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POLYMETHINE DYES. PART II*. THE PHOTOCHROMIC BEHAVIOUR OF SOME CATIONIC DIMETHINE DYES

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ABSTRACT. The photochromic behaviour of some 1-H-indazolo-3–dimethine dyes (1-3) in dimethylformamide and 5-chloro-1,3,3.trimethyl-2-[2-(4-oxo-4-H-1-benzopyran-3-yl)ethenyl]-3-H-indolium perchlorate (4) in 1,2 dichloroethane, acetone and acetic acid has been studied. The reason for the photochromism consists of the Z/E or *cis/trans* isomerisation reaction. The formation of Z configuration at light exposure and thermal re-formation of E configuration at dark is supported by spectroscopic data (UV-VIS, IR and ^{1}H- NMR) and kinetic data. Activation parameters for the *cis-trans* isomerisation have been determined.

INTRODUCTION

The *cis- trans* isomerisation of various unsaturated organic molecules induced by light has been extensively studied because of their involvement in the eyesight and photosynthetic bacteria [1], the photochemical degradation of various stilbenic and polymethine dyes [2] mechanism by which part of the harmful energy of U.V. radiation is dissipated by the body [3]. Many of the applications of cyanine dyes (cationic polymethines) have been explained by their photochromic behaviour [2, 4-6], which has been largely examined [4-7]. Panea [5] has proved unambiguously that the photochromism of 1-H-indazolo-3-dimethine dyes is based on the E - Z or *trans – cis* isomerisation, the direct transformation being induced by light and the reverse transformation taking part thermally, in the dark.

The present work supplements the data on photochromic behaviour of 1-H-indazolo-3-dimethine dyes making use of dimethylformamide as solvent, along with the examination the photochromism of a dye from the class of 4-oxo-4-H-1-benzopyran-3-dimethines in dichloroethane, acetone and acetic acid.

EXPERIMENTAL SECTION

Synthesis of the dyes. Cationic 1-H-indazolo-3-dimethine dyes ***(1-3)*** as perchlorate [5,8.] and 1,3,3-trimethyl-5-chloro-2-[2-(4-oxo-4-H-1-benzopyran-3-yl)ethenyl]-3-H-indolium perchlorate [9] were synthesised and purified according quoted references.

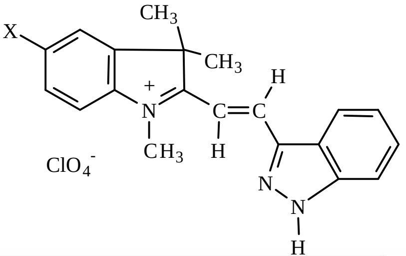
UV-VIS, IR and NMR spectra. Electronic spectra were recorded for all the dyes synthetised in various solvents. We recorded the spectra of more stable *trans*-isomers by using a Specord-UV-VIS Zeiss spectrophotometer or a Jasco V-530 spectrophotometer with the solutions of appropriate concentrations, kept in the dark for a long time. The spectra of the photo-generated isomer (*cis*) were recorded after photoexcitation for a known period of time using either a UV lamp, a tungsten lamp or a blue filter (λ = 450 mn). IR spectra were registered as KBr pellets by using a Zeiss Jena UR-20 spectrophotometer. The ^{1}H-NMR spectra were obtained by means of a Varian Gemini 300 (300 MHz) NMR spectrometer.

Kinetic measurements were performed by spectrophotometrical means, recording the absorbance increase for the thermodynamically stable isomer (*trans*-isomer) in the dark, after the *cis- trans* equilibrium has been shifted to the left and the solution has became practically colourless under irradiation. The photostationary state has been attained. The formation of the more stable and more intense coloured species has been recorded as a function of time at the wavelength corresponding to the peak absorption of each dye. The effect of solvents and temperature has been investigated. Either a Zeiss Spekol or a Jasco V-530 spectrophotometer was used. Both of them were provided with thermostated cell holders. A thermostat has been connected to cell-holder. Three to six replicate runs were performed for each set of experimental conditions. Some of them consisted of several consecutive irradiation and dark reaction of the same dye solution, and some used different solutions with the cell irradiated with light for the same period of time and dark process was monitored. Rate constant determined did not vary to more than 3-4 % for the same experimental conditions. Four ways of irradiation were used: a UV lamp, a tungsten lamp, a tungsten lamp with a blue filter, and a prolonged exposure to daily diffuse light. Reproducible results were obtained with the last two ways of exposure to light. When UV source of light, or repeated irradiation using a ultraviolet or a visible tungsten lamp was used, the systems did not revert to the same value of final absorbance at dark, some irreversible processes took place.

