Com-	mp ,* ° C	λ nm([σ ε)	Found, %		Empirical	Calc., %		d, %
pound		max, (13 5)	C1(N)	s	formula	C1(N)	s	Yiel
IIIa IIIb IIIc Via VIb VIc VIIa VIIc VIIIa	$\begin{array}{c} 295-296\\ 281-282\\ 283-285\\ 273-275\\ 276-277\\ 268-269\\ 256-259\\ 265-267\\ 303-305\\ 313-315\\ \end{array}$	305 (3,37), 400 (3,06) 305 (3,44), 400 (3,10) 305 (3,42), 400 (3,12) 514 (3,62) 514 (3,57) 498 (3,39) 496 (3,40)	$(10,4) \\ 8,8 \\ 8,2 \\ 7,8 \\ 7,4 \\ 7,1 \\ 6,4 \\ 5,7 \\ (12,0) \\ (11,5) \\ (11,5) \\ (10,4) \\ (11,5) \\ (10,4) \\ (11,5) \\ (11,$	16,3 15,2 15,0 14,0 13,7 12,6 10,8 10,2 20,3 19,1	$\begin{array}{c} C_{20}H_{14}CIN_3S_2\\ C_{21}H_{16}CIN_3O_5\\ C_{21}H_{16}CIN_3O_5\\ C_{20}H_{14}CIN_3O_4S_2\\ C_{21}H_{16}CIN_3O_4S_2\\ C_{21}H_{16}CIN_3O_5S_2\\ C_{20}H_{21}CIN_4O_5S_2\\ C_{20}H_{22}CIN_4O_5S_2\\ C_{30}H_{23}CIN_4O_5S_2\\ C_{24}H_{16}N_4O_3\\ C_{25}H_{18}N_4O_2S_3\\ \end{array}$	(10,6) 8,6 8,3 7,7 7,6 7,2 6,2 5,7 (11,9) (11,2)	16,1 15,6 15,0 13,9 13,5 13,1 11,2 10,3 20,3 19,1	64 75 50 65 53 57 87 67 92 80

TABLE 2. Properties of the Synthesized Compounds

*Compounds VI, VII, and VIII were crystallized from alcohol-DMF.

<u>8-R-3-Phenyl-1-[(3-ethylbenzothiazolin-2-ylidenes)methyl]thiazolo[3,4':1,2]pyrimido[6,5-b]quinolinium Perchlorates (VIIa, c).</u> A mixture of 0.35 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium tosylate, 1 mmole of the corresponding perchlorate VI, 10 ml of absolute alcohol, and 2 ml of DMF was heated until the components had dissolved, after which 0.1 g (1 mmole) of triethylamine was added, and the precipitated dye was removed by filtration and crystallized.

2-Thioxo-3-ethyl-5-(1H-8-R-3-phenylthiazolo[3',4':1,2]pyrimido[6, 5-b]quinol-1-ylidene)thiazolidin-4-one (VIIIa, c). A mixture of 0.16 g (1 mmole) of 3-ethylrhodanine, 1 mmole of the corresponding perchlorate VI, and 10 ml of absolute alcohol was heated to the boiling point, and 0.1 g (1 mmole) of triethylamine was added. The precipitated dye was removed by filtration and crystallized.

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THERMOLYSIS AND MASS SPECTROMETRY OF meso-SUBSTITUTED THIACARBOCYANINES

V.	G.	Khesin, R.	D. Raikhina, M. A. Al'perovich,	UDC 668.819.45+547.789.6:
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The pathways of fragmentation of thiacarbocyanine dyes with various electron-donor substituents in the meso position of the polymethine chain under the influence of high temperatures and electron impact were investigated. The results of thermolysis of the dyes are compared with the results of quantum-chemical calculations of the labilities of the bonds in the molecules.

