REACTIONS OF BENZO-1,2,3-DITHIAZOLIUM SALTS AND THEIR SELENIUM ANALOGS WITH AMINES

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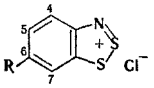
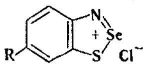
The corresponding 6-arylamino derivatives were obtained by reaction of 6-chloro, 6-bromo, and 6-methoxy derivatives of benzo-1,2,3-dithiazolium and their selenium analogs – benzo-1,2,3-thiaselenazolium, benzo-2,1,3-thiaselenazolium, and benzo-1,2,3-diselenazolium salts – with aromatic amines. The 6-methoxy derivatives also react with acetates of secondary aliphatic amines, whereas in the case of the chloro derivatives attack is directed to the heteroring. 6-Aryl(dialkyl)amino derivatives of dithiazolium and 1,2,3-thiaselenazolium salts are protonated in concentrated sulfuric acid at the exocyclic nitrogen atom. The analogous derivatives of 2,1,3-thiaselenazolium and diselenazolium salts under the same conditions form a tautomeric mixture of dications, the position of the equilibrium between which depends on the substituent. The electronic and PMR spectra of the amination products are presented.

Benzo-1,2,3-dithiazolium cations (I) that contain halogens and alkoxy groups in the 6 position react with anilines to give 6-arylamino derivatives [1, 2]. The electronic and PMR spectra of benzo-1,2,3-thiaselenazolium (II), benzo-2,1,3-thiaselenazolium (III), and benzo-1,2,3-diselenazolium (IV) salts, which we recently synthesized, show that localization of the positive charge in the 6 position of the benzene ring of these compounds is even greater than in the I cations and that they consequently should react readily with anilines.


Ia-j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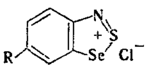
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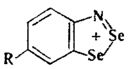
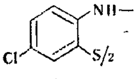

IVa-j

I-IV a $R=H$; b $R=Cl$; c $R=Br$; d $R=CH_3O$; e $R=C_6H_5NH$; f R=p-toluidino; g $=(CH_3)_2N$;

h $R=(C_2H_5)_2N$;. i R=piperidino; j R=


In fact, deeply colored arylamino derivatives IIe, f, IIIe-f, and IVe, f were obtained in the reaction of salts of IIb-d, IIIb-d, and IVb-d with anilines. Analogous reactions involving substitution with aliphatic amines have not been described and do not take place when the investigated cations are treated with amines under the conditions described for the synthesis of arylamino derivatives. It was found that dialkylamino derivatives Ig-i, IIg-i, IIIg, and IVg are obtained when methoxy derivatives I-IV are treated with amine acetates. The reactions proceed more slowly than with aromatic amines under the same conditions but do occur smoothly to give the products in high yields. The structures of salts Ig and IIg were confirmed by alternative synthesis from 3-mercapto-4-aminodimethylaniline hydrochloride and thionyl chloride or selenious acid, respectively.

The use of chloro-substituted salts I-IVb instead of the methoxy derivatives in the reaction with amine acetates leads to the formation of deeply colored substances that do not contain dialkylamino groups (according to the PMR spectra). Salts Ij and IIj, identical to the products of the reaction of Ib and IIb with dialkylamine acetates, were obtained by alternative syntheses from cations Id and IId and 2,2'-diamino-5,5'-diphenyl disulfide.

Signals of the protons of the benzene ring and dialkylamino groups are observed in the PMR spectra of the dialkylamino derivatives obtained (Table 1). The chemical shifts of the protons of the condensed ring in I-IV (g-i) are shifted 0.5-1.2 ppm to strong field as compared with the unsubstituted cations; this provides evidence for strong coupling of the substituent with the benzene ring in the investigated systems.

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TABLE 1. PMR Spectra of 6-Dialkylamino Derivatives of Herz Salts and Their Selenium Analogs

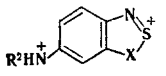
Compound	Solvent (%)	Chemical shifts, δ, ppm				Spin-spin coupling constants, J, Hz	
		4-H	5-H	6-Me$_2$N	7-H	J_{45}	J_{57}
Ig	CF_3COOH	8,27	7,73	3,54	7,71	10	2,5
	H_2SO_4 (70)	8,16	7,70	3,54	7,62	10	2,5
	H_2SO_4 (96)	9,10	8,31	3,51	8,92	9	2,0
IIg	CF_3COOH	8,22	7,60	3,50	7,68	11	2,5
	H_2SO_4 (96)	8,67	8,09	3,53	8,45	9	2,0
IIi	CF_3COOH	8,08	7,68	3,98	7,79	10	2,5
	H_2SO_4 (96)	8,96	8,18	3,84	8,78	9	2,5
IIIg	CF_3COOH	8,41	7,67	3,46	8,00	10	2,0
	H_2SO_4 (70)	8,26	7,64	3,46	7,82	10	2,0
IVg	CF_3COOH	8,28	7,54	3,34	8,02	10	2,2
	H_2SO_4 (96)	8,53	7,93	3,29	8,35	9	2,0

