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 - 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.

In order to determine the character of the Ia - 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 hydroxylaldimines of benzo[b]furan and benzo[b]thiophene [2, 3], are observed in the PMR

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

The decrease in the frequency of the absorption of the C=O 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\(^\circ\) (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), \(\lambda_{\text{max}}\) nm (log \(c\)): 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 POCI\(_3\) was added at 0\(^\circ\) 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\(^\circ\). The mixture was then stirred at 0\(^\circ\) for 2 h and at 50-60\(^\circ\) 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\(^\circ\) to give colorless needles with mp 84\(^\circ\). Found: C 43.8; H 2.1%. C\(_8\)H\(_6\)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\(^\circ\) (from alcohol). Found: C 49.9; H 3.2%. C\(_{13}\)H\(_8\)O\(_2\)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: \(\lambda_{\text{max}}\) 335 nm (log \(c\) 4.28).