We have previously shown [1] by means of gas-chromatographic analysis of the volatile products of the pyrolysis of 3,3'-dialkylthiacarbocyanine halides that in the molecules of these dyes processes involving thermal heterolytic dissociation of the C-C bonds of the external polymethine chain may compete with dealkylation. It seemed of interest to ascertain what effect substituents in the 9 position of the polymethine chain have on the character of the thermal fragmentation of thiacarbocyanines. In this connection, in the present research we investigated the pathways of the thermal transformations of meso-substituted thiacarbocyanine

All-Union State Scientific-Research and Planning Institute of the Photographic Industry, Moscow 125815. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 207-213, February, 1983. Original article submitted November 5, 1981; revision submitted June 15, 1982. TABLE 1. Results of the Quantum-Chemical Calculation [Pariser-Parr-Pople (PPP) Method]



	<i>q_{rs}</i>				<i>l</i> ,	nm	μ , D		
ĸ	C 3(3')	C 10(10')	C _{8(8')}	Сg	C _{8(8')} -C 9	C _{3(3')} -C ₁₀	C _{8(8')} -C 9	C _{3(3')} C ₁₀	
H CH3 OCH3 NH2	0,267 0,264 0,259 0,249	0,010 0,010 0,013 0,009	-0,135 -0,145 -0,168 -0,177	0,139 0,150 0,140 0,139	14,017 14,047 14,139 14,197	14,700 14,700 14,598 14,700	0,384 0,414 0,435 0,449	0,378 0,373 0,359 0,353	

dyes Ia-f:



a R=H; b R=CH₃; c R=C₂H₅; d R=OCH₃; e R=OC₂H₅; f R=NH₂

To evaluate the relative strengths of the bonds in thiacarbocyanines Ia, b, d, f we performed quantum-chemical calculations of the electron density distributions in their molecules in the ${}^{1}S_{0}$ state within the Pariser-Parr-Pople (PPP) approximation by the method described in [2]. The charges on the atoms (q_{rs}) and lengths (l) and dipole moments (μ in debyes) of the bonds in thiacarbocyanines Ia, b, d, f are presented in Table 1.

It is apparent from Table 1 that when methyl, methoxy, and amino groups are introduced in the 9 position of dyes I, the positive charges on the nitrogen atoms of the benzothiazole residues decrease successively as the electron-donor effect of the substituents increases, and the negative charges on the C_8 (C_8 ') atoms and the length of the C_8-C_9 (C_8 '- C_9) bonds increase, in connection with which the polarities of the N- C_{10} (N'- C_{10} ') bonds decrease, and the polarities of the C_8-C_9 (C_8 '- C_9 ') bonds increase. Proceeding from this one might have assumed that the probability of heterolytic elimination of alkyl groups from the nitrogen atoms would decrease as the electron donor character of the substituents in the 9 position increases, whereas the probability of heterolytic dissociation of the C_8-C_9 (C_8 '- C_9) bonds should increase.

To verify this assumption we carried out the thermolysis of dyes Ia-f at atmospheric pressure. The thermolysis conditions and the methods used to establish the compositions and structures of the volatile fragmentation products were similar to those in [3, 4].

Data on the compositions and structures of the volatile products of the thermolysis of Ia [4] and Ib-f are presented in Table 2 with an indication of the relative retention times (α_{rel}) on the gas-liquid chromatograms and the relative percentages of each of the components in the mixtures disregarding the highly volatile compounds. (In addition to the compounds presented in Table 2, alkyl halides, hydrocarbons, and a number of unidentified compounds, the overall amounts of which do not exceed 3%, are formed in the thermolysis of dyes I.)

It is apparent from Table 2 that the ratios of the volatile thermolysis products changes substantially when various electron-donor groups are introduced in the meso position. Thus the relative percentages of benzothiazole (II), 2-ethylbenzothiazole (IV), and o-ethylmercapto-N-ethylaniline (V) in the mixture increase in the case of 9-alkyl derivatives (Ib, c) as compared with chain-unsubstituted dye Ia, while the amounts of 2-methyland 2-propylbenzothiazole (III, VI) decrease. The presence of methoxy and ethoxy groups (Id, e) leads to a sharp decrease in the amount of 2-methylbenzothiazole (III) and an increase in the amounts of IV and VI. The presence of an amino group (If) is responsible for the significant increase in the percentage of IV in the mixture and the decrease (although smaller than in the case of cyanines Ia-e) in the percengage of III, while the relative amounts of the other compounds presented in Table 2 do not change substantially in this case.

