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CONDENSED HETEROCYCLES.

45.* SYNTHESIS AND STRUCTURES OF IMINES OF 2-SELENOLO-3-BENZO[b]FURANALDEHYDE AND 3-SELENOLO-2-BENZO[b]FURANALDEHYDE AND THEIR DERIVATIVES

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A number of new selenolaldimines of benzo[b]furan were synthesized. It was established that they exist in dipolar form with delocalized multiple bonds.

In a previous paper we described the synthesis of imines of 2-mercapto-3-benzo[b]furanaldehyde and 3-mercapto-2-benzo[b]furanaldehyde [1]. It was shown that a thione—enamine tautomeric form with the contribution of a dipolar structure, as in the case of their benzo[b]thiophene analogs [2], was characteristic for them. In order to study the effect of the nature of the exocyclic heteroatom on the structures and properties of aldimines of this type we synthesized a number of isomeric selenolaldimines of benzo[b]furan.

Thus the reaction of 2-bromo-3-benzo[b]furanaldehyde (I) [3] or 3-chloro-2-benzo[b]furanaldehyde (II) [4] with sodium hydroselenide and the subsequent action of salts of primary amines lead to the formation of 2-selenolo-3-benzo[b]furylideneamines III and 3-selenolo-2-benzo[b]furylideneamines IV in high yields (Table 1).

Like their sulfur analogs, selenolaldimines III are stable readily crystallized substances, in contrast to selenolaldimines IV, which are unstable in solutions and therefore cannot be purified by recrystallization and were characterized analytically. We established

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*See [1] for communication 44.

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TABLE 1. Selenolaldimines III,* Diselenides V, and Methylselenolaldimine VI

Compound	mp,† °C	Found, % C	Found, % H	Found, % N	Found, % Se	Empirical formula	Calc., % C	Calc., % H	Calc., % N	Calc., % Se	Yield, %
IIIa	187—192	60,7	4,3	5,0	26,6	$C_{15}H_{11}NOSe$	60,0	3,7	4,7	26,3	70
IIIb	196—200	60,8	4,2	4,7	25,6	$C_{16}H_{13}NOSe$	61,1	4,2	4,5	25,1	78
IIIc	176—180	60,0	4,4	4,2	22,8	$C_{16}H_{13}NO_2Se$	58,2	4,0	4,2	23,9	79
IIId	190—194	61,4	4,4	4,5	24,7	$C_{16}H_{13}NOSe$	61,1	4,2	4,5	25,1	62
IIIe	169—172	62,1	3,7	4,2	23,2	$C_{17}H_{13}NO_2Se$	62,6	4,0	4,3	24,2	71
IIIf	148—151	49,8	4,4	4,4	26,2	$C_{13}H_{13}NO_3Se$	50,3	4,2	4,6	25,5	25
Va	151—155	60,9	4,8	4,8	26,1	$C_{30}H_{20}N_2O_2Se_2$	60,2	3,4	4,7	26,4	31
Vb	166—171,5	59,9	3,7	4,6	24,8	$C_{32}H_{24}N_2O_2Se_2$	61,3	3,9	4,5	25,2	60
Vc	169—172,5	57,4	3,7	4,4	23,7	$C_{32}H_{24}N_2O_4Se_2$	58,4	3,7	4,2	24,0	50
Vd	128—131	60,5	3,8	4,6	24,9	$C_{32}H_{24}N_2O_2Se_2$	61,3	3,9	4,5	25,2	70‡
VI	70,5—71,5	61,5	4,3	4,6	24,9	$C_{16}H_{13}NOSe$	61,1	4,2	4,5	25,1	78

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*Selenolaldimines IVa-f were obtained in 84, 91, 66, 79, 86, and 81% yields, respectively, and decomposed when heated at 80-120°C.

†Solvents: benzene for IIIa-d, $CHCl_3$ for IIIe and Vc, CCl_4 for IIIf and Vb, methanol for Va, d, and ether for VI.

