

SYNTHESIS AND STRUCTURE OF 2-FORMYL-3-HYDROXYBENZO[b]-SELENOPHENE ANILS*

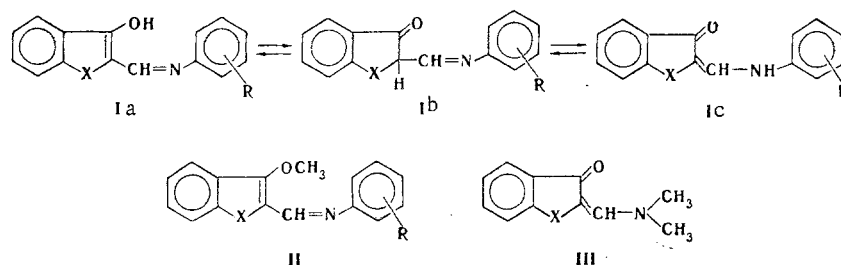
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A number of 2-formyl-3-hydroxybenzo[b]selenophene anils and their derivatives, which model the individual tautomeric forms, were synthesized. A ketone-amine structure was assigned to the anils as a result of physicochemical investigation.

We have previously shown that 2-formyl-3-hydroxybenzo[b]furan and 2-formyl-3-hydroxybenzo[b]thiophene anils (I, X = O, S) have ketone-amine structure Ic in solution, i.e., the possible Ia \rightleftharpoons Ic equilibrium is shifted practically completely to the right [2, 3].

It seemed of interest to study whether the introduction into I of a heteroatom less electronegative than oxygen and sulfur (X = Se) would affect the position of this benzoid-quinoid equilibrium. With this end in mind, we synthesized 2-formyl-3-hydroxy[b]selenophene anils I (X = Se) and also their derivatives II and III, which model the individual tautomeric forms.



I a-c R = H, *p*-Cl, *m*-Cl, *p*-OCH₃, *p*-COCH₃; II R = H, *p*-Cl

In order to determine the character of the Ia \rightleftharpoons Ic tautomeric equilibrium we recorded the electronic, vibrational, and PMR spectra of I-III.

The intensities and positions of the absorption bands in the electronic spectra of I remain practically unchanged as the polarity of the solvent changes and as substituent R in the phenyl ring is varied. This constitutes evidence that I (X = Se) exist in solution as one of three possible tautomeric forms.

The similarity in the spectra of I and III and their clear difference from the spectra of II (Fig. 1) indicate the preferableness of quinoid form Ic (X = Se).

The PMR spectra prove the existence of anils I in form Ic. Two distinct doublets of CH and NH protons with a spin-spin coupling constant of 13 Hz, which coincides in magnitude with the analogous constant observed in the spectra of the quinoid tautomers of the mercapto- and hydroxyaldimines of benzo[b]furan and benzo[b]thiophene [2, 3], are observed in the PMR

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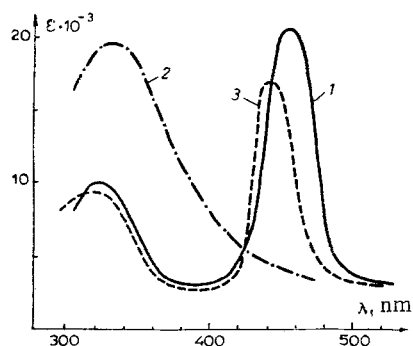


Fig. 1. Electronic absorption spectra in ethanol: 1) 2-formyl-hydroxybenzo[b]selenophene anil (I, R = H); 2) 2-formyl-3-methoxybenzo[b]selenophene anil (II, R = H); 3) 2-(N,N-dimethylaminomethylene)-3(2H)-benzoselenophenone.

spectrum, and this indicates practically complete shifting of the tautomeric equilibrium to favor form Ic. The chemical shift of the signals of the NH protons of I in dimethyl sulfoxide (DMSO) solutions ($\delta \sim 10$ ppm) remains practically unchanged as heteroatom X is varied, whereas the signal of the CH protons of the benzoselenophene derivatives is shifted to weak field as compared with benzofuran and benzothiophene anils [2, 3]. This is probably due to the large anisotropic contribution of selenium as compared with sulfur and oxygen.

The IR spectroscopic data (Table 1) confirm the ketone-amine structure of the 2-formyl-3-hydroxybenzo[b]selenophene anils.

The vibrational spectra of azomethines I (X = Se) contain the strong absorption band of a ring carbonyl group at ~ 1600 cm^{-1} ; this band is observed at 1650 cm^{-1} in the spectrum of III. However, a band at 1590 – 1600 cm^{-1} ($\nu_{\text{C=N}}$) [2, 3] is observed in the spectra of azomethines II.

The decrease in the frequency of the absorption of the C=N bond to 1590 – 1600 cm^{-1} is apparently due to the effect of the selenium atom.

