SYNTHESIS AND STRUCTURE OF ANILS OF 2-FORMYL-3-MERCAPTOBENZO[b]THIOPHENE AND 2-FORMYL-3-MERCAPTOBENZOFURAN*

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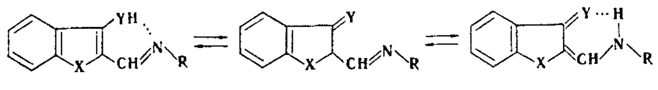
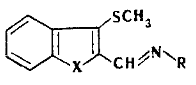
As a result of a study of the electronic, vibrational, and PMR spectra of alkyl- and arylimines of 2-formyl-3-mercaptobenzo[b]thiophene and 2-formyl-3-mercaptobenzofuran and of the spectra of model compounds the thione–enamine structure was assigned to the imines. The stability of the latter structure is in agreement with the results of quantum-mechanical calculations of the energies of atomization of the individual tautomeric forms; the calculations were made by means of the Pariser–Parr–Pople (PPP) method with the Dewar σ,π parametrization.

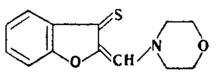
We have previously synthesized aryl- and alkylimines of 2-formyl-3-hydroxybenzofuran and 2-formyl-3-hydroxybenzo[b]thiophene (I, X = O, S; Y = O) and discussed their structure [2, 3]. The aim of the present study was elucidation of the effect of replacement of the hydroxyl group in the indicated compounds by a mercapto group on the position of the possible tautomeric equilibrium and the character of the most stable form.



IA IB IC



II

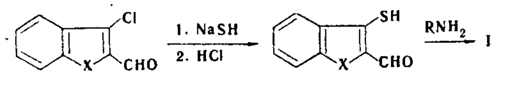


III

X=O, S; Y=S; R=Ar, Alk

The compounds with similar three-center tautomerism (Y = S) that have been studied up to now exist primarily in the form of the thione–enamine tautomer (for example, see [4-7]). However, according to the data in [8, 9], the transition from 3-hydroxythiophenes to the 3-mercapto derivatives promotes stabilization of the heteroaromatic ring, and this makes it possible to hope for more labile character of the tautomeric equilibrium than in the case of the previously studied anils of formyl-3-hydroxybenzofuran and formyl-3-hydroxybenzo[b]thiophene.

Compounds of the I type (Table 1) were synthesized via the scheme



IV V X=O,S

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*Communication XVII from the series "Benzoid-Quinoid Tautomerism of Azomethines and Their Structural Analogs." See [1] for communication XVI.

Rostov State University, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 631-639, May, 1974. Original article submitted July 31, 1973.

TABLE 1. Azomethines of the I–III Type (Y = S)

