MASS SPECTROMETRY OF POLYMETHINE DYES

I. FRAGMENTATION OF UNSUBSTITUTED THIACARBO- AND POLYCARBOCYANINES ON ELECTRON IMPACT

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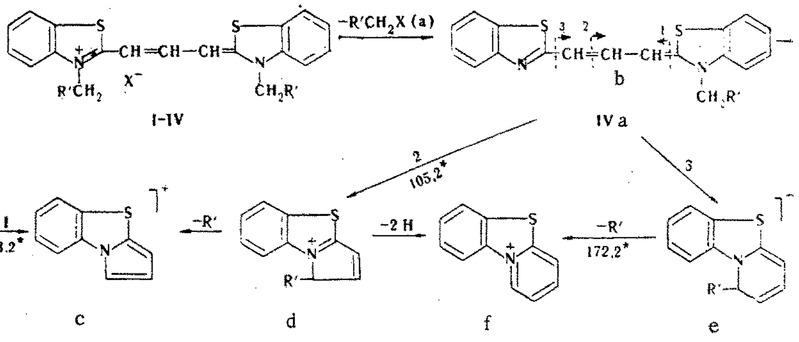
The mass spectra of some unsubstituted (in the heteroresidues and polymethine chain) thiacarbo- and polycarbocyanines were investigated. It was ascertained that the first act of disintegration of the dye molecules is splitting out of an alkyl halide ion to give an anhydro base ion. Some regularities between the structure of the dyes and the fragmentation of the anhydro ions obtained from them are exposed. The peculiarities of the dissociative ionization of the dye molecules as the polymethine chain is lengthened are shown.

The fragmentation of polymethine dyes upon electron impact has not been described in the literature. The present paper is devoted to a preliminary study of the principles of fragmentation upon electron impact of a number of thiacyanine dyes (I-VII) that do not contain substituents in the heteroresidues and the polymethine chain. The structures of the investigated dyes and the mass numbers and intensities of both the characteristic and other ions in their mass spectra are presented in Table 1.

A detailed analysis of the mass spectra of dye IV and its specially obtained anhydro base (IVa) with assignment of the metastable ions and a comparison with the mass spectra of other dyes make it possible to assume the following general scheme for their fragmentation:



I-III R'=H IV, IVa R'=CH$_3$

The dissociative ionization of fragment ions c-f leads, upon subsequent disintegration, to the formation of ions g-k, which are typical for the mass spectra of benzothiazole derivatives [1, 2].

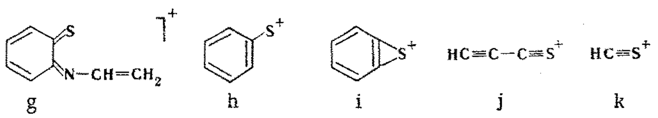


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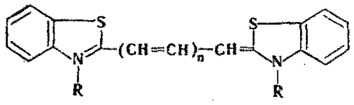
TABLE 1. Mass Numbers (m/e) and Intensities (I/I_{max}, %) of the Ion Peaks in the Mass Spectra of I-VII



Compound		I	II	III	IV	V	VI	VII
	R	CH_3	CH_3	CH_3	C_2H_5	C_2H_5	C_2H_5	C_2H_5
	X	Cl	Br	I	I	1	I	I
	n	1	1	1	I	2	3	5
Characteristic ions	a	50 (100)	94 (29)	142 (57)	156 (56)	156 (100)	156 (46)	156 (100)
	b	322 (21)	322 (39)	322 (40)	336 (60)	362 (20)	388 (—*)	440 (—*)
	c	173 (53)	173 (100)	173 (100)	173 (100)	199 (7)	255 (—*)	277 (—*)
	d	174 (18)	174 (31)	174 (25)	188 (31)	214 (8)	240 (2)	292 (—*)
	e	187 (—†)	187 (—†)	187 (5)	201 (7)	227 (4)	253 (—*)	305 (2)
	f	186 (7)	186 (12)	186 (5)	186 (23)	212 (9)	238 (4)	290 (3)
	g	149 (8)	149 (8)	149 (7)	149 (15)	149 (74)	149 (58)	149 (74)
	h	109 (10)	109 (5)	109 (5)	109 (9)	109 (17)	109 (10)	109 (18)
	i	108 (7)	108 (—†)	108 (—†)	108 (10)	108 (29)	108 (46)	108 (47)
	j	69 (7)	69 (8)	69 (7)	69 (11)	69 (27)	69 (35)	69 (19)
	k	45 (14)	45 (11)	45 (6)	45 (8)	45 (15)	45 (15)	45 (13)
	l	336 (—*)	336 (—*)	336 (—*)	364 (—*)	390 (24)	416 (—*)	468 (2)
	m	36 (—*)	80 (—*)	128 (—*)	128 (6)	128 (14)	128 (11)	128 (13)
	n	35 (—*)	79 (—*)	127 (—*)	127 (—†)	127 (30)	127 (16)	127 (39)
Other intense ions		52 (39)‡ 136 (13) 148 (12) 161 (11)	96 (25)‡ 161 (18) 323 (10)		174 (16) 307 (20) 337 (13)	63 (12) 82 (12) 148 (14) 173 (19) 174 (16) 186 (14) 211 (19)	63 (15) 82 (16) 106 (17) 134 (22) 177 (18) 210 (16) 211 (100)	64 (15) 148 (15) 177 (7) 261 (25) 466 (14)