‡The unrecrystallized stubstance.

TABLE 2. Spectral Characteristics of Selenolaldimines III and IV, Diselenides V, and Methylselenoaldimine VI

Compound	IR spectrum (KBr),* cm⁻¹	UV spectrum,† λ_{max}, nm (log ε)	PMR spectrum, ($CDCl_3$)‡ δ, ppm, TMS: NH, br d	=CH, d (J, Hz)	H_{arom}, m	CH_3, s
IIIa	1644	478 (4,30), 333 (3,96), 297 (4,56), 263 (4,37)	14,14	8,71 (13,8)	7,53—7,17	—
IIIb	1648	484 (4,37), 337 (3,97), 299 (4,70), 266 (4,36)	14,15	8,67 (13,6)	7,48—7,16	2,38
IIIc	1651	478 (4,40), 340 (4,10), 299 (4,70), 270 (4,39)	14,18	8,59 (13,7)	7,47—6,93	3,85
IIId	1641	479 (4,24), 337 (3,88), 297 (4,62), 264 (4,46)	13,74	8,76 (13,4)	7,54—7,19	2,57
IIIe	1640	435 (3,95), 293 (4,11), 266 (sh.) (3,90), 245 (4,02)	12,52 (br.s)	8,30 (13,6)	8,02—7,10	—
IIIf	1642	435 (4,10), 292 (4,55), 266 (4,24), 217 (4,36)	12,31 (br.s)	8,26 (13,6)	7,33—7,08	1,34 t
IVa	1641	548 (—), 385 (—), 312 (—)	15,05	8,53 (13,0)	8,03—7,60	—
IVb	1649	548 (—), 386 (—), 311 (—)	15,08	8,45 (13,0)	7,96—6,58	2,38
IVc	1643	550 (—), 392 (—), 313 (—)	15,20	8,40 (13,4)	8,03—6,72	3,83
IVd	1634	543 (—), 387 (—), 303 (—)	14,47	8,61 (12,8)	8,03—7,18	2,55
IVe	1632	510 (—), 360 (—), 249 (—)	—	—	—	—
IVf	1640	508 (—), 361 (—), 288 (—)	—	—	—	—
Va	1614	349 (sh.) (4,55), 318 (4,60), 239 (sh.) (4,42)	—	8,00, s	7,72—6,82	—
Vb	1616	363 (4,49), 316 (4,55), 244 (4,33)	—	8,01, s	7,66—6,73	3,35
Vc	1612	382 (4,47), 315 (4,47), 250 (sh.) (4,29)	—	8,01, s	7,70—6,76	3,83
Vd	1612	360 (sh.) (4,29), 310 (4,47), 250 (sh.) (4,30) (in CH_2Cl_2)	—	7,84, s	7,73—6,23	2,38
VI	1623	342 (4,28)	—	8,70, s	7,72—7,00	2,18

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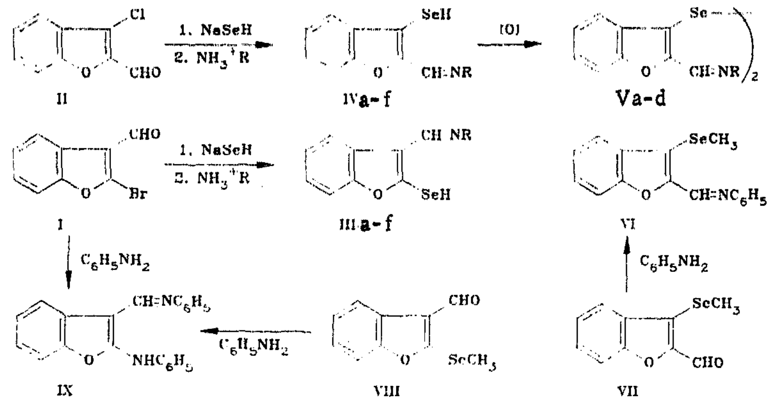
*These are $\nu_{C=N^+}$ bands for III and IV and $\nu_{C=N}$ bands for V and VI.

