Compounds Ib-e (Table 1) were obtained by methods A or B.

4-Phenylazo-3,5-diamino-1,2-dithiolium Bromide (IIa). A 1-g sample of dithiomesoxalic acid diamide phenylhydrazone was dissolved in 20 ml of chloroform, and a solution of 0.6 g of bromine in 50 ml of chloroform was added slowly with stirring and cooling. A light-brown precipitate formed gradually. The mixture was allowed to stand at room temperature for 1-2 h, after which the precipitate was removed by filtration and washed with chloroform and ether. The yield was 1 g.

Compounds IIb-e (Table 2) were similarly obtained.

3-(N-Phenylthiocarbamoyl)-4-phenylazo-5-amino-1,2-dithiolium Bromide (IIIa). A 0.3-g sample of 4-phenylazo-3,5-diamino-1,2-dithiolium bromide was dissolved in 10 ml of methanol or ethanol, 0.24 g of phenyl isothiocyanate was added, and the mixture was heated at 80°C for 1 h, during which a precipitate formed. A small amount of the alcohol was removed by evaporation, and the precipitate was removed by filtration, washed with ether, and air dried. The yield was 0.2 g.

Compounds IIIb,c (Table 2) were similarly obtained.

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STRUCTURES AND REACTIVITIES OF BENZO-1,2,3-DITHIAZOLIUM SALTS AND THEIR SELENIUM ANALOGS

Yu. I. Akulin, M. M. Gel'mont, B. Kh. Strelets, and L. S. Éfros

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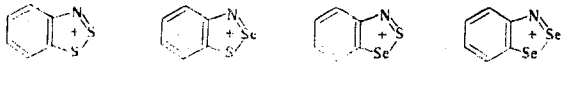
A number of benzo-1,2,3-dithiazolium chlorides (I) and their selenium analogs – benzo-1,2,3-thiaselenazolium, benzo-2,1,3-thiaselenazolium, and benzo-1,2,3-diselenazolium salts – were synthesized. The electronic structures and reactivities of the I cation and salts I-IV are discussed on the basis of a quantum-chemical calculation of cation I and the PMR spectra of salts I-IV. Successive substitution of the sulfur atoms in the I cation by selenium atoms, particularly in the 2 position, substantially increases the degree of transfer of positive charge to the condensed benzene ring. The trend of the nucleophilic reactivities of 6-methoxy derivatives of salts I-IV in the reaction with aromatic amines is the same as the trend of the degree of localization of the positive charge in the 6 position.

In our preceding communications we described the selenium analogs of benzo-1,2,3-dithiazolium salts (I), – benzo-1,2,3-thiaselenazolium (II), benzo-2,1,3-thiaselenazolium (III), and benzo-1,2,3-diselenazolium (IV) salts – and described some of their properties [1-4].



I II III IV

Leningrad Branch, Design Scientific-Research Institute of Synthetic Fibers, Leningrad 195030.

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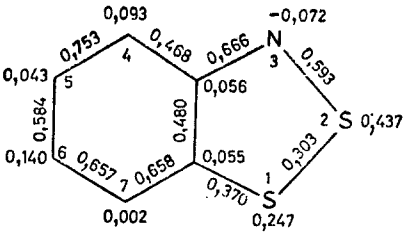


Fig. 1. Charge distribution and bond orders in the benzo-1,2,3-dithiazolium cation (I).

It is known [5, 6] that the positive charge in the I cation is delocalized to a considerable degree due to the condensed benzene ring. Quantum-chemical calculation* by the self-consistent-field (SCF) MO method within the Pariser–Parr–Pople approximation gives a more nearly complete picture of the electron-density distribution.

It is apparent from the molecular diagram (Fig. 1) that the highest positive charge is located on the sulfur atom in the 2 position. Approximately one-third of the charge is distributed nonuniformly in the condensed benzene ring of the cation. The carbon–carbon bonds in the benzene ring are nonequivalent: The 4–5 and 6–7 bonds have higher orders than the 5–6 bond, which is in agreement with the previously expressed assumptions. The electron density distribution presented in the diagram is in good agreement with the experimental data on the nucleophilic reactivities of these cations, according to which substitution in the heteroring takes place in the 2 position and substitution in the benzene ring occurs in the 6 position. The certain amount of negative charge on the nitrogen atom in the I cation indicates the possibility of protonation in the 3 position.

