CONDENSED HETEROCYCLES.

40.* THE STRUCTURE OF 2- AND 3-BENZO[b]THIOPHENALDEHYDES AND THEIR IMINES CONTAINING A HYDROSULFIDE OR HYDROSELENIDE GROUP IN THE ADJACENT POSITION

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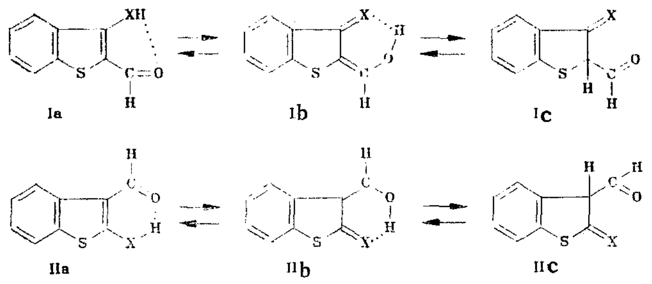
The structure of isomeric selenol(mercapto)aldimines of benzo[b]thiophene and the complexes formed by them was studied by the methods of IR, UV, and ESR spectroscopy and magnetic susceptibility. The influence of the structure of the exocycilic heteroatom on the structure of 2- and 3-benzo[b]thiophenaldehydes containing OH, SH, or SeH groups in the adjacent position, in contrast to their imines, was demonstrated. An analogous change in the nature of the exocyclic heteroatom in complex compounds of selenol(mercapto)aldimines also does not lead to any change in the flat structure of the coordination unit in these complexes.

Earlier [2, 3] we proposed methods for synthesizing 3-selenol-2-benzo[b]thiophenaldehyde (I, X = Se) and 2-selenol-3-benzo[b]thiophenaldehyde (II, X = Se), which, according to the data of the IR and UV spectra, exist primarily in selenone-enol tautomeric form (Ib, IIb). A comparison of these data with the data on the structure of mercapto- and hydroxyaldehydes of the benzo[b]thiophene series permits us to trace the influence of the nature of the exocyclic heteroatom X on the structure of substituted benzo[b]thiophenaldehydes I and II.



I,II X=O, S, Se

Thus, although a selenol-enol form Ib, IIb with a strong intramolecular hydrogen bond is characteristic of isomeric selenol aldehydes I and II (X = Se), mercaptoaldehydes I, II (X = S) are characterized by a thiolaldehyde form Ia, IIa (X = S) with a weak intramolecular hydrogen bond. 3-Hydroxy-2-benzo[b]thiophenaldehyde is characterized by a hydroxyaldehyde tautomeric form Ia (X = O), in contract to its isomer II (X = O), which is characterized by an oxoenol form IIb, but with intermolecular hydrogen bonds.

On the basis of these data it can be concluded that replacement of an oxygen or sulfur atom by a selenium atom in the aldehydes I and II leads to an increase in the fraction of the enol tautomeric form (Ib, IIb) and the strength of the intramolecular hydrogen bond; moreover, the mutual arrangement of the functional groups in the 2- and 3-positions of benzo[b]thiophene has less influence on the structure of I and II than the nature of the heteroatom X. It can also be noted that both aldehydes of benzo[b]thiophene and other five-membered heterocycles are characterized by an S,O-cis-form while the introduction of the XH group into the o-position stabilizes the S,O-trans-configuration of the aldehyde group on account of the formation

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*For communication 39, see [1].

