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Journal of Photochemistry and Photobiology A: Chemistry 128 (1999) 93–96

Journal of Photochemistry and Photobiology A:Chemistry

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Photochemistry of 2-[(1,3,3-trimethylindoline-2(1H)-ylidene)propen-1-yl]-3, 3-dimethylindolino[1,2-b]-oxazolidine in solution

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Received 16 March 1999; received in revised form 27 May 1999; accepted 1 June 1999

Abstract

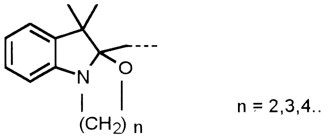
Photochemical behavior of 2-[(1,3,3-trimethylindoline-2(1H)-ylidene)propen-1-yl]-3,3-dimethylindolino[1,2-b]-oxazolidine was investigated in different solvents. The results obtained indicate that in solution the compound may exist in the two forms (closed and open forms) depending on solvent polarity and proticity. Solvent and structure effects on the closed → open form process were studied. The mechanism responsible for the stabilization of the open form is discussed. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Photochemistry; Solvatochromism; Ring-chain equilibrium; Cyanine dyes

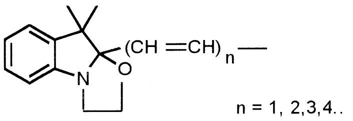
1. Introduction

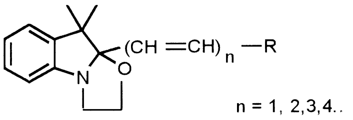
Photochromic compounds attract special attention because they could be applied as optical memory media, for coatings, for windows, photochromic decoration, optical switches and optical filters [1]. The trimethinecyanine dyes, derivatives of 3H-indole, containing the 2-hydroxyethyl group on the nitrogen atom present some photochromic and electrochromic properties [2,3] and could be compared to those of classical photochromic families. This class of compounds has several important structural peculiarities, which give good reasons for more special properties of the compounds:

- a long conjugated system, which easily can be chemically modified through:
    1. extension of the oxazine cycle



    2. extension of the conjugated system
    3. changes of the structural fragment R at the end of the system





- photocoloration and thermodecoloration or thermocoloration are interesting properties of the compounds
- the form of well separated charges gives possibility for the presence of electrochromism and an electric potential in polymer membranes.

In connection with our intentions to use photochromic systems for the construction of light-sensitive molecular devices for us it was very important to know the photochemical behavior of 2-[(1,3,3-trimethylindoline-2(1H)-ylidene)propen-1-yl]-3,3-dimethylindolino[1,2-b]-oxazolidine in polar and non-polar solvents. The ring-chain equilibrium like a photochromic process will depend on the light absorption, the characteristics of the solvents and their participation as subsidiary medium.

This paper evaluates 2-[(1,3,3-trimethylindoline-2(1H)-ylidene)propen-1-yl]-3,3-dimethylindolino[1,2-b]-oxazolidine in terms of color response range on the basis of its solvatochromic behavior.

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PII: S1010-6030(99)00131-8

Table 1
UV spectral data of INO, λ (nm)

C_6H_{12}	EtOH	THF	Dioxane	C_6H_5Cl	CH_3CN	Glycol
525, 564	515, 545	524, 550	524, 552	526, 562	511, 541	525, 575
412	–	424	426	–	420 (w)	–
310, 370	–	310	310	324	310	–
–	285	–	–	–	–	285

2. Experimental

2-[(1,3,3-trimethylindoline-2(1H)-ylidene)propen-1-yl]-3,3-dimethylindolino[1,2-b]-oxazolidine (INO) was synthesized and purified by the procedure described in [2].

Ethanol, acetonitrile, cyclohexane, tetrahydrofuran (THF), dioxane, chlorobenzene, ethylene glycol were used as solvents. All were of spectral grade and used without further purification. The spectral and photochemical measurements were carried out in quartz cells.

A standard OSRAM HBO 200 W/2 low pressure Hg (mercury) vapor lamp (600 mW) was used for all irradiation with filters (λ = 254 nm). The energy absorbed by the sample was determined by measuring the UV light intensity with a power meter in front of the probe.

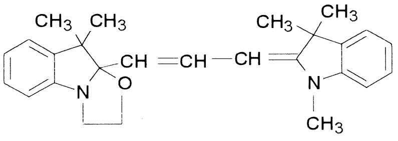
The absorption spectra of the unirradiated and irradiated solutions were measured in the wavelength range 200–800 nm using Perkin–Elmer 19 Spectrophotometer.