In analogy with thiacarbocyanine Ia [4], which is unsubstituted in the polymethine chain, the thermal fragmentation of dyes Ib-f can be represented by the scheme



TABLE 2. Composition of the Principal Products of the Thermolysis of $3,3\,{\rm '-Diethylthiacarbocyanines}~{\rm I}$

In certain increases in the relative amounts of II and IV in the case of meso-alkyl derivatives Ib, c, evidently constitutes evidence for an increase in the lability of the C_2-C_8 bond in the anhydro bases (VII) of these dyes. The formation of a significant amount of 2methylbenzothiazole III (76%) in the thermolysis of unsubstituted thiacarbocyanine Ia was previously explained [4] by dissociation at the C_8-C_9 bond with subsequent migration of a proton from ethyl derivative VIII (R = H) to methylene base IX and dealkylation of the resulting quaternary salt of 2-methylbenzothiazole. The decrease in the relative percentage of III in dyes Ib, c is due to the absence of a hydrogenatom in the 9 position (R = CH₃ and C_2H_5). The increase in the amount of o-ethylmercapto-N-ethylaniline V, which is formed from methylene base IX, is also associated with this. The certain decrease in the amount of VI can be explained by a decrease in the probability of heterolytic dealkylation of carbocyanines Ib, c to give $C_2H_5^+$ cations (see the results of the quantum-chemical calculations). The fact that the ratio of ethane and ethylene in the hydrocarbon fractions of the pyrolyzates is 1:3, whereas it is 1:23 for chain-unsubstituted dye Ia [4], constitutes evidence for this.

The sharp decrease in the percentage of 2-methylbenzothiazole III in the mixtures of volatile products of the thermolysis of meso-alkoxy derivatives (Id, e) of thiacarbocyanines, as well as for Ib, c, is also explained by the absence of a hydrogen atom in the 9 position $(R = 0CH_3 \text{ and } OC_2H_5)$. However, in contrast to the meso-alkyl derivatives, the percentage of V does not increase in this case, but the amount of 2-ethylbenzothiazole IV for Id $(R = 0CH_3)$ and the amount of 2-propylbenzothiazole VI for Ie $(R = 0C_2H_5)$ increase sharply. This fact can be explained by the high lability of the O-Alk bond in the indicated dyes [5], which is responsible for the formation of alkyl cations and the addition of these ions to the anion (z) of the methylene base (see Scheme 1). This is also indicated by the appearance, in addition to ethyl iodine, of the same amount of 2-ethylbenzothiazole IV increases markedly not only in the case of dye Id $(R = 0CH_3)$ but also in the case of dye Ie $(R = 0C_2H_5)$; a significant amount of methyl iodide is formed in the thermolysis of the latter dye.

We assumed that the ethyl groups attached to the nitrogen atoms of the benzothiazole residues, which have little tendency to undergo heterolytic elimination but rather undergo

