10. R. D. Obolentsev and L. N. Gabdullina, in: The Chemistry of Organic Sulfur and Nitrogen Compounds Contained in Petroleum Oils and Petroleum Products [in Russian], Vol. 3, Izd. Akad. Nauk SSSR, Ufa (1960), p. 261.

11. R. D. Obolentsev and L. N. Gabdullina, in: The Chemistry of Organic Sulfur Compounds Contained in Petroleum Oils and Petroleum Products [in Russian], Vol. 4, State Joint Scientific and Technical Publishing House of Petroleum and Fossil Fuel Literature (1961), p. 145.

12. V. Berti, A. Girelli, and A. Ilardi, Fourth International Petroleum Congress [in Russian], Vol. 4, Gostoptekhizdat (1956), p. 375.

13. R. D. Obolentsev, L. N. Gabdullina, G. A. Gailyunas, and M. R. Gaisina, in: The Chemistry of Organic Sulfur Compounds Contained in Petroleum Oils and Petroleum Products [in Russian], Vol. 7, Khimiya, Leningrad (1964), p. 148.

14. E. Whitehead, R. Dean, and F. Fidler, J. Am. Chem. Soc., 73, 3632 (1951).

15. H. A. Benesi, J. Phys. Chem., 61, 970 (1957).

16. A. N. Korepanov, T. A. Danilova, and E. A. Viktorova, Neftekhimiya, 16, 909 (1976).

17. B. G. Eremina, Gas Analysis [in Russian], Goskhimizdat, Leningrad (1955), p. 143.

DEPENDENCE OF THE COMPOSITION OF THE PRODUCTS OF THERMAL

FRAGMENTATION OF THIACYANINE DYES ON THE LENGTH OF THEIR

POLYMETHINE CHAIN

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The pathways of thermal fragmentation of thiacyanine dyes with different lengths of the external polymethine chain were investigated. The results of thermolysis of the thiacyanines are compared with the results of quantum-chemical calculations of their molecules.

When thiapolycarbocyanines I are heated above their melting points, they are converted to dyes with a shorter polymethine chain; when the chain length is increased (when n is increased), the yields of the dyes decrease markedly, and larger amounts of products that absorb in the UV portion of the spectrum, the structures of which have not been established, are formed [1]. In thiapolycarbocyaninium iodide series I when n is increased, the temperature at which the compounds melt (accompanied by decomposition of the dyes) gradually decreases, which constitutes evidence for lability of the bonds.

To estimate the strength of the bonds in dyes I (n = 1-5) we subjected the indicated compounds in the S_0 state to quantum-chemical calculation by the Pariser—Parr—Pople (PPP) method with the program in [2]. The results of the calculation are given in Table 1.

An analysis of the data in Table 1 shows that the magnitude of the positive charge on the nitrogen and sulfur atoms of the thiazole rings and on the odd-numbered carbon atoms of the polymethine chain decreases as the polymethine chain becomes longer; in the case of all of the examined dyes the carbon atoms in the 2 and 2' positions, which are closer to the center of symmetry of the molecule, have the greatest q_r values. The negative charges on the even-numbered carbon atoms change only slightly for the various n values: In contrast to the $+q_r$ values, the $-q_r$ values decrease from the ends to the center of the polymethine chain. It is interesting that the bond orders decrease as the polymethine chain of the thiacyanines becomes longer, and the polarities of the bonds in the thiazole rings increase; the μ values and the uniformity of the p_{rs} values along the polymethine chromophore decrease. In conformity with the F values [3], the ring nitrogen atoms and the carbon atoms in the 8 and 8' positions should be most susceptible to the effect of radical reagents; as n increases, this

ability increases for all of the atoms indicated in Table 1. The magnitude of the boundary electron density (f_E) [3], which is greatest for the α,α' carbon atoms of the external chain and the nitrogen atoms, decreases for the S, N, C_8, and C_8' atoms as the polymethine chain becomes longer and increases for the odd-numbered carbon atoms in the 2, 2', 9, and 9' positions while remaining, in general, insignificant.