Thus, regardless of replacement of heteroatom X in the five-membered ring, a change in the polarity of the solvent, and the structural variations, azomethines I exist in the form of ketone-amine structure Ic.

EXPERIMENTAL METHOD

The UV spectra were recorded with a Specord UV-Vis spectrophotometer. The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra of 0.4 – 0.5 M solutions of the compounds in DMSO were recorded with a Tesla spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

2,3-Dihydro-3-oxobenzo[b]selenophene (IV). This compound, with mp 76° (from water), was obtained by the method in [4].

Azomethines I. A) A solution of equimolecular amounts of IV and the appropriate diarylformamidine [5] in alcohol was refluxed for 30 min. The resulting azomethines were recrystallized successively from 50% aqueous pyridine and aqueous alcohol. UV spectrum (in ethanol), λ_{max} , nm (log ϵ): 325 – 330 (4.00) and 450 – 460 (4.30).

B) A solution of equimolecular amounts of IV and ethoxymethylene aniline [6] in alcohol was refluxed for 30 min. The crystals obtained after the mixture was cooled were recrystallized from aqueous alcohol.

3-Chloro-2-formylbenzo[b]selenophene (V). A 1-ml (0.01 mole) sample of POCl_3 was added at 0° to 1.6 ml (0.02 mole) of dimethylformamide (DMF), after which a solution of 1.97 g (0.01 mole) of IV in 15 ml of DMF was added dropwise at 0° . The mixture was then stirred at 0° for 2 h and at 50 – 60° for 1 h, after which it was poured into a mixture of 100 g of ice and 10 g of sodium acetate, and the precipitate was removed by filtration and steam distilled to give 1.56 g (65%) of aldehyde V. The product sublimed at 50 – 60° to give colorless needles with mp 84° . Found: C 43.8; H 2.1%. $\text{C}_8\text{H}_5\text{ClOSe}$. Calculated: C 44.4; H 2.1%. IR spectrum: $\nu_{\text{C=O}}$ 1655 cm^{-1} .

2-Formyl-3-methoxybenzo[b]selenophene (VI). A 1.5-g (6 mmole) sample of V and a catalytic amount of potassium iodide were added to a solution of 0.15 g (6.5 mmole) of sodium in 18 ml of methanol, after which the mixture was refluxed for 4 h. The hot solution was filtered, and the filtrate was cooled to give 0.8 g (54%) of cubic crystals of VI with mp 96° (from alcohol). Found: C 49.9; H 3.2%. $\text{C}_{10}\text{H}_8\text{O}_2\text{Se}$. Calculated: C 50.2; H 3.4%. IR spectrum: $\nu_{\text{C=O}}$ 1655 cm^{-1} .

Azomethines II. These compounds were obtained by condensation of VI with equimolecular amounts of the appropriate substituted anilines. UV spectrum in ethanol: λ_{max} 335 nm (log ϵ 4.28).

TABLE 1. IR Spectra of 2-Formyl-3-hydroxybenzo[b]selenophene Anils

Compound	R	mp, °C	Empirical formula	Found, %		Calc., %		IR spectra of mineral oil suspensions, cm ⁻¹
				C	H	C	H	
I	H	156	C ₁₅ H ₁₁ NOSe	60,4	3,9	60,0	3,7	1660
I	<i>p</i> -Cl	197	C ₁₅ H ₁₀ NCIOSe	54,1	2,9	53,8	3,0	1670
I	<i>m</i> -Cl	192	C ₁₅ H ₁₀ NCIOSe	53,3	3,5	53,8	3,0	1650
I	<i>p</i> -OCH ₃	165	C ₁₆ H ₁₃ NO ₂ Se	58,2	3,7	58,2	4,0	1655
I	<i>p</i> -COCH ₃	200	C ₁₇ H ₁₃ NO ₂ Se	59,3	3,3	59,7	3,8	1650
II	H	66	C ₁₆ H ₁₃ NOSe	61,1	3,6	61,2	4,1	1590
II	<i>p</i> -Cl	106	C ₁₆ H ₁₂ NCIOSe	55,4	3,1	55,1	3,5	1600

2-(N,N-dimethylaminomethylene)-3(2H)-benzoselenophenone (III). A 2-ml (0.02 mole) sample of POCl₃ and a solution of 4 g (0.02 mole) of IV in 30 ml of DMF were added successively dropwise at 0° to 3.2 ml (0.04 mole) of DMF, after which the mixture was stirred at 0° for 3 h. It was then poured into a mixture of 200 g of ice and 20 g of sodium acetate, and the precipitate was removed by filtration, dried, and crystallized from alcohol to give yellow plates with mp 202° in 80% yield. Found: C 52.1; H 4.1%. C₁₁H₁₁NOSe. Calculated: C 52.4; H 4.4%. IR spectrum: $\nu_{\text{C=O}}$ 1650 cm⁻¹. PMR spectrum: δ 8.07 ppm (singlet, CH) and 3.13 ppm (singlet, CH₃).

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