		<i>m/z</i> 1.12	(*)	(*)	25	87	80	44	44
	eak)	m/z 156	56 29	98	10	88	26	94	17
		F12		188 (28)	190 (38)	175 (45)	189 (8)	254 (4)	238 (*)
	aximum p	Fu	[173] (10)	187 (37)	I	174 (75)	[188] (18)	253 (*)	237 (*)
) eV).	to the m	F10	175 (7)	189 (6)	191 (8)	176 (49)	190 (7)	255 (*)	239 (*)
des (70	nt relative	F ₉	173 (100) 187 (54)	2011 (100 2011 (100	046 (100)	188] (85) 188] (85)	202 (17) 202 (17)	275 (5) 273 (8)	219 (29) 173 (50)
con Lodi	m/z values (intensities of the peaks of the characteristic ions in percen	F.8	188 (31) 202 (15)	216 (52)	1 8 (4) 2 (2 (2 (2) 2) 2 (2	203 (100)	217 (17)	(or) [001	234 (6) 188 (19)
aracteristics of the Mass Spectra of 3,3'-Diethylthiacarbocyaniniu		F ₁	186 (23) 200 (100)	186 (42) 214 (62)	216 (*)	[201] (51)	215 (21)	186 / 971	232 (8) 186 (88)
		F ₆	201 (7) 215 (30)	201 (17) 229 (29)	231 (4)	216 (19)	230 (10) 230 (10)	(11) [107]	247 (6) 201 (17)
		F5		l	352 (*)	337 (39)	351 (4)	l	368 (7)
		F ₄	11	1	380 (*)	365 (26)	379 (25)	1	396 (12)
		F3	307 (20) 321 (*)	335 (16)	337 (*)	322 (11)	[336] (4) [336] (4)	(0) INC	353 (5) 307 (9)
		F_2	336 (60) 350 (23)	[364] (77)	366 (59)	351 (94)	365 (11) 365 (11) 336 (11)	428 (18) 336 (4)	382 (56) 336 (7)
		F	364 (*) ^a 378 (14)	392 (12) 13641 (77)	394 (*1) 394 (*)	379 (10)	393 (4)	l	410 (*)
	S _{1/2}		6 9	00	9	26	22	7	11
			500 650	1150	500	3850	1500	770	1780
	Ç F	ر ۲	200 220	220	110	160	210	110	110
3 3. Ch		×	H CH ₃	C ₂ H ₅	OCH3	NHz	NHCH ₃	OC ₆ H ₅	SCH ₃
TABL	Com-	punod	la Ib	<u>c</u>	Id	ц. Ц.	Ig:	ΗI	li

^aThe asterisk indicates peak intensities $\leq 3\%$ of I_{max} : the [m/z] values are those for alternative structures. ^bThe F₉+H ion.

thermal β decomposition when electron-donor substituents are present in the meso position of the thiacarbocyanines, are the source of the CH₃⁺ ions. The formation of significant amounts of 2-ethylbenzothiazole IV and CH₃I in the case of 9-amino derivative If confirms the validity of this assumption.

The relatively higher percentage of 2-methylbenzothiazole (III) among the volatile products of the thermolysis of dye If as compared with carbocyanines Ib-e is evidently explained by migration of a proton from the amino group to methylene base IX.

Thus the results of a study of the volatile products of the thermolysis of meso-substituted thiacarbocyanines are basically in agreement with the results of quantum-chemical calculations of the effect of electron-donor substituents on the polarities of the bonds in these dyes. The data from a mass-spectrometric study of dyes Ia-d, f as well as Ig ($R = NHCH_3$), Ih ($R = OC_6H_5$), and Ii ($R = SCH_3$), in the case of direct introduction of the dyes into the ion source confirm the conclusions regarding the labilities of the bonds in meso-substituted thiacarbocyanines obtained on the basis of a study of the volatile products of their thermolysis.

The mass spectra of the cyanine dyes do not contain a molecular-ion peak [6,7]; the most intense peaks in the high-mass region correspond to ions of anhydro bases VII $[[M-C_2H_5]^+$ $(F_2)]$ and $[M-C_2H_5I, -C_2H_5]^+$ (F_3) ions, which are accompanied by peaks of $C_2H_5I^+$ ions. On the basis of this, in [6, 7], we expressed the assumption that the first step in the fragmentation of chain-unsubstituted cyanines is pyrolytic splitting out of the substituent from the ring nitrogen atom with subsequent ionization of both fragments. The principal argument in favor of this assumption was the identical character of the mass spectra of thiacarbocyanine Ia and its anhydro base. Further studies of the thermolysis of cyanines, which revealed, in particular, the heterolytic dissociation of the latter in the polymethine chain [1, 3, 4], expanded the concepts of the possible transformations of dyes that precede their ionization.