†The UV spectra were obtained in ethanol (III, V, and VI) and in $CHCl_3$ (IV).

‡A signal at 5.07 ppm (2H, d CH_2) is present in the PMR spectrum of IIIe, and signals at 4.39-4.23 ppm (4H, m, $2CH_2$) are present in the PMR spectrum of IIIf.

that the products of transformation of aldimines IV when they are dissolved in organic solvents are bis(2-benzo[b]furylideneamino) 3,3'-diselenides V* (Table 1).

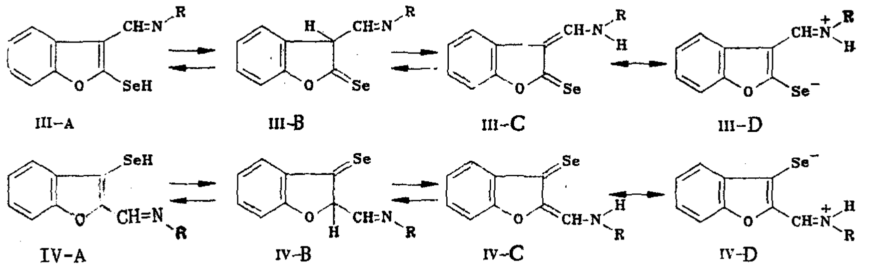


a R=C_6H_5, b R=p-$C_6H_4CH_3$, c R=p-$C_6H_4OCH_3$, d R=o-$C_6H_4CH_3$, e R=$CH_2COC_6H_5$, f R=$CH_2CO_2C_2H_5$

Signals of protons at 7.8-8.0 ppm, which are characteristic for the protons of an azomethine group, are present in the PMR spectra of diselenides V, and the IR spectra contain absorption bands of a C=N group at 1610-1620 cm^{-1}; the UV spectra of the diselenides are similar to the spectrum of 3-methylseleno-2-benzo[b]furylidenephenylamine (VI) (Table 2) obtained by the reaction of 3-methylseleno-2-benzo[b]furanaldehyde (VII) [5] with analine.

It should be noted that the reaction of 2-methylseleno-3-benzo[b]furanaldehyde (VIII) (an isomer of aldehyde VII) [5] with aniline does not lead to 2-methylseleno-3-benzo[b]furylidenephenylamine (an isomer of imine VI). The reaction product is 2-phenylamino-3-benzo[b]furylidenephenylamine (IX), which is also formed by the action of aniline on 2-methylmercapto-3-benzo[b]furanaldehyde [1] or on bromo aldehyde I.

In order to establish the structures of the isomeric selenolaldimines III and IV, which may exist in various tautomeric forms, such as A, B, or C (the latter can be depicted by boundary structure D) or an equilibrium mixture of them, we analyzed their PMR, UV, and IR spectra.



Signals of two protons at 12.3-15.2 ppm in the form of a broad doublet and at 8.2-8.7 ppm in the form of a resolved doublet with spin-spin coupling constant (SSCC) J = 13-14 Hz are present in the PMR spectra of selenolaldimines III and IV (Table 2) at weak field. This character of the spectra may correspond to tautomeric form C or its boundary structure D, and the indicated signals are related to the protons of the NH and CH groups, respectively. However, it is difficult to give preference to any of the structures, viz., C or D, on the basis of the PMR spectra. To solve this problem we used UV spectroscopy.

A keto(thione)-enamine tautomeric form of the C type has usually been ascribed to o-hydroxy(mercapto)aldimines [4, 6], whereas a dipolar structure of the D type has been proposed in the benzene and naphthalene series [7]. This was done on the basis of the similarity between the UV spectra of the aldimines and the spectra of compounds that model one or another tautomeric form. However, this method makes it possible only to reveal the similarity or difference between the aldimines and the model compounds and does not always make it possible to establish the structure of a molecule.

