ABSORPTION SPECTRA OF 2,3-DIHYDROTHIONAPHTHEN-3-ONE AND ITS DERIVATIVES

XII*. DYES FROM 7-BROMONAPHTHO[1,8-bc]THIOPYRAN-3(2H)-ONE

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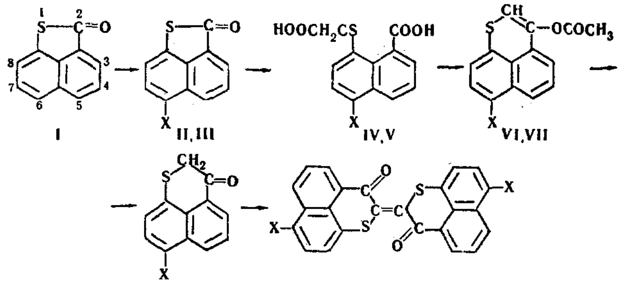
UDC 668.816.5:543.422.6

A number of new thioindigoid dyes have been synthesized. They have been subjected to photochemical isomerization. The absorption spectra of the dyes synthesized have been compared with the absorption spectra of analogous dyes not containing bromine. The spectra of the cis forms are less sensitive to the introduction of a bromine atom than those of the trans forms.

The present paper describes a series of new thioindigoid dyes capable of reversible photochemical cis-trans isomerization. We have shown previously [2] that when naphtho[1,8-bc]thiophen-2(2H)-one (perinaphththiolactone, I) is halogenated, substitution takes place in position 6, and substances II-IV are obtained from I:



II X=Cl; III X=Br; IV X=Cl; V X=Br; VI X=Cl; VII X=Br; VIII X=Cl; IX X=Br;
X X=Cl; XI X=Br; XII X=H

We have now obtained a further confirmation of the structure II by converting it (via IV, VI and VIII) into the dye X, identical according to its absorption spectrum with the 7,7'-dichloroperinaphththioindigo obtained by E. P. Gendrikov by a method eliminating doubt as to the position of the halogen. The absorption maxima of the trans and cis forms of the dyes X and XI in trichlorobenzene are compared with the spectral characteristics of unsubstituted perinaphththioindigo (XII) in Table 1.

The conversions of XII into the 7,7'-dichloro and into the 7,7'-dibromo derivatives are accompanied by practically identical shifts of λ_{max} in the long-wave direction, the spectra of the cis forms being less sensitive to the introduction of a substituent than the spectra of the trans forms.

A series of unsymmetrical dyes with the general formula A, solutions of which in benzene undergo photochemical trans → cis and cis → trans isomerization, has been synthesized by the condensation of IX

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*For Communication XI, see [1].

Rubezhnoe Branch of the Scientific-Research Institute of Organic Intermediates and Dyes. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 8, pp. 1031-1033, August, 1970. Original article submitted March 7, 1969.

TABLE 1. Influence of a Halogen Atom on the Spectrum of the Symmetrical Dye

Dye	trans isomer		cis isomer		$\Delta\lambda$ max trans-cis, nm
	λ_{max}, nm	$\lambda_{max}-\lambda_{max}$ XII, nm	λ_{max}, nm	$\lambda_{max}-\lambda_{max}$ XII, nm	
X*	650	12	520	6,5	130
XI	651	13	521,5	8	129,5
XII	638	0	513,5	0	124,5

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*According to [3], for the trans form of 7,7'-dichloroperinaphththioindigo, λ_{max} 650 nm, ε_{max} $3.0 \cdot 10^4$, and for the cis form λ_{max} 520 nm, ε_{max} $2.0 \cdot 10^4$.

TABLE 2. Properties of the Dyes of General Formula A

Compound	R	trans form		cis form		Empirical formula	Found, %		Calculated, %		$\Delta\lambda$,* nm		Yield, %
		λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$	λ_{max}, nm	$\varepsilon_{max} \cdot 10^{-4}$		C	H	C	H	trans	cis	
XIII	H	598	2,86	485	1,46	$C_{20}H_9BrO_2S_2$	56,84	1,58	56,47	2,13	6	3	56,5
XIV	6-OC_2H_5	587	2,99	470	1,57	$C_{22}H_{13}BrO_3S_2$	56,32	2,43	56,29	2,79	5	0	39,2
XV	4-CH_3; 6-Cl	597	2,71	482	1,39	$C_{21}H_{10}BrClO_2S_2$	53,21	1,96	53,23	2,12	6	3	60,3
XVI	6-Cl	597,5	2,79	485,5	1,55	$C_{20}H_8BrClO_2S_2$	52,42	1,68	52,24	1,75	7	5,5	40,7
XVII	5,6 benzo 7-Cl	622	2,93	511	1,74	$C_{24}H_{10}BrClO_2S_2$	56,78	1,54	56,54	1,97	10	4	49,4
XVIII	6,7-(1'-chlorobenzo)†	615	—	507	—	$C_{24}H_{10}BrClO_2S_2$	55,89	1,78	56,54	1,97	6	3	74,1

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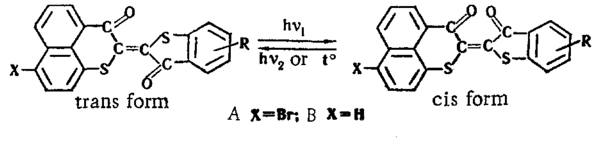
* $\Delta\lambda = \lambda_{max}$ for substance A − λ_{max} for substance B.