Compound	R	X	mp, °C	Empirical formula	Found, %			Calculated, %		
					C	H	S	C	H	S
I a	C_6H_5	O	125—126	$C_{15}H_{11}NOS$	71,4	4,2	12,6	71,1	4,4	12,7
I b	C_6H_5	S	199	$C_{15}H_{11}NS_2$	66,8	4,3	23,6	66,9	4,1	23,8
I c	p-$CH_3OC_6H_4$	O	176	$C_{16}H_{13}NO_2S$	67,7	4,9	11,6	67,9	4,6	11,3
I d	p-$CH_3OC_6H_4$	S	184—185	$C_{16}H_{13}NOS_2$	63,8	4,5	21,2	64,2	4,4	21,4
I e	p-$CH_3C_6H_4$	O	172—173	$C_{16}H_{13}NOS$	71,4	4,8	11,8	71,9	4,9	12,0
I f	p-$CH_3C_6H_4$	S	208	$C_{16}H_{13}NS_2$	67,6	4,7	22,2	67,8	4,6	22,6
I g	p-ClC_6H_4	O	187—188	$C_{15}H_{10}ClNOS$	62,6	3,8	11,5	62,6	3,5	11,1
I h	p-ClC_6H_4	S	195	$C_{15}H_{10}ClNS_2$	59,0	3,2	20,6	59,3	3,3	21.1
I i	m-ClC_6H_4	O	147—148	$C_{15}H_{10}ClNOS$	62,3	3,8	11,3	62,6	3,5	11,1
I j	m-ClC_6H_4	S	199—200	$C_{15}H_{10}ClNS_2$	59,3	3,2	20,6	59,3	3,3	21,1
I k	p-$NO_2C_6H_4$	O	216	$C_{15}H_{10}N_2O_3S$	60,0	3,7	10,5	60,4	3,4	10,7
I l	m-$CH_3C_6H_4$	S	181	$C_{16}H_{13}NS_2$	67,5	4,9	22,9	67,8	4,6	22,6
I m	p-$C_2H_5OCOC_6H_4$	S	187—188	$C_{18}H_{15}NO_2S_2$	63,5	4,6	18,6	63,3	4,4	18,8
I n	p-$CH_3COC_6H_4$	S	201—202	$C_{17}H_{13}NOS_2$	65,1	4,4	20,4	65,6	4,2	20,6
I o	CH_3	S	183—184	$C_{10}H_9NS_2$	57,4	4,5	30,5	57,9	4,4	30,9
I p	n-C_4H_9	S	120	$C_{13}H_{15}NS_2$	62,7	6,2	25,5	62,6	6,1	25,7
I q	$CH_2C_6H_5$	O	144	$C_{16}H_{13}NOS$	72,3	5,0	12,4	71,9	4,9	12,0
I r	$C_6H_5CH_2$	S	181—182	$C_{16}H_{13}NS_2$	67,3	4,8	22,8	67,8	4,6	22,6
III	—	O	163—164	$C_{13}H_{13}NO_2S$	62,7	5.4	12,9	63,1	5,3	13,0
II a	C_6H_5	O	73	$C_{16}H_{13}NOS$	71,7	4,9	11,5	71,9	4,9	12,0
II b	C_6H_5	S	74—75	$C_{16}H_{13}NS_2$	67,6	4,6	22,5	67,8	4,6	22,6
II c	p-$CH_3OC_6H_4$	S	105—106	$C_{17}H_{15}NOS_2$	65,0	4,8	20,1	65,1	4,8	20,5
II d	p-ClC_6H_4	O	105	$C_{16}H_{12}ClNOS$	64,1	3,9	10,5	63,7	4,0	10,6

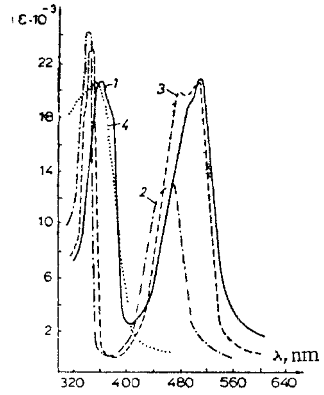


Fig. 1

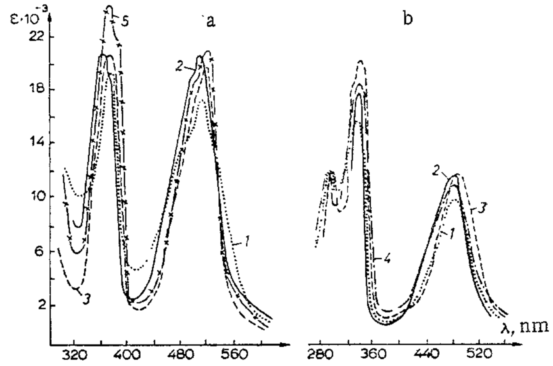


Fig. 2

Fig. 1. Electronic absorption spectra of acetone solutions: 1) 2-(N-phenylaminomethylene)-3(2H)-benzofuranthione (Ia); 2) 2-(N-benzylaminomethylene)-3(2H)-benzofuranthione (Ic); 3) 3-benzofuranthione 2-morpholinomethide (III); 4) 2-formyl-3-methylmercaptobenzofuran anil (IIa).