Valuable information regarding the electron density distribution in cation I and its selenium analogs II–IV can be obtained as a result of an analysis of the ^{1}H NMR spectra of these compounds (Table 1). The interpretation of the spectra of 5- and 6-monosubstituted cations I–IV does not present any difficulties owing to the great difference in the chemical shifts of the ring protons and the spin–spin coupling with characteristic constants. The spectra of the unsubstituted cations are more complex but are interpreted within a first order approximation with an accuracy of ±2 Hz [3]. The signals of the aromatic protons were assigned on the basis of calculation of the spectra of the unsubstituted compounds and on the basis of the spectra of the 5- and 6-monosubstituted compounds. Trifluoroacetic acid and concentrated sulfuric acid were used as the solvent. The spectrum of 6-methoxybenzo-1,2,3-dithiazolium chloride (VII), which is one of the few quite soluble salts, was obtained from a solution in methanol.

It is apparent from Table 2 that the chemical shifts of the aromatic protons of the cations in the 7 position ($\Delta\delta$ = 0.20–0.34 ppm) are the most sensitive to the effect of the solvents. The chemical shifts of the protons in the other positions of the ring are less sensitive: $\Delta\delta$ = 0.04–0.12 ppm.

* The authors thank Professor V. I. Minkin for his calculation.

TABLE 1. PMR Spectra of Benzo-1,2,3-dithiazolium (I), Benzo-1,2,3-thiaselenazolium (II), Benzo-2,1,3-thiaselenazolium (III), and Benzo-1,2,3-diselenazolium (IV) Chlorides in Trifluoroacetic Acid

Compound	Type of heteroring	R	Chemical shifts, δ, ppm				Spin–spin coupling constants, J, Hz†				
			4-H	5-H	6-H	7-H	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	$J_{4,6}$	$J_{5,7}$
I	I	H	8,98	8,34	8,54	8,93	8,8	7.0	8,2	1,2	1,2
II	II	H	8,78	8,09	8,43	8,67	9,0	6,8	8,7	1,2	1,2
III	III	H	9,16	8,18	8,42	9,00	8,8	7,0	8,8	1,2	1,4
IV	IV	H	9,17	8,06	8,52	8,84	9,2	6,9	8,6	1,2	1,2
V	I	4MeO	4,38*	7,54	8,54	8,33	—	7,6	8,2	—	2,0
VI	I	7MeO	8,54	8,28	7,78	4,29*	8,8	7,8	—	1,5	—
VII	I	6MeO	8,70	7,88	4,31*	8,24	9,3	—	—	—	2,2
VIII	II	6MeO	8.54	7,71	4,26*	8,09	9,8	—	—	—	2,2
IX	III	6MeO	8,85	7,74	4,19*	8.42	9,5	—	—	—	2,0
X	IV	6MeO	8,73	7,63	4,22*	8.33	9,4	—	—	—	2,2
XI	I	6MeOOC	9,05	8,86	4,21*	9,57	9,2	—	—	—	1,5

* Chemical shifts of the protons of the substituents.

† $J_{4,7} < 1$ Hz.

TABLE 2. Effect of Solvents on the PMR Spectra of Salts I-IV

Compound	Solvent	Chemical shifts, δ, ppm			
		4-H	5-H	6-H	7-H
VII	CF_3COOH	8,70	7,88	4,31*	8,24
VII	MeOH	8,68	7,82	4,30*	8,42
IX	CF_3COOH	8,85	7,74	4,19*	8,42
IX	H_2SO_4	8,77	7,67	4,13*	8,08
X	CF_3COOH	8,73	7,63	4,22*	8,33
X	H_2SO_4	8,63	7,67	4,17*	8,24
III	CF_3COOH	9,16	8,18	8,42	9,00
III	H_2SO_4	9,11	8,19	8,42	8,80
IV	CF_3COOH	9,17	8,06	8,52	8,84
IV	H_2SO_4	9,05	7,99	8,45	8,64

* Chemical shifts of the protons of the substituents.

It should be noted that replacement of trifluoroacetic acid by sulfuric acid leads to a slight shift of the spectrum to strong field and that the 7H signal of VII in methanol is shifted to weak field with respect to the spectrum in trifluoroacetic acid. This fact indicates unambiguously that protonation of the salts does not occur in acid solvents and that only the monocations are present. The greatest degree of solvation of the heteroatoms in the 1 and 2 positions, on which a large portion of the positive charge is concentrated, also evidently gives rise to the greatest variability in the chemical shift of the closest proton in the 7 position.

A change in the concentrations of the salts has little effect on the chemical shifts of the protons. Thus an increase in the concentration of salt III from 10 to 25% leads to a 0.04 ppm change in the shift of the proton in the 7 position.

The presence of substituents in the investigated cations has a substantial effect on the chemical shifts of the ring protons. Electron-donor substituents in the investigated systems shift the signals of the ring protons to strong field considerably more markedly than in the benzene series. On the other hand, electron-acceptor substituents cause a smaller shift of the signals of the ring protons to weak field. Thus the introduction of a methoxy group in the 4 or 7 position of cations I and II shift the signals of the ring protons to strong field (0.44-0.80 ppm) (Table 1). The analogous change on passing from benzene to anisole is 0.23 ppm. In conformity with the molecular diagram (Fig. 1), the effect of substituents on the chemical shifts of the ring protons is greater within the limits of bonds that have high orders. The difference in the spin–spin coupling constants (SSCC) of the various ortho protons also confirms higher order of the 4–5 and 6–7 bonds.

