SYNTHESIS AND SPECTRAL AND PHOTOCHROMIC PROPERTIES OF 7,7'-DISULFOPERINAPHTHOTHIOINDIGO

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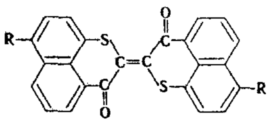
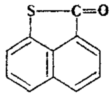
Conditions for the preparation of individual 2-oxonaphtho[1,8-bc]thiophene-6-sulfonic acid were found, and 7,7'-disulfoperinaphthothioindigo (I) was synthesized. The rate of photochemical isomerization of I is higher in dimethylformamide than in water, while the rate of thermal isomerization is lower by a factor of 40 in DMF than in water. A change in the pH of an aqueous solution of I, enriched with the cis form, over the range 1-9 does not affect the rate constant of thermal cis−trans isomerization; at pH 11.2 and 11.6, the constant increases sharply. The solutions are unstable at 11.6 < pH < 1.

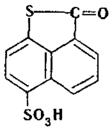
The behavior of dyes of the naphtho[1,8-bc]thiopyran-3-(2H)-one series in organic solvents has been previously studied [1-3]. It was of interest to synthesize a water-soluble dye and investigate its spectral and photochromic properties. For this, we selected dye I.



I $R=SO_3H$; Ia $R=SO_3Na$; II $R=H$



III



IV

In reproducing the known method [4] for the preparation of I, in the step involving the sulfonation of naphtho[1,8-bc] thiophen-2-one (III) we detected the formation of not one, as indicated in [4], but of two isomers of 2-oxonaphtho[1,8-bc] thiophenesulfonic acid (Table 1). It can be assumed that the substituent enters only into the ring that does not contain the carbonyl group, as in all other electrophilic substitution reactions of 1-naphthoic acid [5] and also in the halogenation of III [6]. As an α isomer, 2-oxonaphtho-[1,8-bc] thiophene-6-sulfonic acid (IV) should [7] be formed and hydrolyze more readily than the 8- or 7-sulfonic acid. By moderating the sulfonation conditions, we were able to obtain individual IV, which is converted to the other isomer on heating under the sulfonation conditions. The subsequent successive steps of the process (the production of 4-carboxymethylmercapto-5-carboxynaphthalene-1-sulfonic acid, 3-acetoxynaphtho[1,8-bc] thiopyran-7-sulfonic acid, and dye I) were carried out under the conditions in [4].

The IR spectrum of I differs from the spectrum of unsubstituted perinaphthothioindigo (II) with respect to the presence of the absorption typical for the sulfo group [8] at 645, 680, 1030-1070, 1180, and 1215 cm^{-1}. The broad band at 3300-3500 cm^{-1} attests to the presence of dimeric and polymeric hydrogen bonds, which apparently are also responsible for the insolubility of I in most of the 30 organic solvents tested. While barely coloring alcohols and dioxane, I is more soluble in solvents having two adjacent functional groups: dimethylformamide (DMF) and water. The dye gradually decomposes on heating in ethylene glycol and glycerol to give a complex mixture of products. The principal measurements were therefore carried out in water and DMF solutions (see also Table 2).

The spectra of a solution of I in DMF during trans−cis photoisomerization are presented in Fig. 1. All of the spectra pass through an isosbestic point; this attests to the absence of side photochemical reac-

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TABLE 1. Properties of Isomers of 2-Oxonaphtho[1,8-bc]thiophenesulfonic Acid

Isomer	Band for paper chromatography		Band for electrophoresis in water (pH= 8.2)		UV spectra (in water)	IR spectrum (in mineral oil)
	color	R_f	color	R_f, cm	λ_{max} ($\varepsilon \cdot 10^{-3}$)	ν, cm^{-1}
α	Green	0,775	Green	3,3	256 (17,8); 298 (6,35); 342 (6,64)	620, 655s; 1020, 1040, 1215, 1250, 1380, 1470
β	Blue	0,645	Blue	3,8	226 (8,95); 262 (5); 304, 342 (1,615, 2,06)	620s, 640, 690; 1030, 1050, 1380, 1470

TABLE 2. Comparative Properties of Symmetrical Dyes I and II

Compound	In DMF		$E^{I}_{1/2}$		$E^{II}_{1/2}$	
	λ^{trans}_{max}	λ^{cis}_{max}	in DMF	in water	in DMF	in water
I	275*, ~306, 333, 622	324, 505	0,54	0,168	0,986	1,00
II	270*, ~304, ~326, 624	320, 500	0,68		0,986	

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* The corresponding maximum of the cis form is shifted to the shorter-wavelength side.