On the basis of the results of the calculation it may be assumed that the probability of thermal elimination of an ethyl cation from the ring nitrogen atom and heterolytic dissociation of the C—C bonds of the polymethine chain should decrease in the 3,3'-diethylthiapolycarbocyanine I series as the number of vinylene groups (n) in the external polymethine chain is increased. At the same time, the lability of the bonds in the thiazole rings and the probability of the occurrence of homolytic processes should increase.
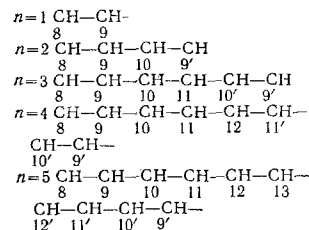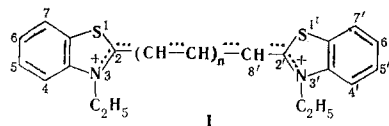
Our study of the volatile products of thermolysis of thiapolycarbocyanines I by gas-liquid chromatography (GLC) and chromatographic mass spectrometry (as in [4]) showed that, as the polymethine chain becomes longer, the overall amount of hydrocarbons (ethylene, ethane, and butane) decreases sharply, chiefly at the expense of ethylene (Table 2). Since the ethyl cation can form only ethylene in the case of deprotonation, these data constitute evidence for a decrease in the rate of heterolytic dealkylation of the dyes as n increases, in agreement with the results of the calculation. In addition to the products identified in the thermolysis of thiacarbocyanine (n = 1), viz, ethyl iodide, benzothiazole (II), 2-methylbenzothiazole (III), 2-ethylbenzothiazole (IV), 2-propylbenzothiazole (V), and o-ethylthio-N-ethylaniline(VI) [5], N-ethylaniline (VII), 2,N-diethylaniline (VIII), 2-phenylbenzothiazole (IX), and 3-ethylbenzothiazolin-2-one (X) are also detected among the volatile products of the thermolysis of thiapolycarbocyanines with n > 1; the ratio of most of these compounds changes regularly for dyes with different polymethine chain lengths (Table 2).

The thermal fragmentation of thiapolycarbocyanines I can be represented by the scheme:
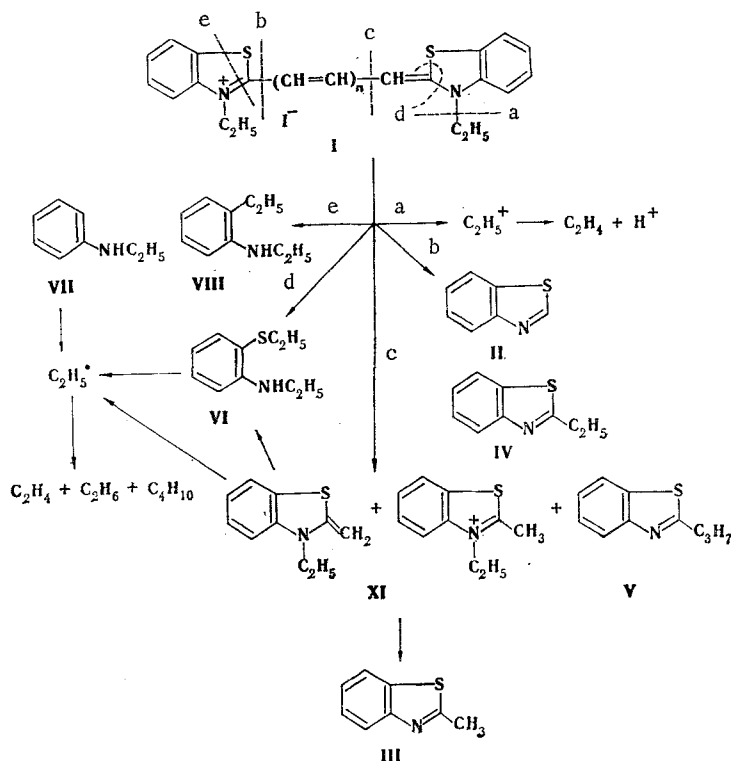
The heterolytic dealkylation of the dyes with the formation of an ethyl cation proceeds via pathway a. Benzothiazole (II) and 2-ethylbenzothiazole (IV, pathway b) are formed in the homolytic cleavage of the C_2—C_8 and C_2'—C_8' bonds. The increase in the percentage of benzothiazole in the mixture as n increases (Table 2) constitutes evidence for an increase in the probability of this process; the increase in the orders of the C_2—C_8 and C_2'—C_8' bonds and the increase in the free valence indexes (F) for the C_8, C_8' and C_2, C_2' atoms as the chain becomes longer (Table 1) suggests that the formation of II and IV does not occur as a result of intramolecular homolysis of the C_2—C_8 and C_2'—C_8' bonds but rather as a consequence of attack by radical agents (H$^\bullet$ and $C_2H_5^\bullet$) at the C_8, C_8' and C_2, C_2' atoms.

