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INVESTIGATION OF THE PATHWAYS OF THERMAL FRAGMENTATION OF THIACARBOCYANINE DYES

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and P. I. Abramenko

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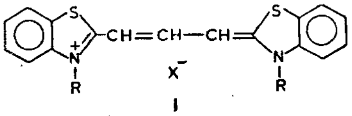
The pathways of the thermal transformations of thiacarbocyanines with various alkyl groups attached to the ring nitrogen atoms of the heteroresidues, of 3,3'-diethylthiacarbocyanine with various anions, and its anhydro base were investigated. The results of the studies are compared with the results of quantum-chemical calculations of the labilities of the bonds in these compounds by the Pariser—Parr—Pople method.

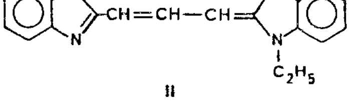
It is known [1, 2] that at high temperatures carbocyanine dyes undergo dealkylation to give anhydro bases. It has also been shown [3] that the corresponding symmetrical dyes are formed in the pyrolysis of unsymmetrical carbocyanines, whereas 2-methylbenzothiazole is detected among the volatile products of the pyrolysis of 3,3'-diethylthiacarbocyanine iodide (I, R = C_2H_5, $\overline{X}$ = $\overline{I}$).



I

It should be noted that the gas—liquid chromatogram of I contains, in addition to a peak of 2-methylbenzothiazole, peaks of other compounds; however, the latter were not identified [3].

In the present research we continued our study of the pathways of the thermal transformations of thiacarbocyanine dyes. It seemed of interest to ascertain whether thermal dealkylation at 300°C and atmospheric pressure is the primary act in the fragmentation, as under mass-spectrometric conditions [2], or whether processes involving cleavage of the C—C bonds of the polymethine chain compete with this reaction.



II

All-Union State Scientific-Research and Design Institute of the Photographic Chemical Industry, Moscow 125167. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1626-1630, December, 1981. Original article submitted December 10, 1980.

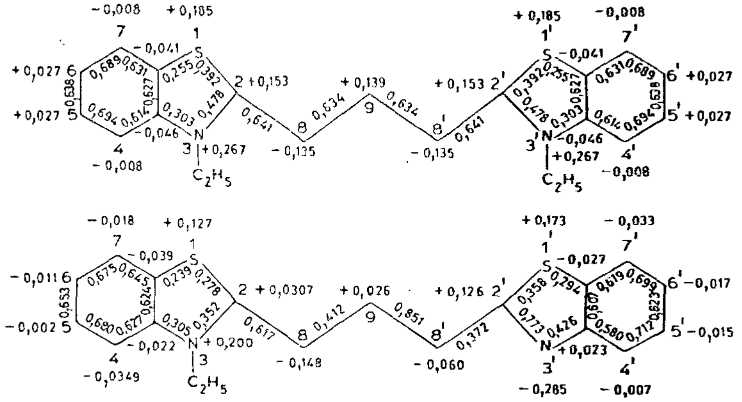


Fig. 1. Molecular diagrams of thiacarbocyanine I and its anhydro base II.

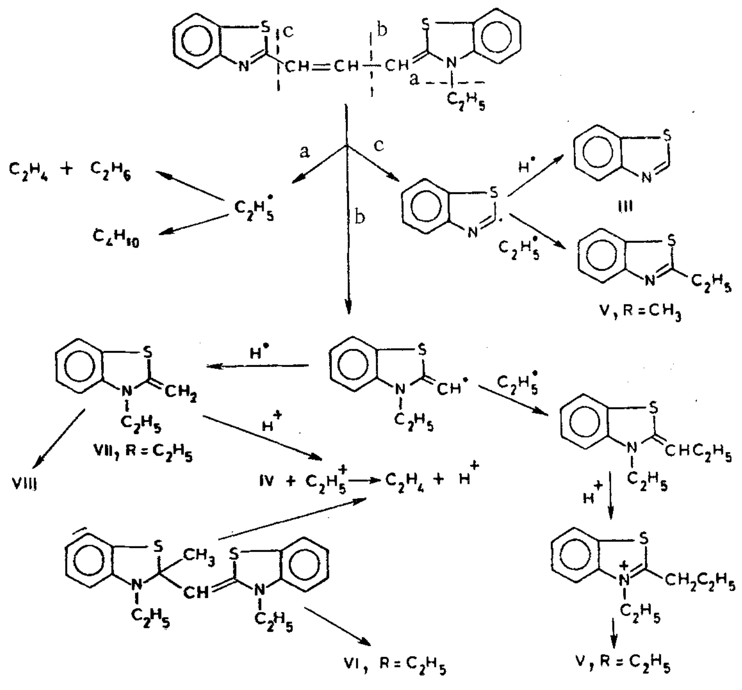
To estimate the strengths of the bonds in thiacarbocyanine I ($R = C_2H_5$) and its anhydro base II we made quantum-chemical calculations of the charges on the atoms (q_r) and the bond orders (p_{rs}) in the indicated compounds. (The method used for the calculations and the parameters used are presented in the experimental section.)