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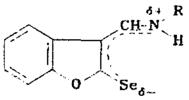
*We were unable to isolate the products of transformation of aldimines IVe and IVf.

An intense long-wave band, the position of which is virtually independent of the temperature and polarity of the solvent but changes as a function of the relative orientation of the selenolo and azomethine groups relative to the ring oxygen atom and the character of the radical attached to the nitrogen atom (Table 2), is present in the UV spectra of selenolaldimines III and IV. An increase in the pH of the medium leads to an ~100 nm hypsochromic shift of this band; the original character of the spectrum is restored when the solution is acidified, and this indicates the existence of an acid–base equilibrium.

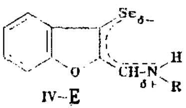
These changes in the UV spectra are in good agreement with dipolar structure D, in which, upon the absorption of light, an electron migrates from the electron-donor Se^- ion to the electron-acceptor $C{=}N^+$ group. Thus an increase in the pH of the medium, which leads to detachment of a proton from the nitrogen atom, decreases the electron-acceptor capacity of the azomethine group in structure D, which should lead [7] and does lead to a short-wave shift of the absorption bands in the UV spectra of aldimines III and IV. Quantum-chemical calculations [6], which predict migration of an electron to the azomethine group in 3-mercapto-2-benzo[b]-furylidene(thenylidene)amines, also constitute evidence in favor of structure D, which also makes it possible to explain other changes in the UV spectra of aldimines III and IV. For example, the bathochromic shift of the bands in the spectra of imines IV as compared with the position of the bands in the spectra of III is due to the closer orientation of the electron-donor ring oxygen atom to the $C{=}N^+$ group in imines IV (in analogy with Woodward's rule for α,β-substituted, α,β-unsaturated carbonyl compounds [8]). The observed hypsochromic shift of the bands on passing from arylimines IIIa-d and IVa-d to alkylimines IIIe, f, and IVe, f is associated with a decrease in the length of the conjugated system in the latter, and the analogous shift of the bands in the UV spectra of the previously synthesized mercaptoaldimines [1] is associated with the lower polarizability and the greater ionization potential of the sulfur atom as compared with the selenium atom [9, 10].

It is difficult to explain the changes in the UV spectra of the aldimines when alkali is added starting from selenone enamine form C, in which, upon light absorption, an electron should migrate from the electron-donor amino group to the electron-acceptor selenone group, since in this case, first of all, the occurrence of any acid–base reaction leading ultimately to a hypsochromic shift of the bands in the spectra of imines III and IV is hardly possible (as a consequence of the low probability of detachment of a proton from the nitrogen atom) and, second, even if detachment of a proton from the nitrogen atom were to occur, a bathochromic shift of the bands, which contradicts the experimental results, would be observed in the UV spectra of selenolaldimines III and IV as a consequence of an increase in the electron-donor capacity of the amino group ($-N^--R$).

Thus, on the basis of the data from the PMR and UV spectra it may be concluded that the structures of selenolaldimines III and IV are described by dipolar structure D, which, with allowance for delocalization of the electrons, can be represented in the form of mesomeric structure E.



III-E



IV-E

A band at 1632-1651 cm^- , which can be ascribed to stretching vibrations of the $C{=}N^+$ bond [2], is present in the IR spectra of imines III and IV; this is in agreement with structures III-E and IV-E. In addition, bands at 1691, 1753, 1690, and 1729 cm^{-1}, respectively, which are due to stretching vibrations of the carbonyl groups of benzolymethyl and carbethoxymethyl residues, also appear in the IR spectra of imines IIIe-f and IVe-f. The other bands in the IR spectra of III and IV do not contradict the data on their structures.

EXPERIMENTAL

The IR spectra of the compounds (KBr pellets) were recorded with a UR-20 spectrometer. The UV spectra were obtained with a Specord UV-vis spectrophotometer. The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with Bruker WM-250 (250 MHz) and Tesla BS-467 (60 MHz) spectrometers with tetramethylsilane (TMS) as the internal standard. The course of the reactions and the individuality of the compounds were monitored by means of thin-layer chromatography (TLC) on Silufol UV-254 plates in $CHCl_3$ or in a $CHCl_3$–hexane system (1:1). The physicochemical characteristics of the synthesized compounds are presented in Tables 1 and 2.