TABLE 2. Characteristics of the Compounds Obtained

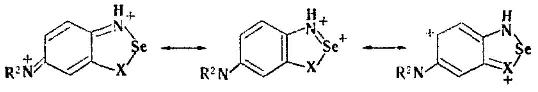
Compound	R	Found, %			Empirical formula	Calc., %			UV spectra		Yield, %
		Cl	N	S		Cl	N	S	solvent (%)	λ_{max}, nm (lg ε)	
Ie	C_6H_5				$C_{12}H_9ClN_2S_2$				CH_3COOH	535 (4,24); 500sh (4,19); 350 (3,84)	80
									H_2SO_4 (100)	410 (3,30); 350 (4,11)	
Ij	$C_6H_5CH_3N$	12,3	10,0	22,2	$C_{13}H_{11}ClN_2S_2$	12,5	9,9	22,6	H_2SO_4 (70)	540 (4,18); 345 (4,15)	76
If	p-$CH_3C_6H_4NH$	12,4	9,8	22,4	$C_{13}H_{11}ClN_2S_2$	12,5	9,9	22,6	CH_3COOH	540 (4,21); 510sh (4,18); 345 (3,89)	82
IIe	C_6H_5NH	11,0	8,8	9,9	$C_{12}H_9ClN_2SSe$	11,2	8,8	10,1	CH_3COOH	545 (4,18); 350 (3,62)	95
									H_2SO_4 (96)	647 (4,08); 405 (3,89)	
IIf	p-$CH_3C_6H_4NH$	10,8	8,6	9,3	$C_{13}H_{11}ClN_2SSe$	10,7	8,4	9,6	CH_3COOH	550 (4,19); 350 (3,63)	92
IIIe	C_6H_5NH	11,0	9,0	9,8	$C_{12}H_9ClN_2SSe$	11,2	8,8	10,1	CH_3COOH	552 (4,11); 370 (3,49); 350 (3,49)	73
									H_2SO_4 (100)	430 (3,65); 360 (4,08)	
IIIf	p-$CH_3C_6H_4NH$	10,6	8,7	9,4	$C_{13}H_{11}ClN_2SSe$	10,7	8,4	9,6	CH_3COOH	550 (4,08); 505sh (3,92); 340 (3,77)	70
IVe	C_6H_5NH	9,8	7,8	—	$C_{12}H_9ClN_2Se_2$	9,8	7,7	—	CH_3COOH	572 (4,08); 380 (3,46); 300sh (3,52)	96
									H_2SO_4 (96)	670 (4,12); 412 (3,75)	
IVf	p-$CH_3C_6H_4NH$	9,3	7,4	—	$C_{13}H_{11}ClN_2Se_2$	9,4	7,4	—	CH_3COOH	590sh (4,06); 570 (4,09); 375 (3,52); 315 (3,60)	92
Ig	$(CH_3)_2N$	15,2	12,2	27,4	$C_8H_9ClN_2S_2$	15,3	12,0	27,6	H_2SO_4 (50)	550 (4,08); 350 (3,20)	85
									H_2SO_4 (96)	410 (3,26); 340 (4,08)	
Ii	$C_5H_{10}N$	12,8	10,0	23,1	$C_{11}H_{13}ClN_2S_2$	13,0	10,3	23,5	H_2SO_4 (50)	565sh (4,06); 530 (4,18)	86
									H_2SO_4 (96)	410 (3,30); 340 (4,04)	
IIg	$(CH_3)_2N$	12,5	10,3	11,2	$C_8H_9ClN_2SSe$	12,7	10,0	11,5	H_2SO_4 (50)	565sh (4,31); 504 (4,38); 370 (3,81)	90
									H_2SO_4 (96)	620 (3,65); 360 (4,05)	
IIh	$(C_2H_5)_2N$	11,5	9,4	10,5	$C_{10}H_{13}ClN_2SSe$	11,6	9,1	10,4	H_2SO_4 (50)	565sh (4,25); 540 (4,32); 370 (3,74)	65
									H_2SO_4 (96)	630 (3,11); 430sh (3,29); 362 (4,10)	
IIi	$C_5H_{10}N$	11,2	8,8	9,9	$C_{11}H_{13}ClN_2SSe$	11,1	8,8	10,0	H_2SO_4 (50)	570sh (4,22); 540 (4,29); 370 (3,69)	86
									H_2SO_4 (96)	625 (2,77); 430 (3,31); 365 (4,17)	
IIIg	$(CH_3)_2N$	12,6	9,6	11,5	$C_8H_9ClN_2SSe$	12,7	10,0	11,5	H_2SO_4 (50)	560sh (4,07); 535 (4,10); 535 (3,71)	88
									H_2SO_4 (96)	430 (3,65); 350 (4,04)	
IVg	$(CH_3)_2N$	10,8	8,8	—	$C_8H_9ClN_2Se_2$	10,9	8,6	—	H_2SO_4 (50)	585sh (4,23); 550 (4,24); 380 (3,79)	94
									H_2SO_4 (96)	640 (3,88); 610sh (3,87); 380 (3,78)	
Ij		19,0	8,0	19,1	$C_{24}H_{14}Cl_4N_4S_4$	20,5	8,1	18,5	CH_3OH	540 (4,50); 510sh (4,45)	75
IIj		18,0	6,8	7,9	$C_{24}H_{14}Cl_4N_4S_2Se_2$	18,1	7,1	8,1	$HCOOH$	545 (4,45); 500sh (4,31); 370 (3,99)	55