The mass-spectral characteristics (total ion currents ΣI , fragmentation selectivities $S_{1/2}$, mass numbers m/z, and relative intensities of the peaks of the characteristic ions in percent) of thiacarbocyanines Ia-d, f-i are presented in Table 3.

The above-noted decrease in the polarities of the N- C_{10} (N' $-C_{10}$) bonds when electrondonor substituents are introduced in the 9 position of the chain is reflected in the appearance of $[M-HX]^+$ (F₁) ions in the mass spectra of the meso-substituted dyes and in the effective formation of CH_3I^+ (m/z 142) and $C_2H_5I^+$ (m/z 156) ions. On the basis of the fact that the formation of CH₃I⁺ ions is also observed in the case of 9-amino- and 9-phenoxy derivatives (If, h) it can be asserted with certainty that the splitting out of a methyl radical occurs as a result of β cleavage in the N-ethyl group of carbocyanines I. Immonium structures can be assigned to the resulting $[M-CH_3I]^+$ (F₄) and $[M-CH_3I-C_2H_4]^+$ (F₅) ions, which are absent in the mass spectra of the chain-unsubstituted dyes. These structures evidently have lower stabilities than the F_2 ions, in connection with which the intensities of the peaks of F_4 ions are generally lower than the intensities of the peaks of F_2 ions even when the peaks of the ions with m/z 142 have considerably higher intensities than the peaks of the ions with m/z 156 (dyes Id, i). The pronounced increase in the mass spectra of the mesosubstituted dyes of structures with six-membered condensed rings (F_7) [6, 7], which, as can be seen from Scheme 2, may be formed via both dissociative ionization of the ion (F_2) of the anhydro base and dissociation of the F4 ion via pathway 3, is an indirect confirmation of the existence of intermediate fragments of the F4 type.

In the mass spectra of the investigated meso-substituted thiacarbocyanines it is interesting to note ions that are also common to those of chain-unsubstituted thiacarbocyanine Ia $([F_{1-3}-R, +H]^+ \text{ and } [F_{6-9}-R, +H]^+)$ and correspond to splitting out of substituent R with simultaneous migration of a hydrogen atom.

The introduction of substituents in the polymethine chain leads to the appearance in the mass spectra of carbocyanines of peaks of $F_{10} - F_{12}$ fragments, which are probably formed by dialkylation of quaternary salt VIII (see Scheme 1).

Peaks of ions with corresponding masses were not observed in the mass spectra of chainunsubstituted thiacarbocyanines [6, 7].

The impossibility of the unambiguous interpretation of the mass spectra of such complex compounds as polymethine dyes, for many of the fragments of which several alternative structures with identical elementary compositions can be proposed, must be emphasized.



The high-resolution mass spectra revealed the doublet character of some of the peaks for the dyes with heteroatomic groupings. Thus the peak with m/z 190 in the case of meso-methoxy-thiacarbocyanine Id has the compositions $C_{10}H_8NOS$ (65%) and $C_{11}H_{12}NS$ (35%), which correspond, respectively, to structures F_{12} and F_8 -R with a completely hydrogenated ring. Similarly, the ratio of the intensities of the $C_{10}H_8N_2S$ (F_{11}) and $C_{11}H_{10}NS$ (F_8 -R, +H) ions amounts to 60 and 40% for the peak with m/z 188 in the case of meso-methylamino derivative Ig.



Ions of this type are singled out by means of brackets in Table 3.