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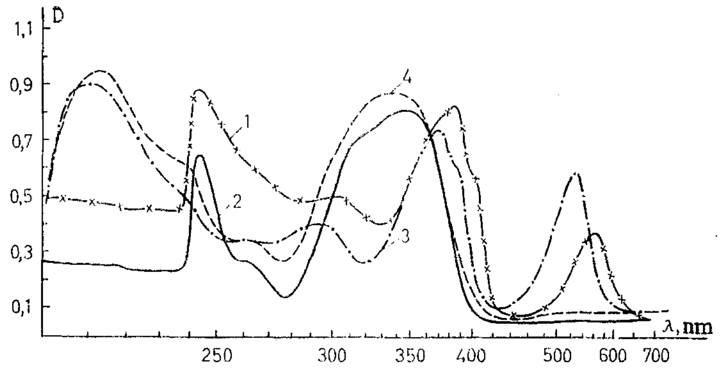
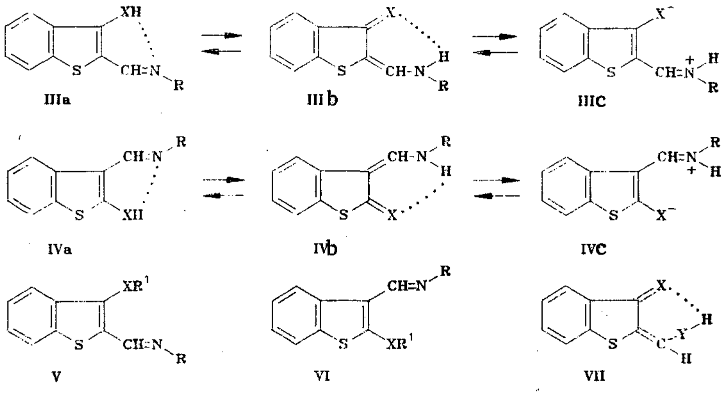


Fig. 1. UV spectra: 1) selenoaldimine (III, X = Se, R — Ph, in $CHCl_3$); 2) Se-methyl derivative (V, X = Se, R = Ph, R^1 = CH_3, in $CHCl_3$); 3) mercaptoaldimine (III, X = S, R = Ph, in ethanol); 4) S-ethyl derivative (V, X = S, R = Ph, R^1 = Et, in ethanol).

of a hydrogen bond and in certain cases a redistribution of the π-electron density in the chelate ring [4].

A series of aldimines (III, IV, X = S, Se) was produced by the interaction of selenol- and mercaptoaldehydes with primary amines or their sodium salts with amine hydrochlorides, in order to determine the influence of the nature of the heteroatom X on their structure.

According to the data of the UV spectra of mercapto(selenol)aldimines III and IV, changes in the temperature (20-60°C) and nature of the solvent (hexane, chloroform, ethanol) actually have no effect on the nature of the spectrum, which is an indication of the stability of one of the theoretically possible tautomeric forms. In a comparison of the UV spectra (see Fig. 1) of S- and Se-alkyl derivatives, for example, V, which are reinforced models of benzoid forms of IIIa, with the spectra of the seleno(mercapto)aldimines III themselves, possessing an analogous substituent at the nitrogen atom, substantial differences were detected — the absence of long-wave maxima at ~500 nm in the spectra of S- and Se-alkyl derivatives V and the presence of a maximum around 340 nm, characteristic of aromatic aldimines. On the basis of this we can conclude that there is no tautomeric form IIIa, both for mercapto- and for selenoaldimines. Analogous data, obtained for selenol(mercapto)aldimines IV, also indicates the absence of the tautomeric form IVa. The presence of a long-wave maximum in the UV spectra of III and IV, judging by the data of [5, 6], is explained by the contribution of the bipolar structure IIIc, IVc to the qunoid form IIIb, IVb.



III—VII X=S, Se; III—VI R=alkyl, aryl R^1=alkyl VII Y=O, N—R

The basis for such a conclusion is the absence of maxima in the visible region in the UV spectra of selenolaldehydes I and II, in contrast to their imines III and IV, although all these compounds have the same chromophore VII, since they exist primarily in the tautomeric form Ib, IIb, and IIIb, IVb. In addition, we might note that the position of the long-wave maximum depends on the nature of the heteroatom X, and as we go from X = S to X = Se a bathochromic shift of ~30 nm is observed.

