

ABSORPTION SPECTRA OF 3-KETO-2,3-DIHYDRO- THIONAPHTHENE AND ITS DERIVATIVES

XIII.* BENZYLIDENE DERIVATIVES OF 5-METHYLBENZO-

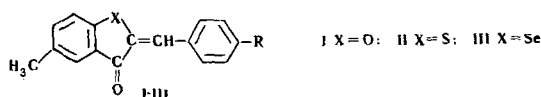
[b]SELENOPHEN-3-(2H)ONE

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The absorption spectra of a number of selenoindogenides specially synthesized for this end were measured. It is shown that the selenoindogenides are photochromic in solution. The absorption maxima of isologous aurones, thioindogenides, and selenoindogenides are compared. It is shown that the magnitude of the shift in the absorption maximum decreases in the heteroatom order $O > S > Se$ on introduction of electron-donor substituents into the 4'-position; the opposite dependence is valid for electron-accepting substituents. The regularities obtained are explained by the difference in the donor properties of the heteroatoms and the introduced substituents. It is shown that λ_{\max} of the selenoindogenides, calculated via an additive scheme, differ from the experimental values by an average of 6.3 nm.

The absorption spectra of aurones (I) and thioindogenides (II) were previously examined in [2].



Selenoindogenides III have been synthesized in this investigation by the condensation of 5-methylbenzo[b]selenophen-3-(2H)one with various aromatic aldehydes. The formation of the benzylidene derivatives of 5-methylbenzo[b]selenophen-3(2H)one proceeds smoothly with yields of 55 to 92%. The absorption spectra of III were measured before and after the action of light. Table 1 indicates that the selenoindogenides in solution have photochromic properties analogous to aurones, thioindogenides, and indogenides [3,4], for which it has been demonstrated [5] that the reason for the photochromy is photochemical cis-trans isomerization. When a solution of 2-(4-dimethylaminobenzylideno)-5-methylbenzo[b]selenophen-3-one prepared in the dark is irradiated with daylight, the intensity of the maxima at 434 and 461 nm decreases (Fig. 1). At the same time, a new, distinct maximum appears at 496 nm which corresponds to the second stereoisomeric form of the substance. The spectrum takes on its original form when a solution irradiated with daylight is stored in the dark.

It is interesting to compare the absorption spectra of the similarly constructed aurones, thioindogenides, and selenoindogenides. Compound III absorbs light at higher wavelengths and less intensely than the corresponding II. An examination of the effect of replacement of the hydrogen in the 4' position on λ_{\max} indicated that the sensitivity to introduction of electron-donating substituents decreases in the heteroatom order $O > S > Se$; the reverse sequence is valid for electron-accepting substituents (Table 2). The relationship between the donor properties of the heteroatom and the substituents introduced apparently plays some role here. When this difference is a maximum ($X = O$, $R = NMe_2$; $X = Se$, $R = NO_2$), the $\Delta\lambda$ value is a

*For Communication XII see [1].

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TABLE 1. Properties of the Selenoindogenides

R	mp, °C	Empirical formula	Element	Found, %	Calculated, %	Spectra in hexane					
						before ir-radiation*		after ir-rad.*		isosbestic point	
						λ_{max} , nm	$\epsilon_{max} \cdot 10^{-4}$	λ_{max} , nm	$\epsilon_{max} \cdot 10^{-4}$	λ , nm	$\epsilon \cdot 10^{-4}$
4-N(CH ₃) ₂	198—198,5	C ₁₈ H ₁₇ NOSe	Se	23,1	23,5	461	3,87	496	1,11	473,6	1,69
4-OCH ₃	168,5—169	C ₁₇ H ₁₄ O ₂ Se	N	4,1	3,9	441	1,63	472	1,09	451,2	0,86
4-OH	252,5	C ₁₆ H ₁₂ O ₂ Se	Se	24,0	23,6	442	—	442	—	461	—
4-H	161—161,5	C ₁₆ H ₁₂ OSe	Se	25,1	25,2	440,5 ‡	0,91	468	0,46	452	0,49
4-Cl	184,5—185	C ₁₆ H ₁₁ ClOSe	Se	26,4	26,3	440	1,08	472	0,58	453,6	0,59
			Cl	23,7	23,6	441,6	—	—	—	—	—
4-NO ₂	263,5—264	C ₁₆ H ₁₁ NO ₃ Se	Se	10,6	10,3	459 ‡	—	488	—	475,2	—
			N	23,0	23,2	—	—	—	—	—	—
2-NO ₂	198,5—199	C ₁₆ H ₁₁ NO ₃ Se	Se	4,1	3,8	440 ‡	—	443	—	468	—
			N	23,0	22,9	—	—	—	—	—	—
3-NO ₂	237—238	C ₁₆ H ₁₁ NO ₃ Se	Se	4,1	4,1	445 ‡	—	475	—	461	—
			N	23,0	22,9	—	—	—	—	—	—

*The most intense long-wave maximum is presented.