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* Intensity less than 2%.

† Intensity less than 5%.

‡ The $[^{12}CH_3{}^{37}Cl]^+$ and $[^{12}CH_3{}^{81}Br]^+$ ions correspond to mass numbers 52 and 96.

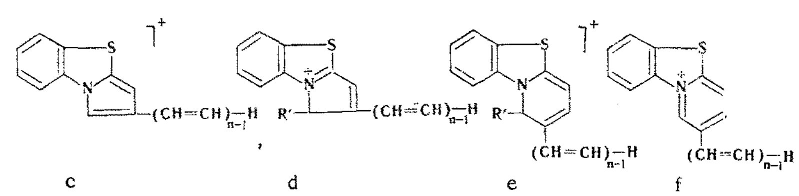
The peaks of $(M-HX)^+$ (ion *l*), $(HX)^+$ (ion m), and $(X)^+$ (ion n) ions in the mass spectra of dyes I-VII are also noteworthy.

The first act in the fragmentation of I-VII is pyrolytic splitting out of alkyl halide RX and formation of the corresponding anhydro base with subsequent ionization, respectively, to ions a and b. In fact, whereas molecular ion M^+ is absent in the mass spectra of dyes I-VII, the intensities of the peaks of ions *a* and b are extremely high or maximal for all of the compounds except VI and VII. The reasons for the decrease in the intensity of the peaks of ions b are examined below. Our proposed sequence of fragmentation of the dyes – pyrolysis followed by ionization – was established with a high degree of confidence in a number of mass spectrometric studies of quaternary salts of heterocycles (see the literature cited in [3]).

The dissociative ionization of ion b of the anhydro base of the dye occurs by cleavage of the carbon–carbon bonds of the polymethine chain in the 1, 2, and 3 directions (see the scheme). Subsequent cyclization of the fragments leads to the formation of more or less conjugated 5-membered (ions c and d) and 6-membered (ions e and f) condensed structures. In addition to cleavage of the carbon–carbon bonds, the formation of ions d and e is accompanied by migration of a hydrogen atom to the neutral residue. Judging from the intensities of the peaks of the corresponding ions, fragmentation via direction 1 to give ion c and, to a lesser extent, via direction 2 to give ion d is preferred for dyes I-IV.

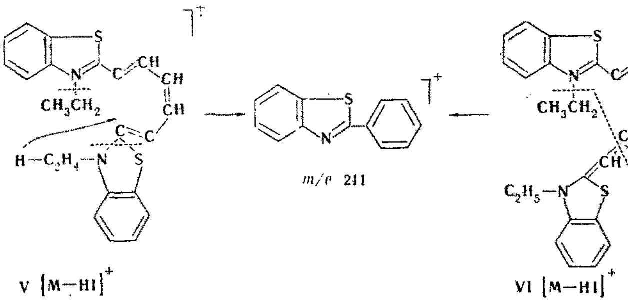
The fragmentation of methohalides I-III, which differ with respect to the character of the anion, proceeds with a high degree of selectivity in a practically identical manner in all cases, and the intensity of the peak of ion a falls in the order $CH_3Cl^+ > CH_3I^+ > CH_3Br^+$.