It is apparent from the molecular diagrams (Fig. 1) that q_r and p_{rs} undergo significant redistribution in the dealkylation of dye I. The positive charges on the N atom bonded to the ethyl group and on the carbon atoms in the 2 and 9 positions decrease. The negative charges on the carbon atoms in the 8 and 8' positions are nonequivalent, and the difference in the orders of the bonds between the carbon atoms of the polymethine chain increases markedly. If one proceeds from the fact that the probability of heterolytic cleavage of the bonds should increase as their polarities increase, it may be assumed on the basis of the results of quantum-chemical calculations that in dye I the ethyl group is more easily eliminated from the nitrogen atom and that the C_2-C_8 and C_8-C_9 bonds are more labile than in the case of anhydro compound II. In turn, homolytic cleavage at the $C_{2'}-C_{8'}$ and C_8-C_9 bonds is evidently more likely in anhydro base II than in I, in conformity with the lower p_{rs} values between the indicated atoms in the II molecule.

On the basis of the data presented above it may be assumed that processes involving heterolytic dissociation of the C–C bonds in dye I may compete with dealkylation. To verify this assumption we carried out the thermolysis of I and II. The thermolysis conditions and the methods used to establish the compositions and structures of the volatile fragmentation products were similar to those in [5]. Data on the compositions and structures of the identified (by GLC) volatile products of the thermolysis of I and II are presented in Table 1 with an indication of the relative retention times (α_{rel}) and relative percentages (C, %) of each of them in the mixture, disregarding the other volatile compounds. In the thermolysis of I and II a number of unidentified compounds, the overall amount of which does not exceed 3%, are formed in addition to the substances presented in Table 1, as well as alkyl halides and hydrocarbons. It is apparent from Table 1 that the compositions of the volatile products of the thermolysis of anhydro base II and thiacarbocyanine I ($R = C_2H_5$, $\overline{X} = \overline{I}$) are identical; however, their relative percentages in the mixtures differ substantially due to the different thermal stabilities of the bonds in these compounds.

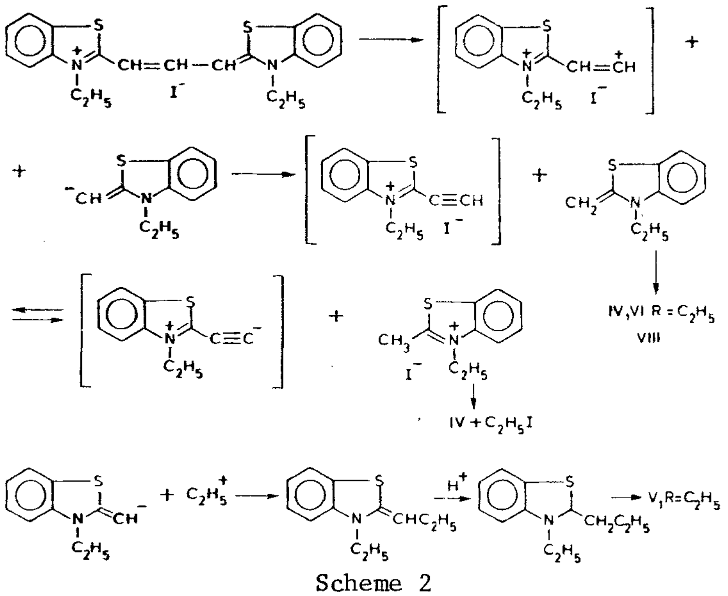
One's attention is also directed to the fact that the overall amount of volatile products formed in the thermolysis, including hydrocarbons, is substantially smaller in the case of the thermolysis of II and, in addition, that the ratio of ethane and ethylene in the hydrocarbon fraction for II is 3:1, as compared with 1:23 for I ($R = C_2H_5$, $\overline{X} = \overline{I}$). Considering the fact that only the ethyl radical can be the source of both hydrocarbons, whereas only ethylene should be formed from the ethyl cation, it may be concluded that homolytic processes involving dissociation of the bonds are more characteristic for II, whereas heterolytic processes are more characteristic for I; this is in agreement with the results of quantum-chemical calculations. In conformity with the data presented and the results of calculations for anhydro base II, Scheme 1 can be proposed for thermal fragmentation.