Fig. 2. Electronic absorption spectra of 2-(N-phenylaminomethylene)-3(2H)-benzofuranthione (a) and 2-(N-n-butylaminomethylene)-3(2H)-benzo[b]thiophenethione (b): 1) in dimethylformamide; 2) in acetone; 3) in benzene; 4) in methanol; 5) in carbon tetrachloride.

Mercapto aldehydes V are rapidly oxidized, and they were therefore subjected to reaction with the appropriate amines immediately after preparation without isolation in pure form.

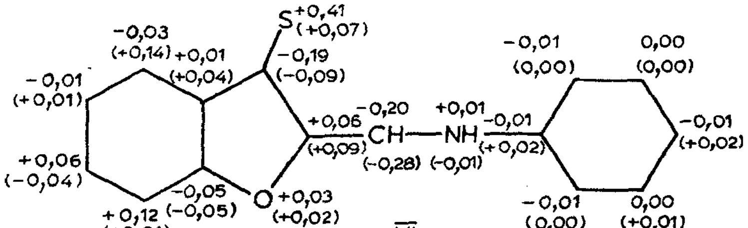
The electronic spectra of all of the compounds of the I type contain a long-wave absorption band at 510–540 nm, which undergoes a hypsochromic shift (30–40 nm) in alkyl- and aralkylimines (Fig. 1 and Table 2). This band is only slightly sensitive to a change in the structure of substituent R and to the effect of a solvent within each heteroaromatic series of anils, although its intensity increases in the spectra of 2-formyl-3-mercaptobenzofuran derivatives as compared with the spectra of the corresponding benzothiophene analogs. The insensitivity of the electronic spectra of compounds of the I type to structural changes (X, R) and to variation of the medium (Fig. 2) attests to stabilization of one of the possible tautomeric forms. It can be identified as a result of a comparison with the absorption spectra of model structures II and III and the results of quantum-mechanical calculations. The experimental electronic spectra of I are close to the spectra of thione–amine structure III (Fig. 1 and Table 2).