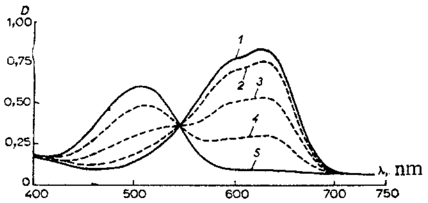

Fig. 1

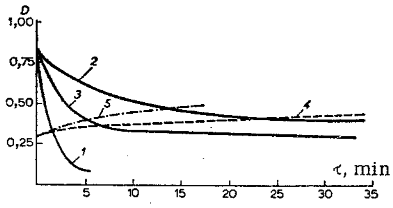

Fig. 2

Fig. 1. Absorption spectra of I in dimethylformamide (c $1.5 \cdot 10^{-4}$ M): 1) solution prepared in the dark; 2) after illumination through a red-light filter for 10 sec; 3) after illumination for 40 sec; 4) after illumination for 100 sec; 5) after illumination for 340 sec.

Fig. 2. Dependence of the optical density on the time for λ^{trans}_{max}: 1) trans → cis isomerization of I in dimethylformamide; 2) trans → cis isomerization of I in water; 3) trans → cis isomerization in water under more powerful illumination; 4) thermal cis → trans isomerization of I in water; 5) photochemical cis → trans isomerization of a solution of I in water. Illumination was realized with a 400-W film projection lamp through an SZS-8 light filter.

tions. Under standard illumination conditions, the trans → cis isomerization of a solution of I in water proceeds much more slowly* (compare curves 1 and 2, Fig. 2), and the degree of conversion does not exceed 45%. An aqueous solution containing 68% of the cis form was obtained when the illumination power was considerably greater. The slower photochemical isomerization in water may be due either to a decrease in the quantum yield of the trans → cis isomerization due to the action of the solvent on one of the elementary steps of the photochemical process or to the rapid reverse thermal cis→trans isomerization in water, or to both of these processes.

We have made rough measurements of the rate of the dark process at room temperature in DMF and in water. The corresponding rate constants are $2 \cdot 10^{-4}$ and $9 \cdot 10^{-3}$ sec^{-1}. Thus the reverse dark reaction occurs in water appreciably faster than in DMF (Fig. 3). If this is the only reason for the incompleteness

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*All of the measurements of the solution in water were made at pH 7.44.

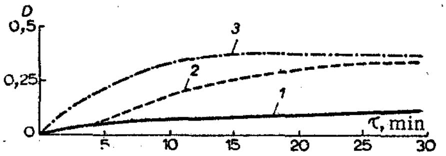


Fig. 3

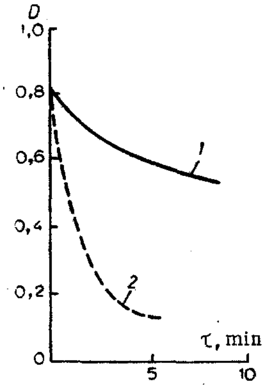


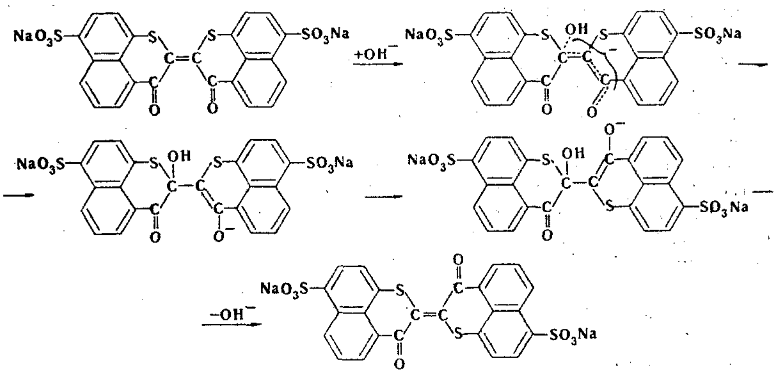
Fig. 4

Fig. 3. Rate of thermal isomerization of I in water: 1) at pH 7.4; 2) at pH 11.28; 3) at pH 11.6.