RESULTS AND DISCUSSION

Photochromism of 1,3,3-trimethyl-2-[2-(1-H-indazol-3-yl)-ethenyl]-5-X-3-H-indolium perchlorate with X = methoxy ***(1)****,* hydrogen ***(2)*** and nitro ***(3)*** groups has been studied in dimethylformamide (DMF).

Figure 1 presents the visible absorption spectrum of *trans* isomer and the spectrum after an exposure to blue light for 45 sec. The points A, B and C represent the absorbance values reached in the dark after a period of 50, 115 and 210 sec, respectively.



(1 – 3)

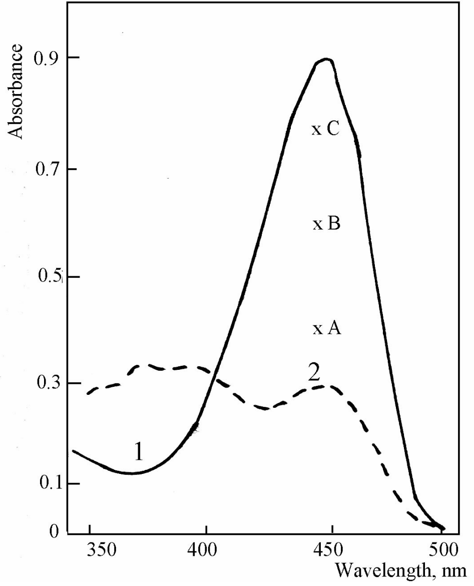


Fig. 1. Absorption spectra for **3** at 20^{o}C in DMF having the concentration of 3.22x10^{-5} M 1- *trans* –isomer, 2- after irradiation.

The shift of the *cis-trans* equilibrium towards the thermodinamically stable isomer at dark follows a first-order kinetics over all experimental conditions employed, even in the cases when some degradation of more coloured species has taken place. The semilogarithmic plots

$$\ln(A_\infty - A) = \ln(A_\infty - A_0) - kt \tag{1}$$

gave straight lines up to 85 – 90 % of reaction, with correlation coefficients of 0.9930 – 0.9990. The value A_∞, A_0 and A stands for the absorbance at the end, at the beginning and at various time intervals from the interruption of light exposure. When repeated irradiation was used, or the reaction time is too long, A_∞ is difficult to obtain. Under such conditions, Guggenheim's method has been used [10] to determine first-order rate constant.

$$\ln(A_{t+\Delta} - A_t) = \ln(e^{-k\Delta} - 1)(A_\infty - A_0) - kt \tag{2}$$

Δ represents a period of time, always the same, having a value of 2 – 3 times larger than the half-life. It is recommended for the first-order reactions when final readings are unknown. Very good correlation coefficients were obtained using the linear equation (2). Table 1 contains the data obtained with the three dyes ***(1-3)***.

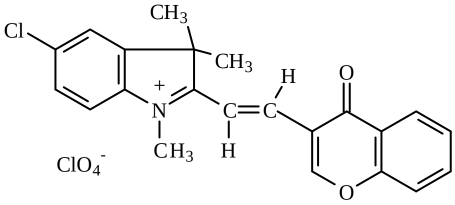
Table 1

Kinetic data on the dark reconversion to *trans* isomer

Substrate	T(K)	10^3k (s^{-1})	Ea ($kJ.mol^{-1}$)	$\Delta H^{\neq}$ ($kJ.mol^{-1}$)	$\Delta S^{\neq}$ ($J.mol^{-1}.K^{-1}$)
1	302.8	0.258	106.4±4.4	104.0±4.3	+30.1±4.5
	312	1.03			
	321.5	3.03			
2	297.7	0.88	94.3±.6.0	91.8±6.0	+5.0±11
		0.89			
		0.90			
	302.8	1.65			
		1.64			
		1.57			
		1.63			
	311.6	4.96			
		4.98			
		4.98			
	316.5	6.92			
		7.06			
		6.88			
	319.0	13,5			
		13.7			
		13.9			
3	293.2	6.60	76.1±.4.0	73.6±.4.0	-35.6±.6.0
	298	9.60			
	303.3	20.1			
	312.3	42.5			

If $\Delta G^{\neq}$ at 298 K were calculated, the following values were obtained for the three compounds: 95.0 ± 5.5, 90.3±4.0 and 84.2± 6.0 $kJ.mole^{-1}$ respectively.