TABLE 2. Spectral Characteristics of Azomethines I, II, and III

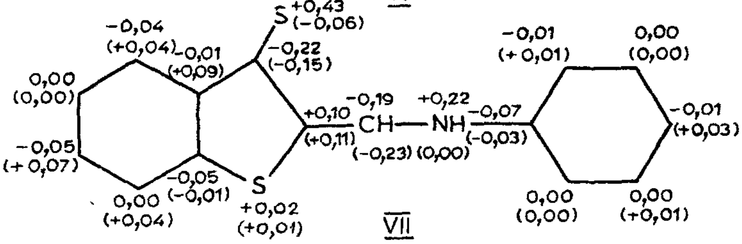
Compound	UV spectra		IR spectra, ν, cm^{-1}	
	solvent	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	mineral oil	perfluorohydrocarbon
Ia	DMF	368 (19,5), 385 (12,8), 510 (17,4)	1590, 1600, 1645	2880, 2950, 3070
	Benzene	368 (21,0), 385 (19,2), 500 (17,3), 522 (19,9)		
	CCl_4	370 (24,5), 385 (21,6), 500 (18,4), 520 (20,3)		
	Acetone	362 (20,8), 378 (18,7), 510 (20,8)		
Ib	DMF	297 (12,8), 365 (12,8), 510 (11,3)	1592, 1632, 1655	2940, 3060
	Benzene	300 (10,2), 375 (19,5), 540 (13,7)		
	Acetone	370 (18,3), 530 (11,5)		
Ic	DMF	375 (14,2), 395 (12,4), 515 (17,2)	1590, 1615, 1650	2870, 2955, 3040
	Benzene	375 (21,2), 390 (19,5), 515 (21,2), 530 (20,4)		
	Acetone	370 (19,0), 385 (17,7), 508 (19,9), 525 (19,6)		
Ie	DMF	370 (18,5), 385 (16,1), 523 (19,7)	1585, 1610, 1650	2870, 2940, 3060
	Benzene	370 (23,1), 387 (20,9), 523 (23,1)		
	Acetone	368 (21,6), 380 (19,3), 515 (23,0)		
If	DMF	300 (12,3), 375 (16,0), 530 (12,8)	1580, 1630	2940, 3040, 3070
	Benzene	302 (11,5), 375 (18,7), 545 (13,4)		
	Acetone	370 (20,7), 532 (14,8)		
Ig	DMF	370 (18,1), 383 (15,8), 520 (19,6)	1580, 1615, 1645	2875, 2955, 3070
	Benzene	370 (22,0), 387 (20,0), 500 (17,6), 525 (20,4)		
	Acetone	370 (22,2), 380 (20,4), 520 (21,7)		
Ih	DMF	297 (10,6), 370 (14,9), 530 (11,3)	1590, 1620, 1640	2950, 3065
	Benzene	300 (11,2), 378 (20,5), 540 (16.5)		
	Acetone	375 (20,1), 540 (13,7)		
Ik	DMF	380 (18,1), 526 (15,1), 558 (18,1)	1600, 1605, 1650	2950, 3045, 3110
	Benzene	386 (16,7), 396 (18,3), 508 (13,7), 535 (17,7)		
	Acetone	390 (21,1), 510 (18,0), 530 (21,1)		
Ip	DMF	297 (11,5), 340 (14,9), 490 (9,0)	1590, 1618, 1650	2965, 3070
	Benzene	300 (11,1), 345 (19,6), 498 (11,2)		
	Acetone	340 (17,5), 485 (10.8)		
	Methanol	292 (11,1), 343 (19,9), 485 (10,2)		
Iq	DMF	338 (18,2), 346 (19,9), 476 (13,7)	1580, 1650, 1640	2950—3000, 3080
	Benzene	300 (18,7), 350 (26,5), 460 (11,5)		
	Acetone	343 (24,9), 450 (12,1), 470 (15.0)		
Ir	DMF	297 (12,6), 343 (19,3), 492 (10,7)	1560, 1600, 1635	2955, 3065
	Benzene	300 (11,9), 350 (22,7), 500 (10,8)		
	Acetone	340 (21,8), 490 (11,5)		
III	DMF	338 (14,8), 347 (17,4), 480 (15,8), 508 (17,2)	1590, 1610, 1640	2890, 2950, 2990, 3050
	Benzene	338 (15,4), 350 (21,7), 490 (16,1), 510 (16,6)		
	Acetone	338 (17.9), 347 (23,2), 480 (19.8), 510 (20,6)		
IIa	Acetone	354 (20,9)	1585, 1620	
IIb	DMF	350 (19,8)	1590, 1615	
	Methanol	348 (18.6)		
	Acetone	350 (15,0)		

The results of a calculation of the energies and intensities of the electron transitions in structures of the IA and IC types are compared with the experimental data in Table 3. It can be seen that only the results of calculation for tautomer IC are in good agreement with the observed electronic absorption spectrum.

The results of redistribution of the π-electron charges on the atoms during electron transitions caused by long-wave ($S_0 \rightarrow S_1$) and short-wave ($S_0 \rightarrow S_2$, the values in parentheses) excitation in molecules of the IC type are shown in the molecular diagrams of VI and VII.



VI



VII

TABLE 3. Calculated and Experimental Characteristics of I and II

Compound*	Calc.	Exptl.
	E, eV (f†)	E, eV(f)
Ia	2,49 (0,20), 3,55 (0,38)	2,44 (0,26) 3,42 (0,34)
Ib	2,50 (0,12), 3,54 (0,48)	2,34 (0,15) 3,36 (0,38)
Iq	2.61 (0,18), 3,80 (0,12)	2,64 (0,28) 3,62 (0,22)
Ip	2,62 (0,11), 3,78 (0,18)	2,56 (0,14) 3,64 (0,11)
IIa	3,62 (0,50)	3,50 (0,81)
IIb	3,46 (0,43)	3,54 (0,25)

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*The numbers correspond to those in Table 1; the spectra were obtained from acetone solutions.

†The oscillator strength.

TABLE 4. Chemical Shifts (δ) of the NH Protons in Compounds of the IB Type in Dimethyl Sulfoxide

X	Y	R	δ, ppm	X	Y	R	δ, ppm
S	O	C_6H_5	10,3	O	O	C_6H_5	10,2
S	S	Alk	14,3	O	S	Alk	12,9*
S	S	C_6H_5	12,3	O	S	C_6H_5	12,1

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*In methylene chloride.