A change in the length of the polymethine chain in the IV-VII molecules has a substantial effect on the character of the primary pathways of dissociative ionization (see Table 1). Whereas the peak of ion c with mass 173 is a maximum in the mass spectrum of dye IV (n = 1), the intensities of the peaks of formal ion c and an ion with mass 173 decrease sharply in the mass spectrum of dye V (n = 2), and these peaks are practically absent in the case of VI and VII (n = 3 and 5). In addition, a gradual decrease in the intensities of the peaks of ions b and formal ions c-f is observed on passing from carbo- to polycarbocyanines IV-VII:

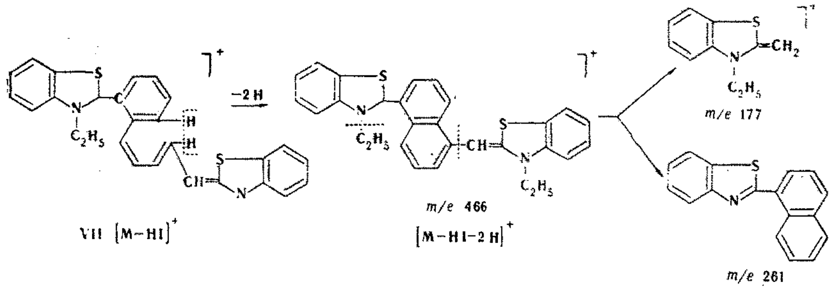


This is evidently associated with an increase in the probability of diverse cleavages of the longer polymethine chain, as evidenced also by an increase in the intensities of the peaks of the g-j ions in the mass spectra of V-VII. The formation of *l*-n ions, which are practically absent in the mass spectra of I-IV, is simultaneously observed in the latter.

The possibility of cyclization within the chain increases as the conjugated chain in the cyanine dyes is lengthened. In a certain sense, the mass spectrum of dicarbocyanine V is intermediate between the mass spectrum of carbocyanine IV and tricarbocyanine VI. On the one hand, the spectrum of V contains an ion peak with mass 173, which is a maximum value in the spectrum of IV and is absent in the spectrum of VI, whereas on the other, an ion peak with mass 211, which is absent in the mass spectrum of IV and is a maximum value in the mass spectrum of VI, is observed. The ion with mass 211 probably has the structure of 2-phenylbenzothiazole formed from fragment ion *l* of V and VI via the scheme



It is apparent from the scheme that this process should be easier for VI than for V, and this is confirmed by the mass spectra. The mass spectrum of pentacarbocyanine VII, in which the peaks of the b-f ions are extremely small but an intense peak with mass 261, which probably corresponds to the 2-α-naphthylbenzothiazole structure, also indicates cyclization within the polymethine chain. The 2-α-napththylbenzothiazole is formed via the following scheme:



This scheme is confirmed by the following data. First, in the series of I-VII dyes, an ion peak from $(M - HX - 2H)^+$ is observed only in the mass spectrum of VII; second, a 2-methylenebenzotriazole ion peak with m/e 177 is present in its mass spectrum. The peak with m/e 177 is also present in the mass spectrum of dye VI but absent in the mass spectrum of V; this is an indirect confirmation of the correctness of the description of the formation of 2-phenylbenzothiazole with respect to the scheme presented above.

However, cyclization within the polymethine chain, which becomes possible as the chain is lengthened, is a more advantageous process than formation of formal ions c-f.

EXPERIMENTAL

The purity of the crystals was monitored by means of the electronic spectra recorded in ethanol with a Hitachi EPS-3T spectrophotometer and by TLC on "Vel'm" silica gel in chloroform–methanol (5 : 1).

The mass spectra were obtained by direct introduction of a 1-2 mg sample into the ion source of a Varian Mat CH-6 mass spectrometer (70 eV, 180°, 100 mA).

3-Ethyl-2-[3'-(2''-benzothiazolyl)allylidene]benzothiazoline (IVa). A 0.42-g (0.001 mole) sample of dye IV was heated in a nitrogen atmosphere with 10 ml of diethylaniline at 230° for 2 h. The diethylanaline was removed by steam distillation, and IV was extracted from the residue with chloroform. The product was purified by chromatography on Al_2O_3 and crystallization to give 0.18 g (52%) of a product with mp 138-139° [from benzene–methanol (1:5)] (see [4]). Absorption spectrum in C_2H_5OH: λ_{max} 460 nm, ε 56,000. Found: C 67.8; H 4.7; N 8.4%. $C_{19}H_{16}N_2S_2$. Calculated: C 67.9; H 4.8; N 8.3%.

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