Photochromism of 5-chloro-1,3,3-trimethyl-2-[2-94-oxo-4-H-1-benzopyran-3-yl) ethenyl]-3-H-indolium perchlorate ***(4)****.* The E(*trans*) configuration relative to ethenylic bridge of *(**4**),* obtained by sinthesys [8], was established based on spectral analysis.



(**4**)

Thus, the relative narrow and intense peak in the visible range (see fig. 2) in dichloroethane (λ_{max} = 410 nm, ε_{max} = 80.000 $M^{-1}cm^{-1}$) is characteristic to E(*trans*) isomer [4,5]. The absorption peak at 983 cm^{-1} on IR spectrum for ν –HC=CH- (ethenylic bridge) or coupling constant of 16 Hz from the corresponding doublets of the bridge hydrohen atoms [5] on NMR spectrum proves the same thing. By exposure to light (blue or U.V.) of *(**4**)* the absorption peak at the in the visible range becomes more extended and little intense (ε_{max} = 40.000 $M^{-1}cm^{-1}$) and slightly hypsochromically shifted by about 15 nm as compared to the one characteristic to *trans* isomer. This is in agreement with the *trans – cis* transformation [4,5]. The photo-product is unstable and changes back to *trans* isomer thermally at dark. Therefore the compound *(**4**)* exhibits photochromic behaviour. The re-conversion to *trans* isomer in the dark has been monitored using 1,2 –dichloroethane, acetone and acetic acid for various temperature values and various ways of irradiation. Figure 2 presents the spectra at several periods after the irradiation with blue light was interrupted in 1,2 –dichloroethane. Two isosbestic points are obvious indicating that only two coloured species are present in the mixture.

To be sure the absorbance values at various concentration obey Lambert-Beer relationship, measurements were made, covering a quite large concentration interval. The linearity was very good up to concentration range of $1.8x10^{-3}$ M. Above that, the Lambert-Beer relationship did not hold, due to some associations of dye molecules. Kinetic measurements were carried out at concentration range far below this limit.

By using 1,2-dichloroetane as solvent and an UV lamp and consecutive exposure to light, to shift the *cis – trans* equilibrium to the left, irreproducible results were obtained, concerning the rate constant and the final value of absorbance. We noticed that the solvent itself undergone some decomposition, which induced irreversible transformation with the dye. It has been revealed by spectrophotometrical means. Several spectra present increasing peaks in the ultraviolet region at successive exposure to ultraviolet light from a Hg-lamp. The spectra are presented in figure 3.

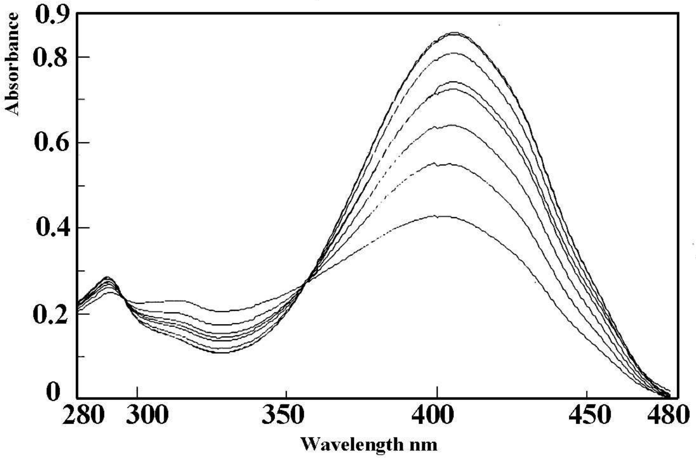


Fig. 2. Electronic spectra of ***4*** at a concentration of 1.07×10^{-5} M in 1,2 dichloroethane at various periods of time after irradiation.

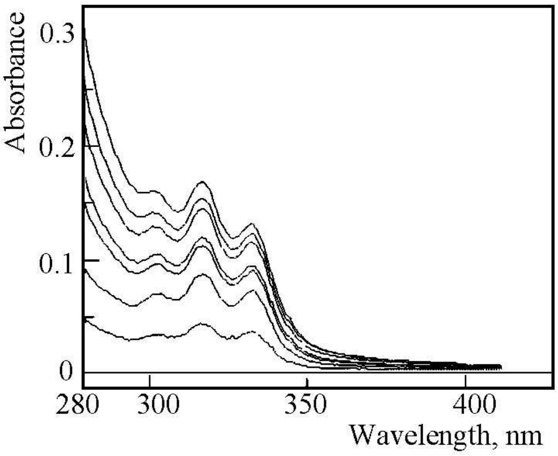


Fig. 3. Absorption spectra of successive irradiated cell of 1,2,dichloroetane. The reference contains unirradiated 1,2,dichloroethane.