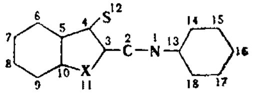
TABLE 5. Differences in the Heats of Atomization of the Quinoid and Benzoid Tautomers of I, with Allowance for the Differences in the Solvation Energies

X	Y	R	$\Delta\Delta H_a$, kcal/mole		
			gas	ε=2,2	ε=48,9
O	O	H	7,4	18,1	21,4
	O	C_6H_5	4,7	16,8	19,9
	S	H	27,7	24,8	21,3
	S	C_6H_5	24,4	21,0	18,4
S	O	H	6,1	17,8	20,9
	O	C_6H_5	3,2	14,7	18,1
	S	H	27,0	24,0	20,8
	S	C_6H_5	24,2	21,3	18,4

Analysis of the magnitude of the increase in the π charges on the atoms makes it possible to draw the following conclusions: 1) the long-wave transitions ($S_0 \rightarrow S_1$) is determined by charge transfer from the sulfur atom to the methylidyne carbon atom; 2) redistribution of the π-electron density from the annelated aromatic system to the methylidyne carbon atom without substantial participation of the electrons of the exocyclic sulfur atom is responsible for the short-wave transition ($S_0 \rightarrow S_2$) (in both cases the π-electron system of the aminophenyl fragment sustains practically no perturbation by the indicated transitions); 3) the absorption at 350 nm for benzoid structure II or IA has the nature of long-wave charge transfer as in the quinoid form ($S_0 \rightarrow S_1$) but is of lower intensity.

The signals characteristic for the splitting of the protons in the > CH–CH–N= group, which corresponds to structure IB, are absent in the PMR spectra of anils I, and this makes it possible to exclude this form from consideration. The PMR spectra of all of the anils confirm structure IC. Thus, there is a signal of an NH proton with J = 13 Hz at weak field (δ > 10 ppm); this is characteristic for the >CH–NH–AB system [10]. Upon deuteration the protons of the methylidine group give a singlet peak (δ ~ 8 ppm). Spectra of this sort are characteristic only for a system of the IC type. In addition to the signals presented above, the PMR spectrum of benzylamino derivative IC contains a doublet at 4.60 ppm from the benzyl group CH_2 protons with J = 4 Hz, which is close to the coupling constant of the benzyl protons of Schiff bases with a thione–enamine structure [11]. After deuteration, the CH_2 protons appear as a singlet. The observed spin–spin coupling constants (SSCC) of (>CH–NH–) and (–NH–CH_2) and their virtual independence on the solution temperature attest to the realization of a single structure – IC – and its high relative stability. One can judge the strength of the intramolecular hydrogen bond in the I molecules from the magnitude of the shift of the NH protons (Table 4). The signal of the NH proton in the spectra of thione compounds (Y = S)

TABLE 6. Distribution of the π Charges in I Molecules in the Ground State



Type	X	Atom No. 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Arylimines																			
IA	O	−0,394	0,314	−0,145	0,118	−0,051	0,025	−0,011	0,028	−0,020	0,032	0,040	0,078	0,118	−0,091	0,040	−0,057	0,020	−0,041
	S	−0,370	0,307	−0,144	0,085	−0,057	0,025	−0,018	0,028	−0,030	0,017	0,110	0,057	0,112	−0,083	0,041	−0,057	0,020	−0,041
IC	O	0,064	0,070	−0,079	0,223	−0,062	0,051	−0,016	0,033	−0,023	0,030	0,028	−0,302	−0,010	−0,006	0,015	−0,016	0,015	−0,022
	S	0,057	0,041	−0,068	0,224	−0,076	0,060	−0,025	0,039	−0,036	0,030	0,070	−0,291	−0,007	−0,011	0,013	−0,013	0,014	−0,021
Alkylimines																			
IA	O	−0,387	0,310	−0,141	0,108	−0,046	0,022	−0,012	0,024	−0,020	0,030	0,041	0,071						
	S	−0,364	0,302	−0,139	0,076	−0,053	0,023	−0,018	0,025	−0,030	0,014	0,110	0,054						
IC	O	0,042	0,074	−0,083	0,227	−0,061	0,051	−0,016	0,033	−0,023	0,030	0,028	−0,302						
	S	0,034	0,046	−0,073	0,225	−0,076	0,060	−0,026	0,038	−0,037	0,030	0,070	−0,293						