TABLE 1. IR Spectra of Selenol(mercapto)aldimines (III, IV) and Their S,Se-Alkyl Derivatives (V, VI)

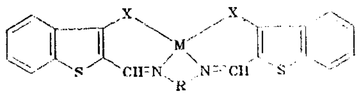
Compound	R[R']	Frequencies of the main bands, cm^{-1}				
III (X=S)	C_6H_5	1645 s.br. 1625 sh.	1600 sh.	1585 s.	1325 s.br.	1315 s.br.
	$p\text{-}CH_3OC_6H_4$	1640 s.br.	1590 s.	1605 sh.	1335 s.br.	1310 s.
	$p\text{-}NO_2C_6H_4$	1630 s.br.	1605 s.br.	1595, 1585	1340 s.br.	1330, 1310
	$\beta\text{-}C_{10}H_7$	1640 s.br. 1620 sh.	1590 m.	1580 sh.	1325 s.br.	1315 s.br.
	$-(CH_2)_2-$	1620 s.br.	1590 m.		1340 s.br.	1300 s.br.
V (X=S)	C_6H_5 $[C_2H_5]$	1620 s.	1585 s.br.	1485 s.	1370 w.	1315 w.
III (X=Se)	C_6H_5	1640 s.br.	1585 s.		1330 s.br.	1315 s.br.
	$-(CH_2)_2-$	1615 s.s.	1585 m.		1340 s.br.	1300 m.
V (X=Se)	C_6H_5 $[CH_3]$	1610 s.	1585 s.	1480 s.		
IV (X=S)	C_6H_5	1640 s.br.	1585 m.	1600 sh.	1325 s.br.	1305 s.
	$p\text{-}CH_3C_6H_4$	1640 s.br.	1585 m.		1325 s.br.	1305 s.
	$\beta\text{-}C_{10}H_7$	1645 s.br. 1625 sh.	1595 w.	1580 sh. 1560 sh.	1325 s.br.	1305 s.
VI (X=S)	$-(CH_2)_2-$ $[C_2H_5]$	1625 s.	1485 w.	1420 s.	1370 m.	1320 sh.
IV (X=Se)	C_6H_5	1640 s.br.	1595 m.	1585 sh.	1330 s.br.	1310 s.
	$p\text{-}CH_3C_6H_4$	1640 s.br. 1610 sh.	1585 s.		1330 s.br.	1310 s.
	$\beta\text{-}C_{10}H_7$	1642 s.br. 1625 sh. 1617 sh.	1595 w.	1580 w.	1340 s.br.	1305 s.
	$-(CH_2)_2-$	1630 s.br.	1590 w.	1560 w.	1340 s.br.	1315 m.

The assignment of the bands in the IR spectra of selenol(mercapto)aldimines is a rather difficult task. The frequencies of the stretching vibrations of the exocyclic C=C bond in form IIIb, IVb, and the C=N bond for form IIIa, IVa are situated rather close together in the region of 1600 cm^{-1}, while the contribution of the bipolar structure may lead to a shift of these frequencies by 30-50 cm^{-1}, for example, for the C=N bond 1610 cm^{-1}, and for $C=N^+$ 1660 cm^{-1} [7, 8]. The absorption band in the region of 1640 cm^{-1} (see Table 1) can be assigned either to the vibrations of the exocyclic C=C bond in form IIIb, IVb [8], or to the stretching vibrations of the $C=N^+$ bond in the bipolar structure IIIc, IVc [7]. In the IR spectra of selenolaldehydes, which are characterized by the selenone-enol form Ib, IIb and the presence of an exocyclic C=C bond, there is no band in the region of 1640 cm^{-1}, while the presence of this bond in the spectra of their imines with the analogous chromophore VII indicates a contribution of the bipolar structure IIIc, IVc to the tautomeric form IIIb, IVb.

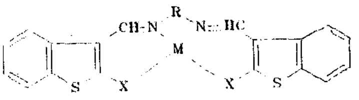
On the basis of these data, this band can be assigned to the stretching vibrations of the $C=N^+$ bond and not to the exocyclic C=C bond. Replacement of the sulfur atom by selenium has practically no effect on the frequency of this band (±5 cm^{-1}), nor does a change in the position of the functional groups in benzo[b]thiophene (compounds III or IV). The nature of the substituent at the nitrogen atom has a more substantial influence (±20 cm^{-1}). We should mention still another strong band, which is split in the form of a doublet, in the region of 1305-1330 cm^{-1}, characteristic of all the selenol(mercapto)aldimines, the frequency of which depends little on the nature of the heteroatom X and the nature of the substituent R at the nitrogen atom. Moreover, this band is absent both in the spectra of S,Se-alkyl derivatives V, VI and in the spectra of a number of other 2,3-substituted benzo[b]thiophenes.