Successive replacement of the sulfur atoms by selenium in amino derivatives I gives rise to a bathochromic shift of the long-wave bands in their electronic spectra (Table 2).

Dissolving of 6-amino derivatives I and III in 100% H_2SO_4 leads to the disappearance of the intense violet coloration, and the color of the solutions increases to yellow, during which the electronic spectrum is similar to the spectra of unsubstituted salts Ia and IIIa in concentrated H_2SO_4. This provides evidence that under these conditions salts Ie-i and IIIe-g are protonated at the amino group to give dications V. In contrast to this, 6-amino derivatives of II and IV, which contain a selenium atom in the 2 position, dissolve in H_2SO_4 with deepening of the coloration to blue and green shades. The original spectra are regenerated when the solutions are diluted with water. The deepening of the coloration in this case can be explained only by protonation of the ring nitrogen atom to give dications VI, the positive charges in which are delocalized and, as shown below, the participation of the amino groups in conjugation is reinforced:



V



VIa VIb VIc

V, VI X=S, Se

However, bands with λ_{max} 360-365 nm, which show that protonation takes place with the formation of dications with structure V, are also observed in the absorption spectra of the solutions of IIg-i and IVg. The ratio (VI/V) of the concentrations of dications VI and V obtained by protonation of salts IIe-i can be judged from the intensity of the bands at 620-650 nm and, respectively, 360-365 nm: an increase in the intensity of the first band is accompanied by a corresponding decrease in the intensity of the second band in the following order of substituents in the 6 position: piperidino, diethylamino, dimethylamino, and phenylamino. In the case of arylamino derivatives IIe, f the short-wave band vanishes completely. The absorption curves of salts IIi and IVg recorded in 50-100% H_2SO_4 have isopiestic points, the presence of which attests to the independence of the ratios of the concentrations of forms V and VI on the acidity of the solution. Thus the fraction of dication VI increases as the basicity of the exocyclic nitrogen atom decreases.

Comparison of the PMR spectra of salts I, II, and IVg in concentrated H_2SO_4 with their spectra in trifluoroacetic and 70% H_2SO_4 (Table 2) confirms the existence in concentrated H_2SO_4 of dications, the signals of the aromatic protons of which are shifted 0.4-1.2 ppm to weak field.

EXPERIMENTAL

The UV spectra of $0.25 \cdot 10^{-4}$ M solutions of the compounds were recorded with an SF-8 spectrophotometer. The PMR spectra were recorded with a Varian HA-100 spectrometer with cyclohexane and methylene chloride as the internal standards.

6-Anilinobenzo-1,2,3-thiaselenazolium Chloride (IIe). A solution of 1 g of aniline in 5 ml of acetic acid was added with stirring and cooling to a suspension of 2.4 g (0.01 mole) of salt IIb in 5 ml of acetic acid, and the mixture was stirred for 12 h. The crystalline precipitate was removed by filtration and recrystallized from acetic acid to give 3.1 g (95%) of violet-bronze crystals of chloride IIe.

6-Arylamino derivatives Ie, f, IIe, f, and IIIe, f were similarly obtained by the action of aniline and p-toluidine on salts Id, IIb, d, IIIb, d, and IVb, d.

