ABSORPTION SPECTRA OF PHOTOINDUCED E ISOMERS OF AURONES, THIOINDOGENIDES, AND SELENOINDOGENIDES

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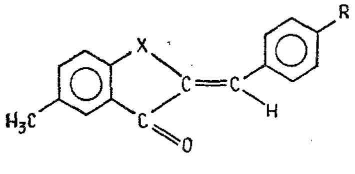
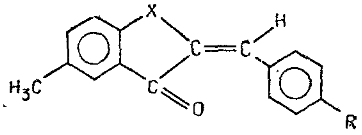
One of the major requirements imposed on photochromic compounds is maximum color contrast between their initial and photoinduced forms [1], in connection with which the study of electronic spectra of both forms of these compounds is of particular interest. Absorption spectra of photoinduced E isomers of aurones (I), thioindogenides (II), and selenoindogenides (III) were investigated in this paper.



Z Isomer



E Isomer

(I) X = O; (II) X = S; (III) X = Se; R = H(a), CH_3 (b), OCH_3 (c), OH (d), NH_2 (e), $N(CH_3)_2$ (f), F(g), Cl(h), NO_2 (i). Z→E isomerization does not occur completely upon irradiation of solutions of initial Z isomers of compounds (I-III) with visible light; the irradiated solutions contain a small amount of the initial Z isomer.

We have observed that in compounds (I-III), as in stilbenes [2, 3] and thioindigoids [4], only the more planar initial Z isomer possesses the ability to luminesce. The intensity of luminescence of the solution decreases regularly with a decrease in concentration of the Z isomer (Fig. 1), which makes it possible to determine the concentration of the initial isomer in the irradiated solution. The method of evaluating the degree of phototransformation based on measurement of intensities of luminescence of the initial form is presented in [5] without consideration, however, of the dependence of intensity of luminescence I_l on the value of optical density of the solution of a wavelength λ of the exciting light [6].

Absorption curves of photoinduced E isomers were calculated with the equation

$$\varepsilon_E = \frac{D_{ZE} - \varepsilon_Z l c_Z D_Z^{\lambda} / D_Z^{\lambda,0}}{l c_Z (D_Z^{\lambda,0} - D_Z^{\lambda}) / D_Z^{\lambda,0}}, \tag{1}$$

in which D_{ZE} is the optical density of the irradiated solution; c_Z is the initial concentration of the Z isomer; D_Z^{λ} is the optical density of the Z isomer in the irradiated solution at a wavelength λ; $D_Z^{\lambda,0}$ is the optical density of a solution of pure Z isomer at a wavelength λ; ε_E and ε_Z are molar extinction coefficients of the E and Z isomers. The optical density of the Z isomer in the irradiated solution was calculated with the equation

$$D_Z^{\lambda} = -\log\left[1 - \frac{I_l\,(1 - 10^{-D_Z^{\lambda,0}})}{I_l^0}\right], \tag{2}$$

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TABLE 1. Absorption Band Maxima of E Isomers of (I-III)

Compound	Band 1		Band 2	
	ν_{max}, cm^{-1}	$\varepsilon_{max} \cdot 10^{-4}$	ν_{max}, cm^{-1}	$\varepsilon_{max} \cdot 10^{-4}$
Ia	25445	0,88	30303	1,90
Ib	25189	1,51	29762	2,15
Ic	24213	2,38	28653	2,52
Id	24814	1,54	29070	1,96
Ie	23753	1,46	28090	1,19
If	21692	3,95	27473	1,10
Ig	25445	1,27	30303	2,40
Ih	25253	1,40	30030	2,90
Ii	24938	0,60	29674	1,70
IIa	22075	0,65	30120	1,75
IIb	21978	1,37	29499	2,30
IIc	21882	1,65	28329	2,25
IId	21930	1,42	28653	2,00
IIe	21368	2,31	27397	1,97
IIf	20534	3,85	26042	2,30
IIg	22173	0,71	30120	1,81
IIh	21978	0,57	29586	2,23
IIi	21413	0,60	30120	2,20
IIIa	21739	0,56	30030	2,12
IIIb	21598	1,10	28249	2,20
IIIc	21645	0,97	28653	2,20
IIId	20408	2,50	25575	2,05
IIIe	21692	0,70	29412	2,40
IIIf	20833	0,55	30488	1,85

TABLE 2. Results of the Comparison of γ_{max} of Bands of Z and E Isomers of (I-III) by the Method of Proportional Response