† Only the new maximum appearing during irradiation is presented.

‡ Compounds slightly soluble in hexane.

TABLE 2. Shift in λ_{max} for I-III* on Introduction of Substituent R Into the 4' Position

X	R	$\Delta\lambda = \lambda_{max}^R - \lambda_{max}^H$, nm				
		N(CH ₃) ₂	OCH ₃	H	Cl	NO ₂
O		61	17	0	3	7
S		30	4	0	3	13
Se		21	1	0	1,6	19

*The spectra were measured in n-hexane.

TABLE 3. Comparison of the Calculated and Experimentally Determined Absorption Maxima of Selenoindogenides

R	λ_{max} , nm					$\Delta\lambda^*$
	solvent	(4-R-C ₆ H ₄ CH ₃) ₂	5,5'-dimethylselenoindigo	calc.	exptl.	
NO ₂	Dichloroethane	342 ^a	574	458	468	-10
Cl	n-Hexane	328 ^a	565	446,5	441,6	4,9
H	n-Hexane	308 ^a	565	436,5	440	-3,5
OH	Ethanol	325 ^a	595	460	460	0
OCH ₃	Dichloroethane	325 ^a	574	449,5	441	8,5
N(CH ₃) ₂	Dioxane	362	566	464	475	-11

* $\Delta\lambda = \lambda_{cal} - \lambda_{exp}$.

maximum. The $\Delta\lambda$ value is a minimum when there is a minimum difference between the donor properties of the heteroatom and the introduced substituent (X = O, R = NO₂; X = Se, R = NMe₂). However, the available data are insufficient to consider this explanation to be proved.

The 2-benzylideno-5-methylbenzo[b]selenophen-3-one molecule can be schematically represented as a combination of half of a stilbene molecule and half of a 5,5'-dimethylselenoindigo molecule. We have calculated the absorption maxima of III by an additive scheme starting from the long-wave absorption maxima

of 5,5'-dimethylselenoindigo and 4,4'-disubstituted stilbenes (Table 3). The average deviation $\left(\frac{\sum |\Delta\lambda|}{n}\right)$ is



Fig. 1. Absorption spectra of 2-(4-dimethylaminobenzylideno)-5-methylbenzo[b]selenophen-3-one in n-hexane: 1) solution prepared in the dark; 2) solution 1 after irradiation with daylight for 5 min; 3) solution 2 after 10-min irradiation.

methylbenzo[b]selenophen-3-one (76.2); 2-(4-methoxybenzylideno)-5-methylbenzo[b]selenophen-3-one (73); 2-(4-hydroxybenzylideno)-5-methylbenzo[b]selenophen-3-one (72.5); 2-(3-nitrobenzylideno)-5-methylbenzo[b]selenophen-3-one (56.3); 2-(2-nitrobenzylideno)-5-methylbenzo[b]selenophen-3-one (67.4).

6.3 nm, which exceeds the experimental error (± 1.0 nm) by a great deal. However, the comparison of the calculated and experimental results should be considered to be satisfactory if one considers the large distance (240–270 nm) between λ_{\max} of symmetrical compounds, the indubitable crudeness of the additive scheme, and the fact that solution of the analogous problem using quantum mechanics does not always lead to the best agreement with the experimental results. However, the major goal – to elucidate a system in the deviations from the additive scheme – could not be reached. This is possibly due to the necessary (because of insufficient experimental data on the spectra of stilbenes) use in Table 3 of various solvents.

EXPERIMENTAL

2-Benzylideno-5-methylbenzo[b]selenophen-3-one. A mixture of 1.05 g (0.005 mole) of 5-methylbenzo[b]selenophen-3-(2H)one, 0.795 g (0.0075 mole) of benzaldehyde, and 2.3 ml of water in 24 ml of acetic acid was heated to 60°, 1.4 ml of concentrated HCl was added, and the mixture was refluxed for 2 h. The mixture was then cooled, filtered, and the residue was washed with water to give 1.06 g (92.4%) of product.

The following compounds were similarly obtained (the percent yield is given in parentheses): 2-(4-dimethylaminobenzylideno)-5-methylbenzo[b]selenophen-3-one (84.1); 2-(4-nitrobenzylideno)-5-methylbenzo[b]selenophen-3-one (55); 2-(4-chlorobenzylideno)-5-

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