† The dye is sparingly soluble in benzene.

with the p-dimethylaminoanils of substituted benzo[b]thiophene quinones (Table 2).



A comparison with the absorption spectra of the dyes of formula B synthesized previously [4] shows that, as in the case of the symmetrical dye XI, the introduction of a bromine atom into the molecule of one of the dyes XIII-XVIII leads to a more pronounced shift in the long-wave direction of λ_{max} of the trans form (shift of 5-9 nm) than λ_{max} of the cis form (shift of 1-6 nm).

EXPERIMENTAL

3-Acetoxy-7-chloronaphtho[1,8-bc]thiopyran (VI). A mixture of 25.3 g (0.085 mole) of S-(8-carboxy-4-chloronaphthyl)thioglycolic acid and 5.3 g (0.065 mole) of CH_3COONa was boiled in 132 ml (1.4 mole) of acetic anhydride for 30 min. Then it was poured into 1300 ml of ice water, and the precipitate was filtered off, washed with water and dried. Yield 23 g (97.5%), mp 105-106°C. After crystallization, mp 112.5-113°C (from ethanol). Found, %: Cl 12.81%. Calculated for $C_{14}H_9ClO_2S$, %: Cl 12.81.

3-Acetoxy-7-bromonaphtho[1,8-bc]thiopyran (VII) was obtained from 5.9 g (0.017 mole) of S-(8-carboxy-4-bromonaphthyl)thioglycolic acid, 18 ml (0.19 mole) of acetic anhydride, and 1 g (0.012 mole) of CH_3COONa in a similar manner to VI. Yield 4.68 g (84.3%), mp 96-99°C. After recrystallization, mp 102°C (from ethanol). Found, %: Br 24.90. Calculated for $C_{14}H_9BrO_2S$, %: Br 24.87.

7-Chloronaphtho[1,8-bc]thiopyran-3(2H)-one (VIII). A solution of 9.44 g (0.034 mole) of 3-acetoxy-7-chloronaphtho[1,8-bc]thiopyran in 1100 ml of glacial acetic acid was treated with 150 ml (1.63 mole) of conc.

HCl and the mixture was boiled for 15 min. Then it was poured into 1500 ml of ice water, and the precipitate was filtered off, washed with water, and dried. Yield 7.7 g (96.2%), mp 104-105°C. After recrystallization from aviation gasoline, mp 103-103.5°C (according to the literature [5] 98°C. Found, %: Cl 15.25. Calculated for $C_{12}H_7ClOS$, %: Cl 15.10.

7-Bromonaphtho[1,8-bc]thiopyran-3(2H)-one (IX) was obtained from 1.12 g (3.48 mmoles) of 3-acetoxy-7-bromonaphtho[1,8-bc]thiopyran, 54 ml of glacial acetic acid, and 24 ml (0.026 mole) of conc.HCl in a similar manner to VIII. Yield 0.92 g (94.8%), mp 121-122°C. After recrystallization from aviation gasoline, mp 132-132.5°C (according to the literature [5] 132-133°C). Found, %: Br 28.51; S 11.47. Calculated for $C_{12}H_7BrOS$, %: Br 28.62; S 11.48.

7,7'-Dichloro-2,2'-bi(naphtho[1,8-bc]thiopyranylidene)-3,3'-dione (X). A solution of 1.5 g (6.4 mmoles) of 7-chloronaphtho[1,8-bc]thiopyran-3(2H)-one in 390 ml of ethanol was treated with 240 ml (0.67 mole) of 10% NaOH solution, and oxidized with air at the boil for 3 hr. Then the precipitate was filtered off and was washed with hot water and hot methanol. Yield 0.85 g (57.0%).

7,7'-Dibromo-2,2'-bi(naphtho[1,8-bc]thiopyranylidene)-3,3'-dione (XI) was obtained from 1.5 g (5.4 mmoles) of 7-bromonaphtho[1,8-bc]thiopyran-3(2H)-one in a similar manner to X. Yield 0.76 g (51.0%). It formed violet prisms from nitrobenzene and did not melt below 400°C. Found, %: C 52.06; H 1.76; Br 28.58. Calculated for $C_{24}H_{10}Br_2O_2S_2$, %: C 52.00; H 1.81; Br 28.83.

2-(7-Bromo-3-hydroxynaphtho[1,8-bc]thiopyranylidene)benzo[b]thiophen-3(2H)-one (XIII). A mixture of 1 g (3.58 mmoles) of 7-bromonaphtho[1,8-bc]thiopyran-3(2H)-one, 1 g (3.54 mmoles) of 2-(p-dimethylaminophenylimino)benzo[b]thiophen-3(2H)-one, and 70 ml of glacial acetic acid was boiled under reflux for 2 hr. The product was filtered off and washed with hot acetic acid and hot methanol. Yield 0.86 g (56.5%), blue powder. It was recrystallized from o-xylene.

The substances given in Table 2 were obtained similarly.

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