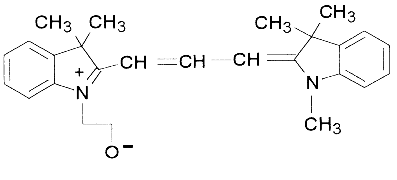
3. Results and discussion

3.1. Spectral investigations

The UV absorption spectra of the compound in different solvents were measured and the spectral data are collected in Table 1.

It was found that the spectra of INO in different solvents exhibit characteristic features of the uncolored (closed) form A (280–330 nm) and colored (open) form B (520–570 nm).

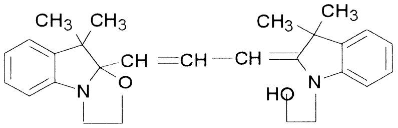




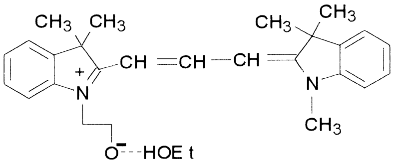
In solution the compound may exist in the two forms – closed and open, depending on the solvent polarity and proticity. In cyclohexane, THF, dioxane the less polar closed form predominates and the equilibrium between the closed and open forms is shifted towards the closed (uncolored) form A.

$$A \rightleftarrows B$$

Analysis of the spectral data obtained and spectral characterization of compounds with similar structure indicate that the closed form can be characterized with an intense absorption maximum at 280–325 nm [2,4]. For comparison, the structure



has λ_{max} at 315 nm [2]. The same absorption maximum is very intense in cyclohexane, THF, CH_3CN, C_6H_5Cl and dioxane and less intense in the other solvents. It can be deduced that in these solvents the closed form predominates to a great extent. The absorption bands of the open form B are in 520–560 nm region [2,4]. The colored form is generally highly polar and the more polar solvents such as EtOH and ethylene glycol shift coloress-colored equilibrium in favor of the colored form. A maximum at 400–420 nm is present in the absorption spectrum of INO in THF, dioxane, cyclohexane and CH_3CN. There are no data in the literature for the assignment of this band. It is important to note that in CH_3CN the absorption maximum is hypsochromic shifted in comparison with that in EtOH. One of the reasons of that fact can be the formation of associates held by intermolecular hydrogen bond (in EtOH and ethylene glycol):



The formation of such associates can explain why in such solvents the open form forms immediately after the dissolution in the solvents. It is obvious that one of the crucial factors determining the transformation of the closed form in to the open form is the polarity of the solvent. The reason for the stabilization of the open form is the whole negative charge at the oxygen atom. Here EtOH or ethylene glycol are proton donors. Such stabilization is not realized in the other solvents. As a proof of the stabilization of the open form we mention the fact that the addition of a strong base (NH_3) to the solution shifts immediately the equilibrium to the closed form.

3.2. Photochemical investigations

Under the influence of UV light a process of formation of the open form takes place. This process is very well expressed in acetonitrile, cyclohexane, and C_6H_5Cl in comparison with the changes in THF and dioxane. In EtOH and ethylene glycol the changes are insignificant (Figs. 1 and 2):

$$A \xrightarrow{h\nu} B$$

The absorption maximum of the colored form increases during irradiation. The presence of isosbestic points is proof