The chemical shifts of the ring protons of all four unsubstituted heterorings I-IV increase in the order 5-H, 6-H, 7-H, and 4-H (Table 1). The trend of the change in the chemical shifts of the protons in this series is not the same as the trend of the changes in the electron densities. This is evidently due to the considerable magnetic anisotropy of the heteroring. Since the 4-H and 7-H α protons are closer by a factor of 1.3-1.35 to the center of the heteroring than the 5-H and 6-H β protons, the contribution of the magnetic anisotropy to the chemical shifts of the α protons should be 2.2-2.4 times greater [7]. This should shift their chemical shifts to weak field (0.6-0.8 ppm).

The possibility of delocalization of the positive charge of the cations in the 4 and 6 positions of the benzene ring in confirmity with resonance structures XII and XIII causes a low-field shift of the protons in these positions with respect to the 7-H and 5-H protons.

XII XIII

X, Y = S, Se

Thus the $\Delta\beta = \delta_{6}H - \delta_{5}H$ and $\Delta\alpha = \delta_{4}H - \delta_{7}H$ differences to a first approximation depend on the electron densities in the corresponding positions of the benzene ring. The $\Delta\beta$ values for the I, III, II, and IV series change in the order 0.2, 0.24, 0.36, and 0.46. In the same series of heterocycles the $\Delta\alpha$ values are 0.05, 0.16, 0.10, and 0.34. The certain degree of disruption in the trend of the $\Delta\alpha$ values is associated with the considerable magnetic anisotropy of the selenium atom, which from the 1 position has a strong effect on the closely situated proton in the 7 position [8].

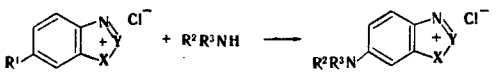
Thus successive substitution of the sulfur atoms in the I cation by selenium atoms, particularly in the 2

TABLE 3. Pseudo-First-Order Rate Constants (K_1) for the Reaction of 6-Methoxy Derivatives VII-X with p-Toluidine at 20°C

Reagents	$K_1 \cdot 10^4$
VII	4,42
VIII	15,30
IX	4,68
X	18,10

position, substantially increases the degree of transfer of the positive charge to the benzene ring. The reason for this is evidently the lower (as compared with the sulfur atom) ability of the selenium atom to form π bonds and, consequently, to localize the positive charge on it, owing to which the specific weight of structures V and VI with charge transfer to the condensed benzene ring increases.

An increase in the transfer of the positive charge to the condensed benzene ring when the sulfur atom is replaced by selenium in the series of I-IV cations should consequently increase their reactivities in nucleophilic substitution reactions. We have observed that all of the 6-halo and 6-alkoxy derivatives of selenium-containing II-IV cations react with aromatic and secondary aliphatic amines to give the corresponding 6-amino derivatives [9].



XIV

X, Y = S, Se; R^1 = Cl, CH_3O; R^2 = R^3 = Alk; R^2 = Ar, R^3 = H

A kinetic study of the reactions of 6-methoxy derivatives (VII-X) of salts I-IV with p-toluidine in acetic acid confirms the above assumption. The selection of 6-methoxy derivatives rather than 6-chloro derivatives for the studies was due to the considerably lower probability of side reactions involving the heteroring.

The pseudo-first-order rate constants (K_1) are presented in Table 3. It is apparent from Tables 2 and 3 that the kinetic data are in good agreement with the conclusions from an analysis of the PMR spectra of salts I-IV.

EXPERIMENTAL

The PMR spectra of solutions of the compounds (0.4 mole/liter) in trifluoroacetic and sulfuric acids were recorded with a Varian HA-100 spectrometer (100 MHz) with cyclohexane and DSS as the internal standards; the chemical shifts are presented on the δ scale with respect to tetramethylsilane.

The synthesis of a number of benzodithiazolium chlorides has been described: Unsubstituted benzo-1,2,3-dithiazolium chloride (I) [10], the 6-carbomethoxy derivative (XI) [11], and the 7-methoxy derivative (VI) [4]. Benzo-1,2,3-thiaselenazolium chloride (II) and 6-MeO-II (VIII) were obtained by the method in [9].