Type of compound	X axis		Y axis		n	r	p	ν_0	Values of t_α	
	isomer	band	isomer	band					calculated	tabular
I	Z	1	E	1	9	0,999	1,005	11,40	7495	5,041
II	Z	1	E	1	9	0,998	1,039	21,27	2722	5,041
III	Z	1	E	1	6	0,982	1,145	6,52	160,9	6,859
I	Z	2	E	2	9	0,999	1,136	0,10	29995	5,041
II	Z	2	E	2	9	0,999	1,180	13,26	29996	5,041
III	Z	2	E	2	6	0,999	1,115	13,40	29999	6,859
I	Z	2	E	1	9	0,918	1,505	296,90	60,3	5,041
II	Z	2	E	1	9	0,796	0,344	4,34	19,6	5,041
III	Z	2	E	1	6	0,544	0,193	192,40	4,64	6,859

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n) number of pairs; r) correlation coefficient; p) sensitivity coefficient; γ_0) free term; t_α) Student coefficient at α = 0.999.

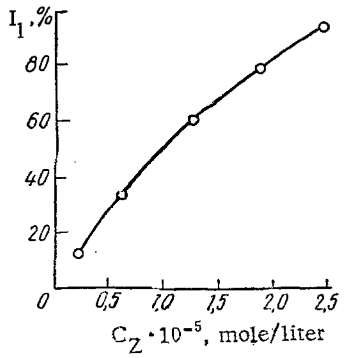
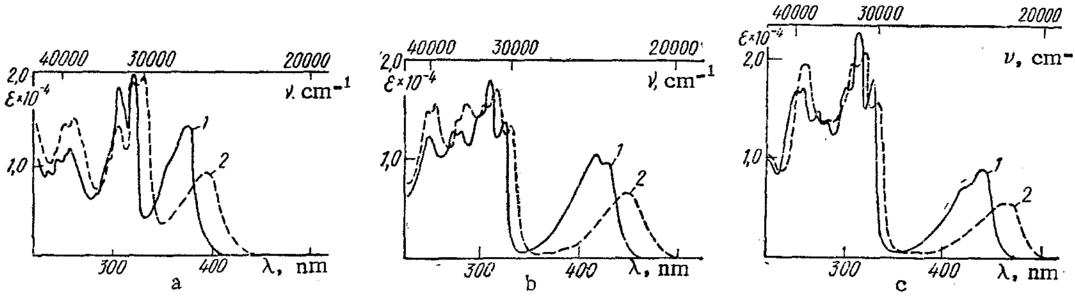


Fig. 1. Dependence of intensity of luminescence I_1 on concentration of initial Z isomer.



a b c

Fig. 2. Absorption spectra: a) 2-benzylideno-5-methylbenzo[b]furan-3-one; b) 2-benzylideno-5-methylbenzo[b]thiophen-3-one; c) 2-benzylideno-5-methylbenzo[b]selenophen-3-one; 1) Z isomer; 2) isomer.

where I_l^0 and I_l are intensities of luminescence of the Z isomer in the initial and irradiated solutions.

The absence of visible changes in spectra of irradiated solutions of (I-III) upon storing in the dark at room temperature for 6 h makes it possible to ignore the opposite thermal E → Z isomerization and the low value of optical density of the irradiated solutions at a wavelength λ makes it possible to ignore the filter effect [7] of the E isomer.

The experimentally measured spectra of Z isomers and calculated spectra of E isomers of (I-III) with R = H are presented in Fig. 2. Absorption bands of the E isomers appear in the longer-wave region and a decrease in absorption intensity and a flattening of the vibrational specture are observed in the first bands, while the second bands retain both the intensity of absorption and the vibrational structure. Analysis of data on spectra of the photoindices (Table 1) and initial [8] forms shows that the effect of substituent R and heteroatoms X on γ_{max} of absorption bands in the series of E isomers (I-III) is similar to the effect of substituents and heteroatoms on the position of absorption maxima of the corresponding bands in the series of Z isomers. Results of comparison of ν_{max} of Z and E isomers of (I-III) by the method of proportional response [9] indicates that the character of electron density redistribution during excitation is identical in the E isomers and the initial Z isomers (Table 2).

Thus, as in the Z isomers [8], the first absorption bands of E isomers (I-III) are associated with redistribution of electron density between the carbonyl group and the heteroatom upon excitation and the second bands are associated with intramolecular charge transfer from the benzylidene portion of the molecule to the carbonyl group.

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