TABLE 1. Charges (q_r) on the Atoms and Bond Orders (p_{rs}) for

```
n=1 CH—CH-
      8   9
n=2 CH—CH—CH—CH
      8   9  10  9'
n=3 CH—CH—CH—CH—CH—CH
      8   9  10  11 10' 9'
n=4 CH—CH—CH—CH—CH—CH—
      8   9  10  11  12 11'
    CH—CH—
    10'  9'
n=5 CH—CH—CH—CH—CH—CH—
      8   9  10  11  12  13
    CH—CH—CH—CH—
    12' 11' 10'  9'
```

I

n	q_r									p_{rs}							
	1,1'	2,2'	3,3'	8,8'	9,9'	10,10'	11,11'	12,12'	13	1—2 / 1'—2'	2—3 / 2'—3'	2—8 / 2'—8'	8—9 / 8'—9'	9—10 / 9'—10'	10—11 / 10'—11'	11—12 / 11'—12'	12—13 / 12'—13'
1	0,185	0,153	0,267	−0,135	0,139	—	—	—	—	0,392	0,478	0,641	0,634	—	—	—	—
2	0,180	0,142	0,261	−0,131	0,134	−0,079	—	—	—	0,382	0,466	0,656	0,618	0,643	—	—	—
3	0,175	0,133	0,254	−0,131	0,126	−0,069	0,130	—	—	0,373	0,456	0,671	0,601	0,568	0,627	—	—
4	0,171	0,124	0,249	−0,133	0,118	−0,067	0,124	−0,057	—	0,345	0,447	0,684	0,584	0,673	0,610	0,643	—
5	0,167	0,117	0,245	−0,135	0,112	−0,065	0,119	−0,053	0,120	0,357	0,438	0,696	0,571	0,688	0,595	0,659	0,626

Dipole Moments of the Bonds and Reactivity Indexes

n	μ, D								F				f_E				
	1—2 / 1'—2'	2—3 / 2'—3'	2—8 / 2'—8'	8—9 / 8'—9'	9—10 / 9'—10'	10—11 / 10'—11'	11—12 / 11'—12'	12—13 / 12'—13'	1,1'	2,2'	3,3'	8,8'	1,1'	2,2'	3,3'	8,8'	9,9'
1	0,055	0,155	0,403	0,384	—	—	—	—	0,354	0,221	0,580	0,457	0,095	0,047	0,118	0,391	0,000
2	0,065	0,160	0,380	0,370	0,298	—	—	—	0,364	0,228	0,595	0,458	0,084	0,067	0,101	0,329	0,012
3	0,071	0,166	0,367	0,362	0,273	0,279	—	—	0,375	0,233	0,608	0,460	0,071	0,078	0,085	0,264	0,031
4	0,080	0,171	0,357	0,354	0,258	0,269	0,253	—	0,385	0,237	0,619	0,462	0,061	0,080	0,072	0,213	0,045
5	0,084	0,174	0,350	0,348	0,246	0,259	0,241	0,242	0,394	0,240	0,629	0,465	0,052	0,078	0,062	0,175	0,054

Heterolytic dissociation of the C_8—C_9 and C_8'—C_9' bonds leads to III, V, XI, and VI according to [5] (pathway c).

The decrease in the amount of benzothiazole V as n increases (Table 2) is due to a decrease in the polarity (μ) of the indicated bonds. However, the increase in the amount of VI is probably associated with an increase in the lability of the C_1—C_2 and C_2—C_3 bonds in the thiazole rings of the dyes and the impossibility of their cleavage via pathway d.
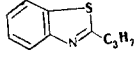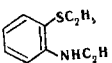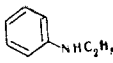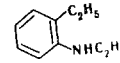
The development and subsequent increase in the percentage of VII and VIII (pathway e) as the chain becomes longer as a result of attack by $H^{\bullet}$ and $C_2H_5^{\bullet}$ on the endocyclic sulfur and nitrogen atoms correlate with the increase in F for these atoms.

