filtration, dried, and chromatographed on Al_2O_3 in chloroform. Workup gave IIIa, with mp 184-186°, in 21% yield. Found, %: N 2.6; S 14.3. $C_{24}H_{17}NO_5S_2$. Calculated, %: N 3.0; S 14.2.

A similar procedure was used to obtain 3,7-di(tolylsulfonyl)phenoxazine (IIIb), with mp 212-214°, in 25% yield. Found, %: N 2.9; S 13.5. $C_{26}H_{21}NO_5S_2$. Calculated, %: N 2.98; S 13.7.

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BASICITIES AND STRUCTURES OF 2-(N-ARYLAMINOMETHYLENE)-3(2H)-BENZO[b]-THIOPHENONES, -BENZO[b]FURANONES, AND -BENZO[b]SELENOPHENONES*

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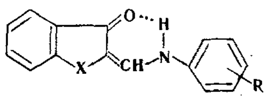
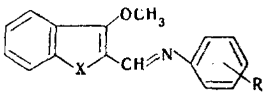
The ionization constants of the conjugate acids of the reaction series 2-(N-arylaminomethylene)-3(2H)-benzo[b]thiophenones, -benzo[b]furanones, and -benzo[b]selenophenones were determined by potentiometric titration in anhydrous acetonitrile. The electronic and vibrational spectroscopic data showed that the protonation center in the molecules of these compounds is the carbonyl oxygen atom. It was established by correlation analysis that N-aryl substituents affect the protonation center primarily via an induction mechanism.

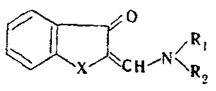
We have previously shown that 2-(N-arylaminomethylene)-3(2H)-benzo[b]thiophenones, -benzo[b]furanones, and -benzo[b]selenophenones exist in the form of enamino ketone structures I in the solid state and in solution [2-4]. The strong polarization of the amino enone system of π bonds leads to induction of a considerable negative charge on the carbonyl oxygen atom [5, 6]. This provides a basis to expect that precisely the carbonyl oxygen atom in I will be the protonation center.



I



II



III

I-III a X=O; b X=S; c X=Se

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*Communication XVIII from the series "Basicities and structures of azomethines and their structural analogs." See [1] for communication XVII.

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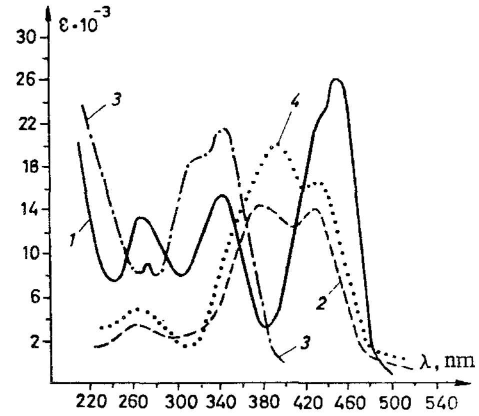


Fig. 1. Electronic absorption spectra in acetonitrile: 1) 2-(N-phenylaminomethylene)-3(2H)-benzo[b]thiophenone; 2) its conjugate acid IV; 3) 2-formyl-3-methoxybenzo[b]thiophene phenylimine; 4) its conjugate acid V.