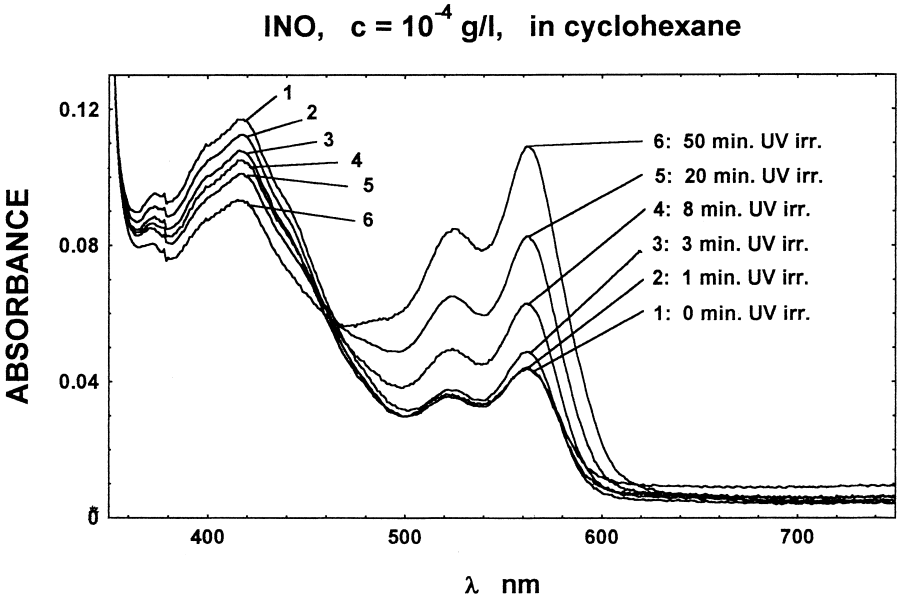


Fig. 1. UV spectra of INO in cyclohexane, $c = 1 \times 10^{-4}$ m/l, measured at different times after start of UV irradiation.

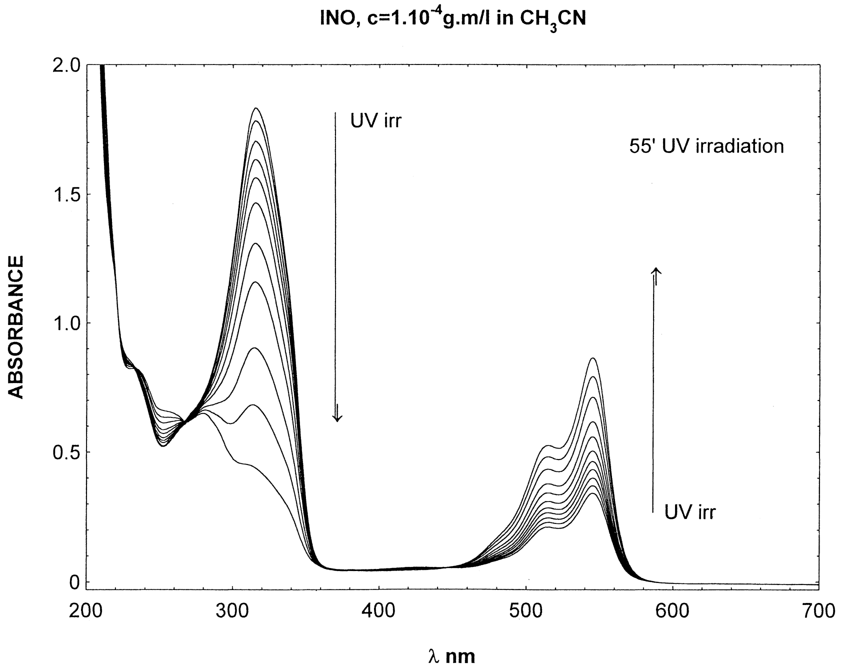


Fig. 2. UV spectra of INO in acetonitrile, $c = 1 \times 10^{-4}$ m/l, measured at different times after start of UV irradiation.

for the transformation only between the forms A and B one into the other (Table 2, Fig. 3). After 24 h, the irradiated solutions do not show reverse formation of the initial closed form A.

In EtOH and ethylene glycol the equilibrium is shifted strongly (above 90%) to the open form. That is the reason for the weak effect of the UV light. But there is no photochemical degradation process during the irradiation. One drop NH_3(25%) added to the irradiated solution causes the decrease of the intensity of the maximum of the open form and increase of the maximum of the closed form. If such solution is irradiated again, there is not effect on the formation of the open form. The presence of the base is a very strong factor, having an influence on the equilibrium. As a result, the π-conjugation between both the parts is achieved. Strong evidence for the existence of only two forms and the presence only of the process: 'closed – open' forms is found in the isosbestic points. From the results it can be seen that the colored species are not formed as rapidly in cyclohexane, THF, dioxane as in ethanol and chlorobenzene. This strongly suggested that the formation of the open form is through the cleavage of the C(spiro)–O bond of the oxazoline ring, since

Table 2
Photochemical data for INO in CH_3CN. $\varepsilon_{\mathrm{formA}}$ ($\mathrm{dm}^{-3}\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$) = 21 500, $\varepsilon_{\mathrm{formB}}$ ($\mathrm{dm}^{-3}\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$) = 9250