Of extreme interest is the formation in the thermolysis of thiazyanines with n > 1 of 2-phenylbenzothiazole, the amount of which increases as n increases to n = 4. The development of this compound was recorded in the mass spectra of thiapolycarbocyanines when the dyes were introduced directly into the ion source of the mass spectrometer and is explained by cyclization of the polymethine chain [6]. Thus, just as in the case of electron impact, in the thermolysis of dyes I with n > 1 a benzene ring is evidently formed via, for example, the scheme:
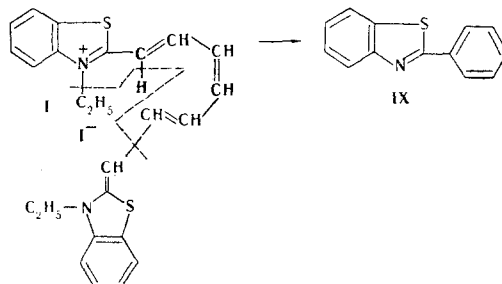
The amount of 3-ethylbenzothiazolin-2-one (X) also increases on passing from thiacarbo- to thiapentacarbocyanine. We found that its percentage depends on the length of time that samples of starting dyes I (particularly those with n = 4 and 5) are stored in air. Consequently, benzothiazolin-2-one X can be regarded as an impurity that is formed as a result of

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TABLE 2. Volatile Products of the Thermolysis of 3,3'-Diethyl-thiapolycarbocyaninium Iodides I

	hydrocarbons		II	V	VI	VII	VIII
	total amount	C_2H_4 : C_2H_6					
1	36	20:1	1	18	2	—	—
2	8	5:1	1,2	9	5	—	2,5
3	6	1:1	2	7	12	1,5	3,5
4	3	1:2	4,5	5,5	20	7	5,6
5	2,6	1:5	11	5	30	13	12

*These are the percentages of the thermolysis products in the mixtures with respect to 2-methylbenzothiazole (III) determined from the heights of the chromatographic peaks.

hydrolysis or oxidation of the dye during storage (see [7]). The question of the possibility of its thermal formation as a result of reaction of the dyes with the crystallization water or adsorbed oxygen remains unanswered.

EXPERIMENTAL

Chromatographic analysis was carried out with a Khrom 3-1KZ chromatograph with a flame-ionization detector; the pyrolysis temperature was 300°C. The analysis of the hydrocarbon fraction of the pyrolysate was carried out with a column (l = 3 m, d = 0.3 cm) filled with Porapak Q (60-80 mesh); the thermostat temperature was 40°C, the carrier gas was nitrogen, and the flow rate was 20 ml/min. The analysis of the high-boiling fraction of the pyrolysate was carried out with a column (l = 2 m, d = 0.3 cm) filled with Cellite 545 (50-60 mesh); the stationary phase was Apiezon L (15% based on the mass of the packing), the thermostat temperature was 130°C, the carrier gas was nitrogen, and the flow rate was 20 ml/min.

The chromatographic mass spectra were measured with an MAT-311A spectrometer with a Varian Aerograph 3700 chromatograph with a capillary column with a length of 25 m (0.25 mm); the phase was OV-101, the injector temperature was 300°C, the column temperature was 80-220°C (10 deg/min), the carrier gas was helium (2 ml/min), the ionizing-electron energy was 70 eV, and the source temperature was 150°C.

LITERATURE CITED

1. M. A. Al'perovich, R. D. Raikhina, V. G. Khesin, T. D. Medvedeva, and I. I. Levkoev, Dokl. Akad. Nauk SSSR, 222, 118 (1976).
2. V. A. Kosobutskii, Master's Dissertation, Rostov-on-Don (1974).
3. K. Fukui, T. Yonezawa, and H. Shingu, J. Chem. Soc., No. 20, 722 (1952).
4. M. A. Al'perovich, V. G. Khesin, R. D. Raikhina, and T. D. Medvedeva, Khim. Geterosikl. Soedin., No. 12, 1620 (1981).
5. V. G. Khesin, M. A. Al'perovich, and P. I. Abramenko, Khim. Geterotsikl. Soedin., No. 12, 1626 (1981).
6. K. K. Zhigulev, F. L. Kolodkin, R. D. Raikhina, M. A. Al'perovich, and I. I. Levkoev, Dokl. Akad. Nauk SSSR, 215, 347 (1974).
7. A. Munter and W. Cooper, Chem. Phys. Lett., 22, 212 (1973).