6-Dimethylaminobenzo-1,2,3-thiaselenazolium Chloride (IIg). A 2.4-g (10 mmole) sample of salt IId was added to 10 mmole of dimethylamine acetate in 10 ml of dimethylacetamide (DMA), and the mixture was stirred at 20 deg C for 16 h. The precipitate was removed by filtration and recrystallized from acetic acid to give 2.9 g (90%) of green crystals of chloride IIg. Dimethylformamide (DMF) or 2 ml of acetic acid can be used instead of DMA.

6-Dialkylamino derivatives Ig-i, IIg-i, IIIg, and IVg were similarly obtained by the action of dimethylamine, diethylamine, and piperidine acetates on salts Id, IId, IIId, and IVd.

6-Dimethylaminobenzo-1,2,3-dithiazolium Chloride (Ig). A 1.2-g (5 mmole) sample of 4-amino-3-mercaptodimethylaniline hydrochloride was refluxed for 3 min in 10 ml of thionyl chloride, after which the mixture was cooled and treated with 20 ml of ether. The precipitate was removed by filtration and recrystallized from acetic acid to give 0.4 g (34%) of chloride Ig.

6-Dimethylaminobenzo-1,2,3-thiaselenazolium Chloride (IIg). A 0.65-g (5 mmole) sample of selenious acid was added to 1.2 g (5 mmole) of 4-amino-3-mercaptodimethylaniline hydrochloride in 8 ml of acetic acid, and the mixture was stirred for 2 h. The precipitate was removed by filtration and recrystallized from formic acid to give 1.25 g (80%) of chloride IIg, which, with respect to its electronic spectrum, was identical to the chloride obtained by the first method.

2,2'-Dithiobis[6-(4-chlorophenylamino)benzo-1,2,3-dithiazoliun] Chloride (Ij). A) A 10-mmole sample of Ib was added to 12 mmole of dimethylamine (diethylamine) acetate in 10 ml of DMA, and the mixture was stirred for 24 h. The precipitate was removed by filtration and crystallized from formic acid to give 2.9 g of chloride Ij. Compound IIj was similarly obtained from salt IIb.

B) A 2.2-g (10 mmole) sample of salt Id was added to 1.6 g (5 mmole) of 2,2'-dithiobis(4-chloroaniline) in 10 ml of acetic acid, and the mixture was stirred for 48 h. The precipitate was removed by filtration and recrystallized from formic acid to give 2.5 g of chloride Ij. Compound IIj was similarly obtained from salt IId. The compounds obtained by methods A and B were identified from their electronic spectra.

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QUINONEIMINES AND QUINONEDIIMINES OF THE DIBENZO[ce][1,2]THIAZINE 5,5-DIOXIDE SERIES

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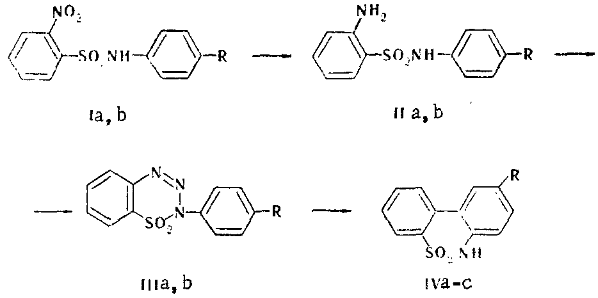
9(H)-Oxodibenzo[ce][1,2]thiazine 5,5-dioxide and its 9(H)-phenylsulfonylimino-substituted derivative were synthesized. It is shown that the direct bond between the quinoid ring and the substituent attached to nitrogen leads to a decrease in the redox potential of the system and a simultaneous increase in the electrophilic properties of the quinoneimine.

In order to determine the factors that affect the redox potentials of quinoneimines we synthesized heterocyclic quinoneimines of the dibenzo[ce][1,2]thiazine 5,5-dioxide (VIII) series, in which a direct bond between the substituent attached to the nitrogen atom and the quinoid ring is realized. The synthesized compounds are of interest in connection with the possibility of the use of the high reactivities of quinoneimines for the synthesis of biologically active compounds [1].

The starting 9-R-dibenzo[ce][1,2]thiazine 5,5-dioxides (IV) were synthesized by cyclization of 2-aminophenylsulfonyl(4-R-anilides) by the Ullmann–Gross method [2] via the following scheme:



Ia, b

II a, b

IIIa, b

IVa-c

I-IV a R = OCH_3; b R = $NHSO_2C_6H_5$; IV c R = OH

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