ib** in acetonitrile. Dye concentration: 2.9×10^{-5} M and 1.4×10^{-6} M, respectively. $\lambda_{em} = 565$ nm.

was detected by varying the emission wavelength from 550 to 650 nm [6]. This suggests that for **I**, emission is due to only one excited species.

In order to understand the particular behaviour of **I**, the emission characteristics of the three analogues must now be compared.

Firstly, the shape of the emission spectra, which exhibited a single band, was very similar (Fig. 4). The emission maximum wavelength was found to be around 560 nm for the three analogues (Table 1). In every case, it was independent of the excitation wavelength, which was arbitrarily set at the absorption maximum. This suggests that the emitting species was similar for the three compounds. Consequently, emission arose from the *cis*, *cis* conformer, which is the only structure possible for **IIb** and **IIIb**.

Secondly, more information can be extracted from the comparison of the fluorescence quantum yields of the three compounds, measured by exciting at the absorption maximum. Tables 1 and 2 revealed surprising similarities between series **I** and **II**. Most of the quantum yields were very
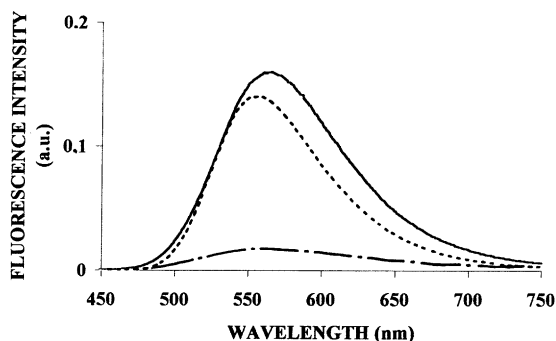

Fig. 4. Emission spectra of **Ib** (1.8×10^{-6} M, full line), **IIb** (7.4×10^{-7} M, dotted line) and **IIIb** (9.5×10^{-7} M, broken line) in acetonitrile. $\lambda_{ex} = 438$, 466 and 434 nm, respectively. The absorbance of each solution being similar ($A = 0.05$) at the excitation wavelength, the fluorescence intensities may be compared.

close, [1] they rose with solvent polarity, then decreased in protic media. This suggests that the emission processes are quite similar for compounds **I** and **II**. At first sight, this hypothesis seems reasonable since the same excited *cis*, *cis* species are involved in both cases. However, it must not be forgotten that the proportion of the *cis*, *cis* isomer in the ground state is only 10% for compound **Ia**. This means that either the *cis*, *cis* rotamer of **I** is more emissive than **II**, or an efficient *cis*, *trans* to *cis*, *cis* photoisomerization takes place in solutions of **I**.

Another striking feature is that the quantum yield of **IIIb** is collapsed by an order of magnitude compared to that of **Ib** and **IIb**. One explanation is that the fluorescence efficiency is at its best when the excited state is close to planar. The dyes of series **I** and **II** can easily take up this optimal conformation while **III** would be sterically prevented from doing so. This also agrees with the observation that the emission spectrum of **IIIb** is the widest (see the FWHM in Table 1), since fluorescence may arise from many conformations, none of them being the most favourable. Finally, the Stokes shifts decreasing in the order **IIIb** > **Ib** > **IIb** also support the fact that relaxation from the Franck–Condon state involves bigger conformational changes for the two first members of the series.

4. Conclusions

The presence of rotamers often complicates the analysis of the spectroscopic and photophysical behaviour of some compounds. Conversely, optical spectroscopy is often well-suited to give evidence about this phenomenon, which is sometimes difficult to detect by other methods. In particular, fluorescence spectroscopy has been widely used to prove the existence of ground-state conformeric equilibria in solutions. In recent years, it has been extensively applied to the study of *trans*-stilbene analogues containing a wide range of aryl moieties ([17–29] and references cited therein). In this work, infrared spectroscopy yielded the best arguments to distinguish between two rotamers in compounds **Ia** and **Ib**. Absorption and emission spectroscopies also proved to be informative, provided that attention is paid to small variations. We intend to use these methods to investigate the effect of rotamerism on ion recognition. In an earlier work [6] **Ib** was studied as a fluoroionophore. Comparison of these results with those obtained with blocked analogues **IIb** and **IIIb** are presently underway.

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[1] The value given by Barnabas et al for **IIa** in acetonitrile (0.29) differed markedly from that reported by us for **IIb** (0.14), whereas no difference was encountered in series **I** between the diethylamino and the crown analogues. This discrepancy prompted us to measure the quantum yield of **IIa**, which was found to be 0.16. Note that this value is very close to that reported for **Ia** according to the same procedure.

Acknowledgements

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