Consequently, the nature of the heteroatom X has a substantial effect on the structure of the aldehydes I and II, while analogous replacement of the sulfur atom by selenium does not lead to such a change in the structure of their imines III and IV.

By the reaction of selenol(mercapto)aldimines with transition metal acetates we obtained a series of complex compounds VIII, IX, some of which we discussed earlier [2, 3].



VIII



IX

VIII, IX X=S, Se; M=Ni, Cu, Zn, Cd R=$-(CH_2)_2-$; o-phenylene

TABLE 2. Magnetic Properties of Complex Compounds (M = Cu, R = —$(CH_2)_2$—)

IX, X=Se			VIII, X=Se			VIII, X=S		
T, K	$\chi \cdot 10^6$	μ_{eff} M_B	T, K	$\chi \cdot 10^6$	μ_{eff} M_B	T, K	$\chi \cdot 10^6$	μ_{eff} M_B
297,5	1319	1,80	295,5	1432	1,84	295,9	1534	1,89
246,5	1699	1,83	238,3	1750	1,83	253,5	1779	1,90
221,3	1818	1,80	230,8	1796	1,82	216,0	2060	1,89
204,3	1988	1,80	203,0	2062	1,83	204,5	2121	1,87
182,3	2204	1,80	163,9	2510	1,82	184,8	2337	1,86
165,3	2494	1,81	137,0	2913	1,79	157,7	2737	1,82
130,5	2999	1,79	99,0	3900	1,77	85,5	4902	1,84
85,5	4684	1,80	81,5	4798	1,77			

The ESR spectra of complexes of divalent copper VIII, IX indicate the appearance of a chelate ring, namely, the formation of a Cu—N bond. Thus, four lines characteristic of complexes of divalent copper were recorded in the spectra; their presence was due to interaction of the spin of the unpaired electron of copper with the ^{63}Cu and ^{65}Cu nuclei ($J = {}^3/{}_2$), while the formation of a supplementary hyperfine structure was due to interaction of the unpaired electron of copper with two equivalent ^{14}N nuclei, which is also an indication of coordination of the copper atom with nitrogen atoms.

The data of IR spectra confirm the formation of complex compounds, namely, the presence of coordination of metal atoms with selenium (sulfur) and nitrogen atoms and the formation of a coordination unit MN_2S_2 and MN_2Se_2. Thus, in the IR spectra of complexes of copper and nickel VIII, a series of bands associated with the formation of the M—Se bond, 365, 340, 302, 280, 235, 225 cm^{-1} (M = Cu) and 380, 350, 330, 285, 230 cm^{-1} (M = Ni), as well as a number of bands that can be attributed to the formation of an M—N bond, 585, 565, 515, 440 cm^{-1} (M = Cu) and 605, 560, 513, 435 cm^{-1} (M = Ni), are observed: Moreover, all the bands enumerated above are absent in the spectrum of the initial ligand. The formation of complexes is also indicated by a shift of the band from ~1640 to ~1600 cm^{-1}, the appearance of a band in the region of 1475 cm^{-1}, and the appearance of the broad band 1340 cm^{-1}, characteristic of their ligands.

Analogous differences were detected in a comparison of the IR spectra of the isomeric ligand with the spectra of its complexes IX (X = Se). In the IR spectra of complexes containing sulfur atoms (VIII, IX, X = Se), new bands appear at 620, 585, 550, 380, 295, 255, 210 cm^{-1}, due to the formation of bonds, for example: Cd—N and Cd—S; the same changes occur in the region of 1650-1300 cm^{-1}.