is at weaker field by ~2 ppm as compared with the corresponding signal of keto amines (Y = O). This is evidence for the presence of a stronger hydrogen bond in molecules of the first type. The signals of the protons of the amino group are also similarly shifted to weak field when aryl radical R is replaced by alkyl groups; this is a consequence of reinforcement of the intramolecular hydrogen bond in derivatives of aliphatic amines. Replacement of the cyclic heteroatom does not have a substantial effect on the magnitude of the NH shift and, consequently, on the energy of the intramolecular bond.

The thione–amine structure of I is also confirmed by their IR spectra (Table 2), which contain a band at 1630–1650 cm^{-1}, corresponding to the stretching vibrations of a conjugated exocyclic C–C bond, which appears at 1640 cm^{-1} in the spectrum of III. The band at ~1640 cm^{-1} is absent in the spectra of azomethines II (with an imine structure), but the absorption at 1610–1620 cm^{-1} that is characteristic for the C=N bond in azomethines of this type [6] is observed.

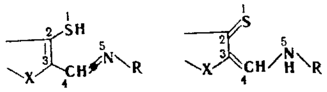
In order to interpret the experimental results that we obtained, we estimated the relative stabilities of tautomers IA and IC and of the corresponding 3-hydroxy compounds [2, 3] (X = O, S; Y = O, S) by means of the Pariser–Parr–Pople (PPP) self-consistent field (SCF) MO method with the Dewar σ,π parametrization [12–14]. The differences in the heats of atomization ($\Delta\Delta H_a$) of the quinoid and benzoid forms, with allowance for the differences in the solvation energies of the indicated tautomers, are presented in Table 5. The calculations in all cases predict the complete preferableness of the ketone- and thione–enamine form IC, regardless of the character of the heteroatom in the ring. The introduction of a phenyl group in place of an alkyl group as a substituent attached to the nitrogen atom does not have a substantial effect on the position of the equilibrium. In all cases, replacement of the noncyclic oxygen atom by a sulfur atom stabilizes the structure of the IC type.

The results of the calculation of the heats of solvation predict that the solvation energy of the quinoid tautomers in the case of the 3-hydroxy derivatives is higher (by 18–21 kcal/mole) than that of the benzoid tautomers in a solvent with a high dielectric permeability. In the case of mercaptoazomethines less polar solvents stabilize the quinoid structure better than highly polar solvents. The data in Table 6 reflect the distribution of the π charges in the ground state of the structures of I, calculated with the Dewar parametrization for the quinoid and benzoid structures. It can be seen that the nature of the heteroring and the amino group has relatively little effect on the charge distribution in each tautomeric form.

A study of the calculated geometrical characteristics of benzoid and quinoid tautomers IA and IC also reveals a similar peculiarity (Table 7). In the case of the benzoid tautomers, the geometry of the mercaptovinyl fragment of the IA molecule is retained, regardless of which ring includes it. The same is valid for the quinoid tautomers with respect to the aminothione fragment of IC. A similar pattern is observed for the 3-hydroxy derivatives of I (Y = O).

All of the results of the calculations presented above confirm the experimental conclusion that compounds of the I type

TABLE 7. Calculated Bond Lengths in the Mercaptovinylimine and Aminothione Fragments of the Tautomers of I (Y = S)



Compound	X	R	Bond length, Å			
			1–2	2–3	3–4	4–5
IA	O	H C_6H_5	1,740 1,737	1,364 1,366	1,452 1,447	1,293 1,302
	S	H C_6H_5	1,748 1,764	1,365 1,366	1,458 1,453	1,289 1,289
IC	O	H C_6H_5	1,598 1,598	1,463 1,464	1,350 1,350	1,411 1,411
	S	H C_6H_5	1,597 1.597	1,467 1,467	1,350 1,350	1,415 1,415

exist primarily in the IC form in both the gas phase and in media with different polarities, regardless of the variations of the structural fragments of the molecules.