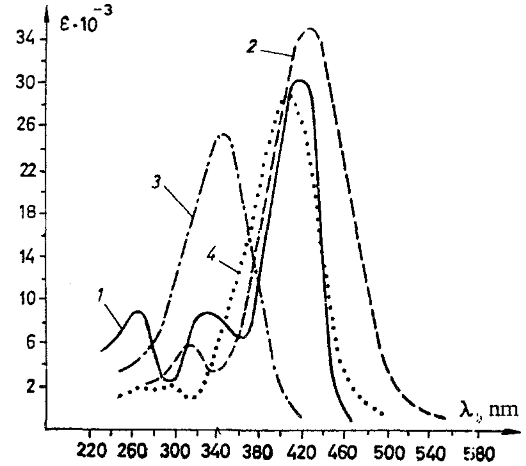


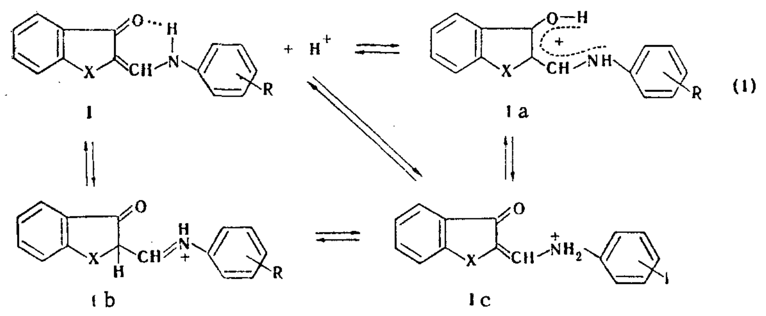
Fig. 2. Electronic absorption spectra in acetonitrile: 1) 2-(N-phenylaminomethylene)-3(2H)-benzo[b]furanone; 2) its conjugate acid VI; 3) 2-formyl-3-methoxybenzo[b]furan; 4) its conjugate acid VII.

TABLE 1. Ionization Constants of the Conjugate Acids of I-III in Acetonitrile at 25°C

Compound	X	Substituent R										
		H	p-OCH₃	p-CH₃	m-CH₃	p-Cl	m-Cl	p-Br	p-COCH₃	p-COOC₂H₅	m-NO₂	p-NO₂
I	O	7,65	8,34	7,95	7,66	7,17					6,29	5,97
	S	7,03	7,52	7,34	7,06	6,67	6,24	6,56		6,06	5,72	5,40
	Se	6,74	7,34			6,28	6,07		5,77			
II	S	10,01	10,41	10,31		9,31				9,04		
	Se					8,73						

Compound	X	Substituents R_1 and R_2			
		CH_3, H	CH_3, CH_3,	CH_3, C_6H_5	C_4H_8O
III	O			8,29	
	S	9,21	9,40	8,81	9,16
	Se		9,58		

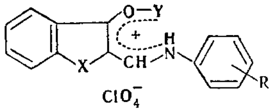
The goal of the present research was to estimate the basicities of heterocyclic enamino ketones I, to compare them with the basicities of compounds that model fixed benzenoid II and quinoid III structures, and to study the effect exerted by substituents R in the N-aryl ring on the ease of protonation of I and II.



(1)

Enamino ketones I have three potential protonation centers: the carbonyl oxygen atom adjacent to heteroatom X, the carbon atom, and the amine nitrogen atom, to which possible conjugate acids Ia, Ib, and Ic correspond. As compared with Ia, the last two structures are unfavorable because of the disruption in these cases of the system of conjugated bonds. Until now it has not been possible to establish the formation of structure Ic [7]. The choice between Ia and Ib was made on the basis of electronic and vibrational spectroscopic data. The electronic spectra in acetonitrile of bases I and II and the corresponding conjugate acids IV-VII are presented in Figs. 1 and 2. Salts IV and V, taken as a pair, have almost identical spectra, just as the spectrum of VI is similar to the spectrum of VII. The electronic spectra of these salts differ considerably from the spectra of II and contain the long-wave absorption band at 430-450 nm that is also characteristic for bases I. This confirms the identical structures of IV and V and VI and VII; this can be realized only in the case of protonation of enamino ketones I at the carbonyl oxygen atom.

The IR spectra of perchlorates IV and V have identical characteristic bands corresponding to the vibrations of bonds of the conjugate protonated enamino ketone system (1630, 1660 cm^{-1}). The spectra of salts VI and VII (ν 1620, 1650-1660 cm^{-1}), which correspond to structure Ia, are also similar to one another. Compounds Ib would have higher-frequency absorption at 1700 cm^{-1} [7].



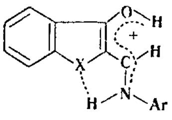
IV–VII

IV, V X=S; VI, VII X=O; IV, VI Y=H; V, VII Y=CH_3

Thus the most basic center in the molecules of I is the carbonyl oxygen atom, and the corresponding conjugate acid has structure Ia.