τ_{irr} (min)	Abs closed form	$c = 1 \times \mathrm{x}\, 10^{-4}$ m/l closed form	Abs open form	$c = 1 \times 10^{4}$ m/l open form	% closed form	% open form
0	1.83	0.87	0.32	0.34	87	13
1	1.78	0.85	0.38	0.41	85	15
3	1.70	0.81	0.42	0.45	81	19
5	1.62	0.77	0.45	0.48	77	23
7	1.55	0.74	0.48	0.53	74	26
10	1.48	0.70	0.51	0.55	70	30
15	1.30	0.62	0.58	0.62	62	38
20	1.15	0.55	0.61	0.66	55	45
30	0.90	0.43	0.70	0.75	43	57
40	0.69	0.32	0.78	0.84	32	68
55	0.45	0.21	0.86	0.92	21	79

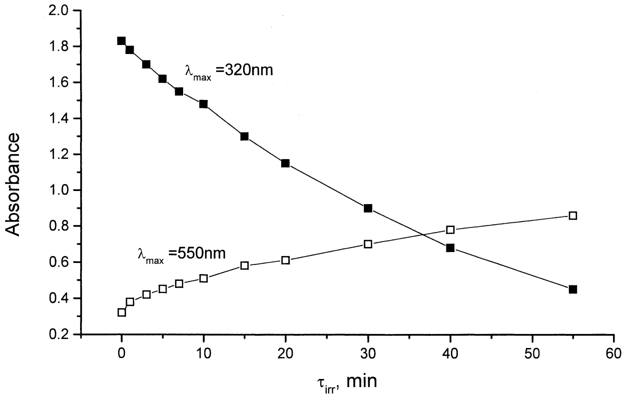


Fig. 3. Dependence Abs/τ_{irr} INO in acetonitrile, $c = 1 \times 10^{-4}$ m/l. ■ – form A and □ – form B.

this process is known to be very sensitive to the type of solvent – especially proton donors (e.g. EtOH) and aromatic solvents (e.g. C_6H_5Cl) [1].

The stabilization of the closed form on the base of the specific properties of the solvents is not effective. That fact allows formation of the isomeric forms of the close form. As that is showed on the base of X-ray investigation for the similar compounds the spiro C atom is located slightly out of the plane of oxazoline ring by 0.41 Å – the ring in nearly in an envelope form. The geometry around N atom is markedly pyramidal [3]. These and other facts show that the oxazoline ring contains a considerable strain. That strain would cause the bond cleavage on the influence of the solvent. The cleavage of the spiro bond causes the change of hybridization of spiro C atom from sp^3 to sp^2 and subsequently changes in molecular conformation and geometry. In open form the pyroline ring is planar and two methyl groups are symmetrically located with respect to the pyroline ring plane. Then stabilization from the molecules of the solvents is considerable.

Spectra of the colored forms of INO were obtained by irradiation of the solution at 254 nm and subsequently recording the UV–VIS absorbance. This was repeated until no further spectral changes were evident. It can be seen from these spectra in cyclohexane, THF and dioxane that the absorption maximum at 400–425 nm decreases during the irradiation in conformity with the increase of the absorption of the open form. The spectral picture can be explained if we consider that this band is characteristic of the isomeric forms of the closed form. During the UV irradiation the formation of the open form can be realized through these forms. The analysis of the results in a wide set of solvents show that in the less polar solvents there is no specific intermolecular interactions and the changes are determined by the dielectric constant of the solvents. The dipolar molecules of the open form are strongly solvated in more polar solvents inhibiting the dark decoloration to the closed form. In this connection the stabilization of the open form with proton-donor solvents such as EtOH and glycol is effective. This experimental fact as well as the strong evidence for the existence of only two forms and the presence only of the process closed–open form is found in the isosbestic points as a proof. The close form A will be stable in non-polar solvents and the contribution of bipolar structure of the open form B becomes noticeable as the polarity of the medium increases. But here in INO there is a second double bond and the explanation of that needs more data. This fact shows that in INO there takes place other processes, which are connected with the spending of the absorbed light [3].

The colored species seemed indefinitely stable in the dark at ambient temperatures as no changes in the color and in the absorbance were detected.

The results show that the dominant photochemical process is the formation of the open form. This is a ‘clean’ reaction, as illustrated by the presence of the isosbestic points (Table 2, Figs. 2 and 3). The fact that these compounds are also photochromic in dilute solutions and in solid polymer matrix [4] demonstrates the molecular character of the process.

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