Ethylene, ethane, and butane (pathway a) are formed as a result of splitting out of an ethyl radical and its subsequent disproportionation and dimerization. In the homolytic



Scheme 1

cleavage of the C_8—C_9 bond (pathway b) one observes the formation of a radical of the methylene base, the acceptance by which of a $C_2H_5^•$ radical and subsequent transformations may lead to 2-propylbenzothiazole V (R = C_2H_5), whereas the addition of an H$^•$ radical may lead to methylene base VII (R = C_2H_5), its dimer, and products of transformation of the latter, viz., IV and VI (R = C_2H_5) and VIII, in accordance with [5]. One also cannot exclude the possibility of heterolytic dissociation of II at the C_8—C_9 bond; however, data that make it possible to prefer one of the possible cleavage mechanisms are not yet available. Benzothiazole III and 2-ethylbenzothiazole V (R = CH_3) may be formed as a result of homolysis of the $C_{2'}$—$C_{8'}$ bond (pathway c). The presence among the volatile products of the thermolysis of 3,3'-diethylthiacarbocyanine (I, R = C_2H_5, $\overline{X} = \overline{I}$) of compounds that are characteristic for homolytic cleavage of anhydro base II (for example, III, ethane, and butane) is explained by the formation of the latter during heterocyclic elimination of an ethyl group from the ring nitrogen atom. In addition, the relatively small percentage of homolytically formed hydrocarbons in dye I (R = C_2H_5, $\overline{X} = \overline{I}$) as compared with II constitutes evidence that processes that involve heterolytic cleavage of the C_8—C_9 bond are more characteristic for it (Scheme 2).



Scheme 2

TABLE 1. Volatile Products of the Thermolysis of Thiacarbocyanines I and Anhydro Base II

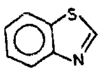
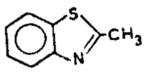
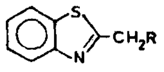
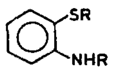
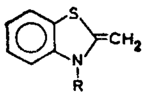
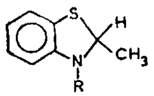
Starting compounds	Thermolysis products (C, %/α_{rel})					
	 III	 IV	 V	 VI	 VII	 VIII
I, R=CH_3, $\bar{X}=\bar{I}$	2/0,89	68/1	24/1,5	6/1,3	0,1/12	0,01/1,33
I, R=C_2H_5, $\bar{X}=\bar{I}$	2/0,89	76/1	18/2,1	4/1,8	0,1/16	0,01/1,45
I, R=C_3H_7, $\bar{X}=\bar{I}$	1/0,89	90/1	5/4,1	3/5,1	0,1/23	0,01/2,2
I, R=C_4H_9, $\bar{X}=\bar{I}$	1/0,89	95/1	4/7,2	1/11,5	0,1/31	0,01/3,8
II	1/0,89	77/1	1/2,1	16/1,8	5/16	1/1,45

TABLE 2. Ratios of the Volatile Products of the Thermolysis of Thiacarbocyanine I ($R = C_2H_5$) as a Function of the Nature of the X Anion

I	VI : V	Ethane: ethylene
I	1 : 4	1 : 23
Br	1 : 1	1 : 10
Cl	70 : 1	1 : 5

The fact that the principal volatile product of the thermolysis of dye I ($R = C_2H_5$, $\overline{X} = \overline{I}$) is 2-methylbenzothiazole IV (C = 76%) is evidently explained by a significant shift of the equilibrium between methylene base VII and ethiodide IV to favor the latter. The schemes of the thermal transformations of thiacarbocyanine dyes that are unsubstituted in the polymethine chain presented above are general in character, since the analogous V, VI, and VII and the corresponding alkyl iodides, alkanes, and alkenes are formed when the alkyl substituents attached to the nitrogen atoms are varied. It is interesting that the character of the anion has a substantial effect on the ratio of the volatile products of the thermolysis of 3,3'-diethylthiacarbocyanine (Table 2).