2-Selenolo-3-benzo[b]furylideneamines (IIIa-f) and 3-Selenolo-2-benzo[b]furylideneamines (IVa-f). A solution of 5.5 mmole of aldehyde I or II in 20 ml of methanol was added in an argon atmosphere to a hot solution of 0.66 g (6.4 mmole) of NaSeH in 20 ml of anhydrous ethanol, after which the mixture was refluxed for 20 min and then treated with 30 ml of water. The mixture was cooled to 5°C, and a threefold excess of the salt of the appropriate amine (in the preparation of imines IIIa-d and IVa-d), 0.94 g (5.5 mmole) of α-aminoacetophenone hydrochloride (in the case of imines IIIe and IVe), or 0.77 g (5.5 mmole) of glycine ethyl ester hydrochloride (in the case of IIIf and IVf) in 30 ml of water was added. The mixture was stirred for 30 min, after which it was diluted with 100 ml of water, and the resulting precipitate was separated and dried over P_2O_5. Aldimines IIIa-f were recrystallized.

Bis(2-benzo[b]furylidenephenylamino) 3,3-Diselenide (Va). A 0.45 g (1.5 mmole) sample of aldimine IVa was added to 100 ml of methanol, and the mixture was allowed to stand for 3 h. It was then heated and filtered, and the filtrate was allowed to stand at –15°C for 5 days. The resulting precipitate was separated.

Bis[2-benzo[b]furylidene(p-methylphenyl)amino] Diselenide (Vb). A 0.47 g (1.5 mmole) sample of aldimine IVb was added to 50 ml of CCl_4, and the mixture was allowed to stand for 3 h. It was then heated and filtered, and the filtrate was evaporated to 20 ml. The concentrate was cooled, and the resulting precipitate was separated.

Bis[2-benzo[b]furylidene(p-methoxyphenyl)amino] 3,3'-Diselenide (Vc). This compound was similarly obtained (as in the case of Vb) from 0.50 g (1.5 mmole) of imine IVc in $CHCl_3$.

Bis[2-benzo[b]furylidene(o-methylphenyl)amino] 3,3'-Diselenide (Vd). A 0.47 g (1.5 mmole) sample of imine IVd was added to 50 ml of methanol, after which the mixture was allowed to stand for 3 h. It was then cooled, and the resulting precipitate was separated.

3-Methylseleno-2-benzo[b]furylidenephenylamine (VI). A 0.46 ml (4.9 mmole) sample of aniline was added to a solution of 0.82 g (3.4 mmole) of aldehyde VII in 50 ml of benzene, and the mixture was refluxed for 2 h with a Dean–Stark adapter. It was then cooled, washed with water, and dried with $MgSO_4$. The benzene was evaporated, and the residue was recrystallized twice from ether.

2-Phenylamino-3-benzo[b]furylidenephenylamine (IX). A 0.9 ml (9.7 mmole) sample of aniline was added to a solution of 1.59 g (6.7 mmole) of aldehyde VIII in 50 ml of benzene, and the mixture was refluxed for 2 h with a Dean–Stark adapter. It was then evaporated, and the residue was refluxed with 40 ml of ethanol. The mixture was cooled, and the resulting precipitate was separated and recrystallized from propanol to give 0.91 g (43%) of amine IX. A 0.21 g (30%) sample of amine IX, with mp 160-163°C, was obtained when a mixture of 0.50 g (2.2 mmole) of bromo aldehyde I and 0.42 ml (4.4 mmole) aniline in 40 ml of ethanol was refluxed for 40 min with subsequent similar workup of the reaction mixture. The results of elementary analysis, the melting point, and the spectral characteristics of amine IX were identical to the data in [1].

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