EXPERIMENTAL

The absorption spectra in the UV and visible regions were recorded with a Specord UV-vis spectrophotometer. The IR spectra were obtained with a UR-20 spectrometer. The PMR spectra of 15-20% solutions of the compounds were obtained with a Tesla BS-407-C spectrometer (80 MHz) at 25° with hexamethyldisiloxane (HMDS) as the internal standard.

In the calculations of the relative stabilities of the benzoid and quinoid tautomers by means of the PPP method, allowance for the solvation energy was made with a formula that is a development of the well known Born equation for the solvation of an ion:

$$E_{\text{solv}} = -\frac{1}{2}\left(\sum_{\mu} q_{\mu}^{2}\gamma_{\mu\mu} + 2\sum_{\mu<\nu}\sum q_{\mu}q_{\nu}\gamma_{\mu\nu}\right)\left(1-\frac{1}{\varepsilon}\right),$$

where q_μ is the charge on atom μ and ε is the dielectric permeability of the solvent. The details of the calculations by the Dewar method are set forth in greater detail in [16]. The calculations were performed with the program composed by V. A. Kosobutskii.

The electronic absorption spectra and the characteristics of the excited states were calculated by the standard PPP method within the approximation of a variable β constant [17] with allowance for 20 singly excited configurations. The two-electron coulombic integrals ($\gamma_{\mu\nu}$) were calculated from the standard Mataga–Nishimoto formula [18]. We presented the principal parameters used in the calculation of the spectral characteristics in [19, 20].

2-Formyl-3-mercaptobenzo[b]thiophene (V, X = S) and 2-Formyl-3-mercaptobenzofuran (V, X = O). These compounds were obtained from chloro aldehydes IV (X = S [15] and O [3]) in analogy with the method in [7]. A solution of 0.03 mole of sodium hydrosulfide in 2.5 ml of water was added to a cooled solution of 0.01 mole of aldehyde IV in 80 ml of acetone, and the mixture was then heated on a water bath for 2 h. It was then cooled, and the precipitated sodium chloride was removed by filtration. The filtrate was vacuum evaporated, and the residue was diluted with ice water and neutralized carefully with 15% hydrochloric acid. The resulting yellow flakes of aldehyde V were extracted rapidly with ether. The ether extracts were combined, dried with anhydrous Na_2SO_4, and used immediately for the preparation of anils I.

2-Formyl-3-(methylmercapto)benzo[b]thiophene (VIII) and 2-Formyl-3-(methylmercapto)benzofuran (IX). A 1-ml (0.011 mole) sample of dimethyl sulfate was added with stirring to a solution of 0.01 mole of aldehyde V in 20 ml of 5% alkali, whereupon yellow methylation products VI or VII precipitated. The yield was ~60%. Two recrystallizations from alcohol gave yellow crystals. Compound VIII: mp 80-81°; IR spectrum: 1670 cm^{-1} (C=O). Found %: C 58.0; H 4.1; S 30.5. $C_{10}H_8O_2S$. Calculated %: C 57.7; H 3.9; S 30.8. Compound IX: mp 72°; IR spectrum: 1680 cm^{-1} (C=O). Found %: C 62.1; H 4.0; S 16.6. $C_{10}H_8O_2S$. Calculated %: C 62.3; H 4.2; S 16.8.

Imines I and III were obtained by reaction of solutions of the aldehydes in ether with the appropriate amines and recrystallization from ethanol or propyl alcohol. Compounds I were obtained as shiny orange or red-brown substances.

Azomethines II were synthesized by reaction of equimolecular amounts of aldehydes VIII or IX with the appropriate amines in alcohol. Crystallization from alcohol gave light-yellow crystals in 60-70% yields.

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