Fig. 4. Change in the optical density of an aqueous solutions of I with time: 1) observed; 2) calculated.

of the trans → cis isomerization, by subtraction of the rate of the reverse thermal cis→trans isomerization in water from the rate of the trans → cis photoisomerization in DMF, we obtain the rate of trans → cis isomerization in water. The change in the optical density of a solution in water, which was found by calculation (curve 2) and observed experimentally (curve 1), is presented in Fig. 4. Since photoisomerization actually proceeds more slowly than one would have expected, it is clear that the quantum yield of the trans–cis isomerization falls on passing from a DMF solution to an aqueous solution, i.e., a third variant of the solvent effect is realized. A hypothesis regarding the shortening of the lifetime of the singlet excited state of the trans form of thioindigo dyes under the influence of hydroxyl-containing solvents was previously stated in [9, 10]. Since not only alcohols have this effect [9-11] but, as seen from the present research, water does also, it should be assumed that the elementary process that is competitive with the fluorescence and trans–cis isomerization, is the photophysical (rather than photochemical) degradation of the electron energy from the first singlet level, which promotes an intermolecular hydrogen bond.

The insolubility of indigoid and thioindigoid dyes in water previously made it impossible to obtain reliable data on the effect of the pH of the medium on the rate of the catalytic cis → trans isomerization [10]. A convenient object for investigation is the I-Ia system. We were able to show that changes in the pH (for pH 1-9) do not substantially affect the rate constant for thermal isomerization. Thus the rate constants $8 \cdot 10^{-3}$, $9 \cdot 10^{-3}$, $5 \cdot 10^{-3}$, $6 \cdot 10^{-3}$, $7 \cdot 10^{-3}$, and $8 \cdot 10^{-3}$ sec^{-1} correspond to pH values of 1, 1.6, 3.1, 4, 6, and 9. Consequently, in this interval the rate of cis → trans isomerization is independent of the proton concentration in water. However, at pH values of 11.3 and 11.6 (Fig. 3) there is a sharp increase in the rate of cis → trans isomerization, respectively, to $33.4 \cdot 10^{-3}$ and $196 \cdot 10^{-3}$ sec^{-1}; this is probably explained by the catalytic effect of the hydroxide ion.



EXPERIMENTAL

2-Oxonaphtho[1,8-bc]thiophene-6-sulfonic Acid. A 1-g (5.4 mmole) sample of naphtho[1,8-bc]thiophen-2-one was sulfonated with 5.92 g of 100% sulfuric acid (60.4 mmole) at room temperature for 144 h. The reaction mass was poured over ice, and the mixture was treated with an aqueous solution of 9.4 g (55.4 mmole) of $Ba(OH)_2 \cdot 8H_2O$. The $BaSO_4$ was removed by filtration, 2.15 g of NaOH was added to the filtrate, and the mixture was evaporated. The yield was 1.4 g (93%).

Photoisomerization was carried out at room temperature in a 20-m-long glass cuvette; illumination through a red-light filter was performed with the apparatus described in [12] by placing the cuvette containing the solution in front of the inlet into the monochromator. Intensified illumination was realized with two incandescent lamps with an overall power of 1000 W.

Measurement of the Rate of Thermal cis→trans Isomerization of 7,7'-Disulfoperinaphthothioindigo. A solution of 1.5 mg of I in 50 ml of twice-distilled water was poured into a Petri dish with a 2-mm layer, and the dish was placed in a water-cooled (to 12-14°) vessel and illuminated through a red-light filter for 15 min with a 500-W incandescent lamp. A 3.0 ± 0.03-ml sample of the isomerized solution was then mixed rapidly with 6.0 ± 0.03 ml of aqueous perchloric acid solution (pH 1*), the mixture was placed in a cuvette, and the optical density was measured in the region of the absorption of the trans form (600-610 nm). The subsequent measurements were made after 5, 10, 20, 40, and 60 min. The absorption spectrum, which was measured after the solution had stood for 24 h in the dark, did not change after additional refluxing of the solution and corresponded to the spectrum of the pure trans form. The measurements at pH 1.6, 3.1, and 6 (these values were achieved with $HClO_4$) and pH 9, 11.2, and 11.4 (with LiOH) were made similarly.

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*A pH-340 pH meter was used to measure the pH values. A calomel electrode was used as the comparison electrode, and the measurements were made with a glass electrode.