A detailed comparison of the chromatograms of the volatile pyrolysis products (Table 2) and the mass spectra (Table 3) of the thiacarbocyanines is difficult, since the intensities of the peaks of the ions that correspond to II (m/z 135), III (m/z 149), IV (m/z 163), and VI and IX (m/z 177) are generally close to one another in the mass spectra of the investigated thiacarbocyanines. The peak of the ion of o-ethylmercapto-N-ethylaniline V (m/z 181) is absent in the mass spectra of dyes Ia-d, f-h, and this constitutes evidence for its appearance only under severe thermolysis conditions at atmospheric pressure [8]. The mass spectrum of 9-methylmercaptothiacarbocyanine Ii, in which the peak of the ion with m/z 181 amounts to 4.6% of Σ I, constitutes an exception; however, in this case the cited peak evidently corresponds to the structure of the 2-methylmercaptobenzothiazole ion.

Thus, despite a number of differences, the above-presented data from the mass spectrometric study not only confirm the conclusions regarding the principal pathways of the thermal fragmentation of 9-substituted thiacarbocyanines but also give additional information regarding these thermolysis products that cannot be recorded by pyrolytic gas chromatography.

EXPERIMENTAL

The mass spectra were measured with a Varian MAT CH6 spectrometer at an ionizing-electron energy of 70 eV, a cathode emission current of 1.5 A, and an ionization chamber temperature of 110-220 °C. The high-resolution mass spectra were measured under the same conditions with a Varian MAT 311A spectrometer with resolution M/ Δ M = 25,000.

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RESEARCH ON THE CHEMISTRY OF HETEROCYCLIC QUINONEIMINES.

REACTION OF 3-PHENOTHIAZINONE WITH ALKOXIDES

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Nucleophilic substitution of hydrogen to give 1- and 2-mono- and 1,7-dialkoxy-3-phenothiazinones, as well as a mixture of dimers, when 3-phenothiazinone is treated with alkali metal alkoxides. The effect of the nature of the alcohol, the alkali metal cation, and the solvent on the reaction was investigated.

Very little study has been devoted to the reactions of quinoneimine systems with charged nucleophiles. In the present research we investigated the reaction of a heterocyclic quinoneimine, viz., 3-phenothiazinone, with alkali metal alkoxides, which is of particular interest in view of the great practical value of diphenazones [1].

It is known that quinones react with alcohols in the presence of Lewis acids under mild conditions to give products of nucleophilic substitution of hydrogen and dihydro compounds [2]. We have shown that 3-phenothiazinone does not react with alcohols even under activation (by means of H^+ and BF_3) conditions. However, nucleophilic substitution of hydrogen both in the quinoneimine and benzenoid fragments of the 3-phenothiazinone molecule to give three reaction products (II-IV), as well as a mixture of dimers (Scheme 1 and Table 1), occurs when solutions of 3-phenothiazinone in the corresponding primary alcohols are refluxed with the alkoxides.



II—IV a R=CH₃; b R=C₂H₅; c R=n-C₃H₇; d R=n-C₄H₉; e R=n-C₈H₁₇; f R=CH₂C₆H₅; g R=CH₂CH=CH₂

In the case of the reaction with sodium methoxide the IIa:IIIa:IVa product ratio is 9:4:1. The formation of only products of self-condensation was observed in the reaction of 3-phenothiazinone with sodium tert-butoxide; Farina and Valderrama [3] also were unable to obtain the tert-butoxy derivative from benzoquinone by means of nucleophilic substitution.

In addition to a multiplet of aromatic protons at 7.5-8.2 ppm and signals of protons of alkyl groups, two singlets at 6.9 and 7.1 ppm, which belong, respectively, to the 4H and 1H protons of the quinoneimine fragment of the molecule, are observed in the PMR spectra of products II; this indicates that the substituent enters the 2 position. In contrast to the PMR spectra of II, two doublets with spin-spin coupling constant (SSCC) J = 1.5 Hz are observed in the spectra of III. The signal of the 4H proton is found at 6.2 ppm in this case, i.e., it is shifted 0.7 ppm to strong field as compared with the signal of the 4H proton of II. The signal of the 2H proton is observed at 6.6 ppm. The observed differences in the PMR

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