2-Amino-3-methoxythiophenol (XVI). An 18-g (0.1 mole) sample of 2-amino-4-methoxybenzothiazole (mp 150-152°C) was refluxed for 8 h with a solution of 100 g of potassium hydroxide in 100 ml of water, after which the mixture was cooled and neutralized carefully with a solution of 125 ml of concentrated hydrochloric acid in 150 ml of water to pH 9. It was then filtered, and the filtrate was treated with 30 ml of acetic acid and worked up to give thiophenol XVI, which was extracted with 200 ml of benzene. The benzene extracts were dried with sodium sulfate, after which they were saturated with dry hydrogen chloride to give colorless crystals of the hydrochloride of XVI with mp 135-142°C. The yield was 13.5 g (70%). Found: N 7.2; S 16.5%. $C_7H_{10}ClNOS$. Calculated: N 7.3; S 16.7%.

4-Methoxybenzo-1,2,3-dithiazolium Chloride (V). A 1.9-g (10 mmole) sample of the hydrochloride of 2-amino-3-methoxythiophenol XVI was sprinkled into 15 ml of refluxing thionyl chloride in a flask equipped with

a reflux condenser, and the mixture was refluxed for 5 min. It was then cooled, treated with 15 ml of ether, and filtered to give 1.4 g (64%) of dark-brown crystals of chloride V. Found: Cl 16.4; N 6.5%; S 30.2%. $C_7H_6ClNOS_2$. Calculated: Cl 16.1; N 6.4; S 30.4%.

o-Aminoselenophenol Hydrochloride (XVII). An 11.4-g (5 mmole) sample of o-nitrophenyl selenocyanate was placed in a 0.5 liter three-necked flask equipped with a stirrer, dropping funnel, and reflux condenser, 300 ml of water was added to the flask, and 30 g (0.46 g-atom) of powdered zinc was sprinkled in with stirring. The mixture was then heated to the boiling point, the heating unit was removed, and a solution of 16 g (0.4 mole) of sodium hydroxide in 20 ml of water was added gradually. The mixture was then refluxed with stirring for 2 h, after which it was cooled, and the solution was decanted and treated with a solution of 48 g (0.2 mole) of crystalline sodium sulfide in 100 ml of water. The resulting precipitate was removed by filtration in a carbon dioxide atmosphere. The filtrate was acidified successively with hydrochloric acid and acetic acid to pH 6-7. The precipitated yellow o-aminoselenophenol was extracted with 100 ml of butyl acetate, and the extract was dried with sodium sulfate and treated with hydrochloric acid to give yellowish hydrochloride XVII, which was washed with absolute ether and dried in vacuo to give a product with mp 142-147°C (dec.). The yield was 6.8 g (65%). Found: Cl 16.8; N 6.6%. C_6H_5ClNSe. Calculated: Cl 17.0; N 6.7%.

Benzo-1,2,3-thiaselenazolium Chloride (III). A 2.1-g (10 mmole) sample of o-aminoselenophenol hydrochloride was added to 20 ml of refluxing thionyl chloride in a flask equipped with a reflux condenser, during which foaming was observed. The mixture was then refluxed for 10 min, after which it was cooled and treated with 40 ml of ether. The precipitated yellow crystals of chloride III were removed by filtration to give 1.6 g (69%) of a product with mp 150-156°C (dec.). Found: Cl 15.4; N 6.1%. $C_6H_4ClNSSe$. Calculated: Cl 15.0; N 5.9%.

Benzo-1,2,3-diselenazolium Chloride (IV). A 1.3-g (10 mmole) sample of selenious acid was added with stirring and cooling (with ice water) to 2.1 g (10 mmole) of o-aminoselenophenol hydrochloride in 30 ml of formic acid, after which the mixture was stirred for 15-20 min. It was then treated with 50 ml of ether, and the precipitate was removed by filtration, crystallized from formic acid–ether (1:2) or formic acid–acetic anhydride (1:2), washed with ether, and dried in vacuo to give 2.3 g (81%) of brown crystals of chloride IV with mp 132-138°C (dec.). Found: Cl 12.5; N 5.0%. $C_6H_4ClNSe_2$. Calculated: Cl 12.5; N 4.9%.

Kinetics of the Reaction of Chlorides VII-X with p-Toluidine. The kinetics were studied spectrophotometrically with an apparatus operating in accordance with the "injection" method. Equal volumes (5 ml) of solutions of the appropriate salt (10^{-4} mole/liter) and p-toluidine (1 mole/liter) were sucked into two thermostatted syringes. After a temperature of 20°C was established in the syringes, the solutions were injected into the thermostatted cuvette of a Spectromom-202 spectrophotometer. The monochromatic light passing through the cuvette and corresponding to the absorption maximum of the final products was conveyed to a photoelectronic multiplier, in which it was converted to an electrical signal and recorded on the diagram ribbon of a recorder (KSP-4). The rate constants were calculated as pseudo-first-order constants by the Guggenheim method. It was demonstrated by preliminary experiments that the reaction goes to completion and that the concentration of the resulting 6-(p-tolylamino) derivatives is equal to the concentrations used for the study of the 6-methoxy derivatives.

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