Investigation of the complexes (XIII, IX, X = Se; IX, X = S; M = Cu, Ni) by the method of static magnetic susceptibility showed that the magnetic susceptibility of copper complexes obeys the Curie—Weiss law ($\chi = C/T + \Theta$)'. The weak temperature dependence of the magnetic moment μ_{eff} (see Table 2) is evidence of the absence of spin—spin exchange and a small influence of spin—orbit interaction. Consequently, the data on the magnetic susceptibility of the investigated copper complexes indicate a flat structure of their coordination unit, which is also confirmed by the diamagnetism of the analogous nickel complexes.

A comparison of the data on the structure of the complexes with the coordination units MSe_2N_2 and MS_2N_2 with the results obtained earlier for structurally analogous copper and nickel hydroxyaldiminates based on benzo[b]thiophene permits us to conclude that the replacement of the donor oxygen atoms by sulfur or selenium atoms does not lead to any change in the flat structure of the coordination unit in these complexes.

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer 577 spectrometer, pressings with CsI, UV spectra on a Specord UV-vis spectrophotometer (hexane, chloroform, ethanol). The ESR spectra were recorded on an RE-1306 radiospectrometer, working frequency 9.46 GHz. The magnetic susceptibility was measured on a modernized Faraday balance, with a standard $HgCo(NCS)_4$.

Selenol(mercapto)aldimines III, and IV, their alkyl derivatives V and VI, and the complex compounds VIII and IX were produced by the methods of [2, 3]. The data of elementary analysis and the melting points of the selenol(mercapto)aldimines synthesized for the first time are

TABLE 3. Characteristics of Selenol(mercapto)aldimines IV (X = Se) and III, IV (X = S)

Compound	R	mp, ℃	Found, %				Empirical formula	Calculated, %			
			C	H	N	S(Se)		C	H	N	S(Se)
III (X=S)	C_6H_4	175—177	66,7	4,0	5,4	23,9	$C_{15}H_{11}NS_2$	66,9	4,1	5,2	23,8
	p-$NO_2C_6H_4$	199—203 (dec.)	57,1	3,3	8,7	20,6	$C_{15}H_{10}N_2O_2S_2$	57,3	3,2	8,9	20,4
	m-$NO_2C_6H_4$	187—189 (dec.)	57,0	3,4	9,0	20,5	$C_{15}H_{10}N_2O_2S_2$	57,3	3,2	8,9	20,4
	o-C_6H_4	171—173	62,3	3,6	6,0	28,1	$C_{24}H_{16}N_2S_4$	62,6	3,5	6,1	27,8
	$—(CH_2)_2—$	194—196 (dec.)	58,0	3,8	6,9	31,4	$C_{20}H_{16}N_2S_4$	58,3	3,9	6,8	31,1
IV (X=S)	C_6H_4	150—152	67,1	4,0	5,1	23,8	$C_{15}H_{11}NS_2$	66,9	4,1	5,2	23,8
	p-$CH_3C_6H_4$	221—222	67,6	4,3	5,2	22,9	$C_{16}H_{13}NS_2$	67,8	4,6	5,0	22,6
	o-HOC_6H_4	159—160	63,0	3,8	4,7	22,8	$C_{15}H_{11}NOS_2$	63,2	3,9	4,9	22,5
IV (X=Se)	C_6H_4	149—151	56,8	3,6	4,3	9,9 (25,3)	$C_{15}H_{11}NSSe$	57,0	3,5	4,4	10,1 (25,0)
	p-$CH_3C_6H_4$	189—192	57,8	3,4	4,5	9,9 (24,1)	$C_{16}H_{13}NSSe$	58,2	3,9	4,2	9,7 (23,9)
	o-$CH_3C_6H_4$	176—179	58,0	3,6	4,4	9,8 (23,8)	$C_{16}H_{13}NSSe$	58,2	3,9	4,2	9,7 (23,9)

cited in Table 3. The characteristics of the remaining selenol(mercapto)aldimines, the structure of which is under discussion, are cited in [2, 3].

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