With the blue filter or exposure to diffuse daylight, reproducible results were obtained even when 4 – 5 successive irradiation - dark periods were used. With acetone or acetic acid as solvents, only these ways of exposure to light were used. Figure 4 presents the automatically recorded values of absorbance versus time for the re-conversion to *trans* configuration, illustrating an exponential shape.

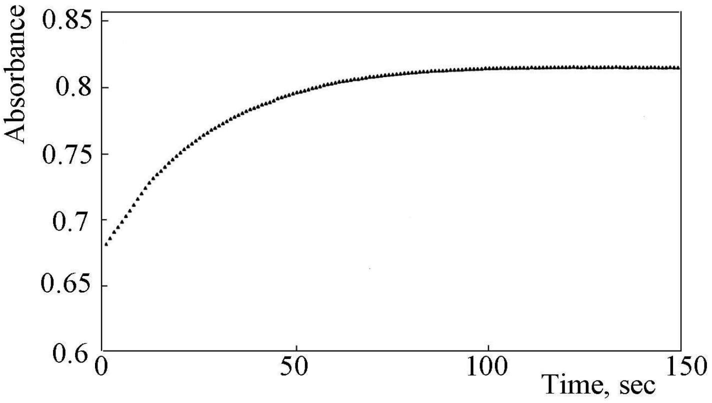


Fig. 4. The evolution of absorbance after irradiation in acetone as solvent.

All kinetic measurements lead to first-order dependence. The linear dependence described by equation (1) was obtained in all the experiments undertaken, correlation coefficients between 0.9960 and 0.9990 were obtained. The results are collected in table 2. Activation parameters were calculated by means of Arrhenius and Eyring equations. Different values were obtained for the solvents employed. It is clear that acetone, a polar solvent, interacts more strongly with activated state, the ionic twisted state of the dye, which is better solvated as compared to a non-polar solvent. This is responsible for unfavourable entropy change, and causes some decrease in activation energy. In the case of acetic acid, a more polar and protic solvent, with possibilities of hydrogen bonding, the mentioned effects are still increased. An important decrease of activation energy as compared to the others has been found. If one calculates the Gibbs free energy of activation, quite close values are obtained for the isomerisation in the three solvents.

Table 2.

First-order rate constants (10^2 k sec^{-1}) for *cis–trans* thermal isomerisation in different solvents and different temperature values and activation parameters.

Temp. (K)/ Solvent	1,2 Dichloroethane	Acetone	Acetic acid
293	0.95	2.16	2.89
294	1.03		
295		2.70	3.11
296	1.30		3.50
297			3.85
298	1.72	2.88	3.90

Temp. (K)/ Solvent	1,2 Dichloroethane	Acetone	Acetic acid
299			3.96
300	2.11	2.96	
301	2.40		
302			
303	3.00	4.86	
304			
305.5		5.3	
308		7.87	
Ea kJ.mole^{-1}	87.8±4.0	6o.2±3.0	29.3±2.8
$\Delta H^{\neq}$ kJ.mole^{-1}	85.4±4.0	57.8±3.0	27.7±2.7
$\Delta S^{\neq}$ J.mole^{-1}K^{-1}	2±3	-79±4	-182±13
$\Delta G^{\neq}$kJ.mole^{-1} at 298 K	84.8±5.0	81.3±3.6	81.9±7.6

CONCLUSIONS

The present study evidentiates the photochromic behaviour of dimethine dyes, having only one stereogenic double bond between the two heterocyclic parts of dye molecule.

The reaction at dark is quite slow to be followed by means of classical spectrophotometrical methods. The spectroscopic measurements (^{1}H-NMR, UV-VIS and IR) of starting material kept in the dark for a long time indicate a E(*trans)* configuration. On the other hand, on the electronic spectra two isosbestic points apear, indicating the involvement of two species in the photochemical-thermal equilibrium.

The broader absorption band and the smaller molar absorptivity for the photo-product as compared to the starting configuration, is in agreement to the fact that the photo-produced isomer is in Z(*cis*) configuration [4].

Kinetic parameters determined here are in accordance with the isomerisation reaction Z(*cis*) – E(*trans*) [4] and the previous conclusions obtained by Panea [5] for other solvents.

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