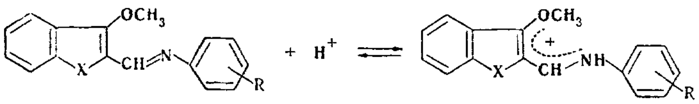
The ionization constants of the conjugate acids of I, II, III in acetonitrile at 25°C are presented in Table 1. On comparing the pK_a values in series of corresponding compounds I (X = O, S, Se), one may note that the basicities increase in the order Se < S < O. According to the PMR spectral data [2-4], the strength of the intramolecular hydrogen bond in the molecules of I is practically independent of the nature of heteroatom X and, consequently, cannot have a substantial effect on the relative basicities of I as X is varied.

Conjugate acids Ia can exist in the form of trans isomers Id. In this case stabilization of the molecule due to an NH...X intramolecular hydrogen bond develops. This bond should be strongest in benzofuran derivatives and weakest when X = Se. This phenomenon may become the reason for the decrease in basicities in the order O > S > Se that is actually observed. On the other hand, the conjugate acids of fixed enamino ketone structures III are incapable of this sort of stabilization, and the basicities of III change in conformity with the electronegativity of heteroatom X: O < S < Se (Table 1). Compounds III are more basic than the corresponding I because of the absence of an intramolecular hydrogen bond in fixed form III.



Id

A rather marked increase in basicity as compared with I, and even with III, is observed for compounds with azomethine structure II. The difference in the nature of the reaction center in isoelectronic molecules of the conjugate acids of I (III) and II is manifested here.



II

IIa

The former dissociate via a mechanism of the type observed for OH acids (I), whereas, on the other hand, IIa are NH acids and correspond to stronger bases with an imine center (2).

TABLE 2. Correlation Parameters of Equations (3)

Reaction series	Type of σ	ρ	R	S	δ_{pk}	$\delta\ \rho$	pK^0 calc.
I, X=O	σ	2,064	0,994	0,24	0,04	0,094	7,65
	σ^0	2,210	0,982	0,41	0,07	0,175	7,71
	σ^+	1,567	0,977	0,46	0,07	0,140	7,38
	σ^-	1,529	0,972	0,51	0,09	0,152	7,67
I, X=S	σ	1,951	0,995	0,20	0,03	0,064	7,00
	σ^0	2,092	0,988	0,33	0,04	0,111	7,06
	σ^+	1,430	0,963	0,57	0,06	0,134	6,77
	σ^-	1,445	0,976	0,46	0,06	0,110	7,00
	σ_I	2,100	0,796	1,27	0,21	0,532	7,21
I, X=Se	σ	2,003	0,998	0,07	0,02	0,060	6,77
	σ^0	2,247	0,990	0,17	0,05	0,161	6,88
	σ^-	1,370	0,949	0,39	0,10	0,226	6,77
	σ^+	1,181	0,969	0,30	0,07	0,151	6,50
II, X=S	σ	2,060	0,988	0,19	0,04	0,162	9,91
	σ^0	2,229	0,995	0,12	0,03	0,114	10,00
	σ^-	1,570	0,958	0,35	0,08	0,236	9,97
VIII	σ	2,224	0,991	0,07	0,02	0,062	8,97
	σ^-	1,696	0,909	0,36	0,08	0,162	8,94

TABLE 3. Correlation Parameters of the Yukawa—Tsuno Equation (5)

Reaction series	ρ^0	$r_{Y\text{-}T}$	R	S	δ_{pk}	δ_{ρ^0}	pK^0calc
I, X=O	1,990	0.302	0.988	0.23	0.06	0,205	7.70
I, X=S	1,895	0,289	0,994	0,16	0.03	0,107	7,05
I, X=Se	2,207	0,037	0,990	0,12	0.06	0,266	6.88
VIII	2,393	0,163	0,969	0,10	0,06	0,189	9,09

TABLE 4. Correlation Parameters of Eq. (6)

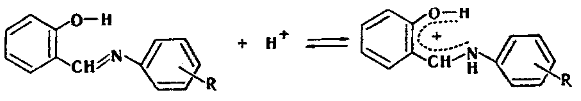
Reaction series	ρ_I	ρ_c	R	S	δ_{pk}	$\delta\rho_I$	$\delta\bar{\rho}_c$	pK°, calc.
I, X=O	1,603	1,469	0,972	0,36	0,12	0,324	0,285	7,69
I, X=S	1,657	1,290	0,979	0,30	0,08	0,197	0,162	7,06
I, X=Se	1,760	1,288	0,968	0,25	0,18	0,523	0,259	6,89
VIII	2,150	1,438	0,934	0,38	0,12	0,275	0,179	9,13