The percentage of o-ethylmercapto-N-ethylaniline (VI), which is formed from methylene base VII [5], with respect to 2-propylbenzothiazole, the formation of which is primarily associated with dissociation of the C_8—C_9 bond in the starting dye, increases successively on passing from the iodide to the bromide and chloride, and the relative percentage of ethylene in the mixture with ethane decreases. These data constitute evidence that in the indicated series of dyes I ($R = C_2H_5$, $\overline{X} = \overline{I}, \overline{Br}, \overline{Cl}$), on the one hand, the probability of thermal dealkylation of the dye increases as compared with the competitive dissociation of the C_8—C_9 bond in it, whereas, on the other, the equilibrium between methylene base VII and the ethylhalide of IV is shifted to favor VII (Scheme 2) (see [5, 6]).

EXPERIMENTAL

The quantum-chemical calculations were made within the Pariser—Parr—Pople approximation by the method described in [4]. The $\gamma_{\mu\nu}$ integrals were calculated from the Mataga—Nishimoto formula. The resonance integrals were calculated within the "variable β" approximation [8, 9]. The principal parameters were taken from [10] and the tables of Hinze and Jaffe [11] by the Pariser—Parr procedure [12] (for nitrogen in heteroresidues), while the constants for the C—S bond were taken from [13]. All of the rings were regarded as regular polygons with bond lengths of 1.40 Å. Values of 1.48 and 1.36 Å, respectively, were assumed for the lengths of the C—C and C=C bonds, while a value of 120° was assumed for the bond angles. As proposed in [14], the geometrical characteristics (in the calculations) were rescaled. Chromatography was carried out with a Chrom 3-IKZ chromatograph with a pyrolytic adapter and a flame-ionization detector.

The conditions used for the analysis of the hydrocarbon fraction of the pyrolyzate were as follows: The column was 3-m long and had a diameter of 3 mm, the stationary phase was Porapak Q (60-80 mesh), the thermostat temperature was 40°C, and the carrier-gas (nitrogen) flow rate was 20 ml/min.

The following conditions were used for the analysis of the high-boiling fraction of the pyrolyzate: The column was 2-m long and had a diameter of 3 mm, the solid support was Cellite-545 (50-60 mesh), the stationary phase was Apiezon L (15% of the mass of the packing), the thermostat temperature was 130-170°C, and the carrier-gas (nitrogen) flow rate was 20 ml/min.

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SYNTHESIS OF THIAPENTA- AND THIAHEXACARBOCYANINE DYES FROM ALKOXY-SUBSTITUTED POLYMETHINE SALTS WITH DIMETHYLAMINE RESIDUES

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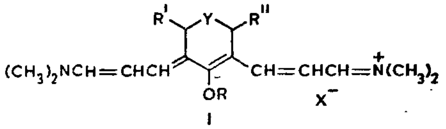
The possibility of the use of alkoxypolymethine salts with dimethylamine residues to obtain thiapenta- and thiahexacarbocyanine dyes is demonstrated. The synthesis of a number of meso-alkoxythiapentacarbocyanines that contain various condensed rings in the 12 and 14 positions of the polymethine chain was realized, and their photographic properties were investigated. It was established that the dyes obtained are effective infrachromatic sensitizers. The electronic absorption spectra of the synthesized compounds were measured.

Polymethine dyes are starting compounds for the preparation of various cyanine dyes. Pentacarbocyanines that are unsubstituted in the chain can be synthesized by the condensation of quaternary heterocyclic salts that contain an active methyl group with salts of dianils, bis(tetrahydroquinolides) [1], or di(N-alkyl)anils [2] of nonatrienedial. Pentacarbocyanines with condensed rings in the chromophore are formed when salts of di(N-alkyl)anils or bis(tetrahydroquinolides) of substituted nonatrienedials are used [3].

In the present research we studied the possibility of obtaining dyes from readily accessible and stable alkoxypolymethine salts with dimethylamine residues (I), which were recently synthesized in [4, 5].



I

$R=CH_3$, C_2H_5, C_4H_9; R' and R''=H, CH_3; $X=CH_3SO_4$, $C_2H_5SO_4$, I, BF_4; $Y=CH_2$, $CHCH_3$, $CHC_4H_9\cdot t$, O

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*Deceased.

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