The parameters of correlation equations of the (3) type for the pK_a values of I and II are presented in Table 2.

$$\lg K = \lg K^0 + \rho\sigma. \tag{3}$$

We used the most diverse sets of σ constants (σ, σ^-, σ°, σ_I, and σ^+) for the correlations. The best correlation coefficients were observed in all cases when substituent R constants partially or completely free of the effects of direct polar conjugation were used: Hammett σ' for series I and inductive σ° for II (X = S).

The results of Table 2 display the similarity in the protonation of I and the reaction series of o-hydroxy azomethines with variable R in the aniline fragment, for example, VIII [8]. Despite the fact that VIIIa are NH acids (4), the correlations of series I and VIII are of the same nature.


(4)

VIII VIII a

To estimate the electronic effects of conjugation we analyzed the pK_a values of I by means of an equation of the Yukawa—Tsuno type (5):

$$\lg K = \lg K^0 + \rho^0(\sigma^0 + r\Delta\sigma_c^-). \quad (5)$$

The results of the correlations are presented in Table 3. The r values, which characterize the conjugation of the substituents with the reaction center, are low in all series I (X = O, S, Se) and in VIII, and this constitutes evidence in favor of the small contribution of the C effect of the electron-deficient substituents to the change in the free energy of reaction (1). It should be noted that this effect is weakened in the I series from oxygen to selenium.

An analysis of the ionization constants from Eq. (6) confirms the conclusion that conjugation effect of substituents R play a lesser role in reaction series I than the inductive effect (Table 4):

$$\lg K = \lg K^0 + \rho_I\sigma_I + \rho_c\sigma_c^-, \quad (6)$$

where $\bar{\sigma}_c = \bar{\sigma} - \sigma_I$.

The ρ_c constants are lower than the inductive constants (ρ_I). An analogy in the results for reaction series I and salicylal imines VIII also shows up here.

EXPERIMENTAL

The electronic absorption spectra were obtained with a Specord UV-vis spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer.

Compounds I-III and VIII were previously synthesized [2-4, 8].

2-Formyl-3-methoxybenzo[b]thiophene p-Carbethoxyphenylimine (II, X = S, R = $COOC_2H_5$). A mixture of 1 g (5.2 mmole) of 2-formyl-3-methoxybenzo[b]thiophene and 0.86 g (5.2 mmole) of ethyl p-aminobenzoate in 20 ml of ethanol was refluxed on a water bath for 20 min, after which it was cooled, and the precipitate was recrystallized from ethanol to give yellow needles with mp 92° in 83% yield. Found, %: C 67.1; H 4.9; S 9.1. $C_{19}H_{17}NO_3S$. Calculated, %: C 67.2; H 5.1; S 9.5.

Perchlorates IV-VII. A small excess of 70% perchloric acid was added with stirring and cooling to a benzene solution of the appropriate compound of the I or II type, and the resulting precipitates were removed by filtration and recrystallized from ethanol. Compound IV had mp 193°. Found, %: C 50.6; H 3.0; Cl 9.7; S 8.8. $C_{15}H_{12}ClNO_5S$. Calculated, %: C 50.9; H 3.4; Cl 10.0; S 9.1. Compound V had mp 132°. Found, %: C 52.0; H 3.5; Cl 9.5; S 8.5. $C_{16}H_{14}ClNO_5S$. Calculated, %: C 52.3; H 3.8; Cl 9.6; S 8.7. Compound VI had mp 183°. Found, %: C 53.1; H 3.8; Cl 10.2. $C_{15}H_{12}ClNO_6$. Calculated, %: C 53.3; H 3.6; Cl 10.5. Compound VII had mp 141°. Found, %: C 54.9; H 4.0; Cl 9.9. $C_{16}H_{14}ClNO_6$. Calculated, %: C 54.6; H 4.0; Cl 10.1. The ionization constants of the conjugate acids were determined by potentiometric titration in anhydrous acetonitrile by the method in [9]. The average accuracy was ±0.03 pK units.

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