ABSORPTION SPECTRA.

XVIII.* NATURE OF THE LONG-WAVE BAND OF THE Z ISOMERS OF PHOTOCHROMIC AURONES, THIOINDOGENIDES, AND SELENOINDOGENIDES

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The first band in the absorption spectra of the Z isomers of aurones, thioindogenides, and selenoindogenides is due to an electronic transition that is associated primarily with charge redistribution on the heteroatom and the carbonyl group. The effect of a substituent in the 4' position plays a secondary role. The low sensitivity of the spectra of selenoindogenides to the effect of substituents is due to the saturation of the acceptor center (carbonyl group) by electrons drawn off from the heteroatom during interaction of the $2\pi p_z$ electrons of selenium with the π system of the molecule.

This research was devoted to a study of the spectral characteristics of the thermodynamically stable Z isomers of photochromic aurones (I), thioindogenides (II), and selenoindogenides (III) [2, 3] (Tables 1, 3, and 4†); this is important in the search for substances with maximum light contrast.

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*See [1] for communication XVII.

†Information on the new derivatives is presented in Table 2.

TABLE 1. Maxima of the Absorption Bands of the Z Isomers of I-III in Octane

Compound	Band 1			Band 2		
	λ_{max}, nm	ν_{max}, cm^{-1}†	$\varepsilon_{max}\cdot 10^{-4}$	λ_{max}, nm	ν_{max}, cm^{-1}†	$\varepsilon_{max}\cdot 10^{-4}$
Ia	376	26596	1,60	322	31056	2,33
Ib*	380	26316	2,14	326	30675	2,29
Ic	393	25445	3,30	335	29851	2,44
Id*	385	25974	2,19	332	30120	2,02
Ie*	402	24876	2,00	340	29412	1,15
If	437	22883	4,80	345	28986	0,91
Ig*	375	26667	1,58	322	31056	2,40
Ih	379	26385	2,03	324	30864	3,06
Ii	383	26110	1,25	327	30581	1,77
IIa	434	23041	1,18	324	30864	1,76
IIb*	436	22936	1,73	330	30303	2,29
IIc	438	22831	2,09	341	29326	2,34
IId*	436	22936	1,91	338	29586	2,03
IIe*	448	22321	2,72	350	28571	1,86
IIf	464	21552	5,00	365	27397	1,59
IIg*	433	23095	1,16	324	30864	1,81
IIh	437	22883	1,24	329	30395	2.11
IIi	447	22371	1,02	324	30864	2,03
IIIa	440	22727	0,91	326	30675	1,86
IIIc	442	22624	1,63	344	29070	2,22
IIId	441	22676	1,38	340	29412	2,14
IIIf	461	21692	3,87	375	26667	2,07
IIIh	442	22624	1.08	332	30120	2,21
IIIi	459	21786	0,76	322	31056	1,50

*Theses compounds were synthesized in the present research.

†The calculated wave numbers are presented in Table 1. The mean experimental error in the determination was 50 cm^{-1}. The spectra were measured with an SF-8 spectrophotometer.

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TABLE 2. Characteristics of Compounds Synthesized by the Method in [2]*

Compound	mp, °C	Empirical formula	Found, %				Calculated, %				Yield, %
			C	H	N	S	C	H	N	S	
Ib	105,5	$C_{17}H_{14}O_2$	81,30	5,52	—	—	81,58	5,64	—	—	84,3
Id	263	$C_{16}H_{12}O_3$	76,27	4,68	—	—	76,18	4.79	—	—	81,4
Ie	229	$C_{16}H_{13}NO_2$	76,39	5,18	5,41	—	76,48	5.21	5,57	—	87,2
Ig	141	$C_{16}H_{11}FO_2$	75,29	4,27	—	—	75,58	4.36	—	—	96,3
IIb	147	$C_{17}H_{14}OS$	76,52	5.27	—	11,95	76,66	5,30	—	12,04	82,0
IId	245	$C_{16}H_{12}O_2S$	71,50	4,38	—	12,09	71,62	4,50	—	11,95	54,0
IIe	175	$C_{16}H_{13}NOS$	71,77	4,83	5,10	12,10	71.88	4,90	5.24	11,99	67,4
IIg	180	$C_{16}H_{11}FOS$	71,15	5,92	—	12,00	71.09	4,01	—	11.86	94.0

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*To obtain absorption spectra of the pure Z isomers of I-III, all of the operations prior to the measurements were accomplished in the dark.

TABLE 3. Effect of Heteroatom X on the Position of the Maxima of the Absorption Bands of Isomers of I-III*

R	$\Delta\nu'_X$, cm^{-1}		$\Delta\nu''_X$, cm^{-1}	
	band 1	band 2	band 1	band 2
H	3555	192	3869	381
CH_3	3380	372	—	—
OCH_3	2614	525	3692	781
OH	3038	534	3298	708
NH_2	2555	841	—	—
$N(CH_3)_2$	1331	1589	1191	2319
F	3572	192	—	—
Cl	3502	469	3761	744
NO_2	3739	−283	4324	−475

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*The $\Delta\nu_{X'}$ value is the difference between the absorption maxima of the aurone and the thioindogenide with identical substituents, and $\Delta\nu_{X''}$ is the difference between the absorption maxima of the aurone and the selenoindogenide with identical substituents.

TABLE 4. Effect of Substituents R on the Position of the Maxima of the Absorption Bands of the Z Isomers of I-III*

R	$\Delta\nu_O$, cm^{-1}		$\Delta\nu_S$, cm^{-1}		$\Delta\nu_{Se}$, cm^{-1}	
	band 1	band 2	band 1	band 2	band 1	band 2
H	0	0	0	0	0	0
CH_3	280	381	105	561	—	—
OCH_3	1151	1205	210	1538	103	1605
OH	622	936	105	1278	51	1263
NH_2	1720	1644	720	2293	—	—
$N(CH_3)_2$	3713	2070	1489	3467	1035	4008
F	−71	0	−54	0	—	—
Cl	211	192	158	469	103	555
NO_2	486	475	670	0	941	−381

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*The difference between the absorption maxima of unsubstituted and substituted aurones is designated by $\Delta\nu_O$, as compared with $\Delta\nu_S$ for the thioindogenides and $\Delta\nu_{Se}$ for the selenoindogenides.

TABLE 5. Results of a Comparison of the $\Delta\nu_{max}$ Values of the First Absorption Bands of the Z Isomers of I-III by the Proportional Response Method

Compound type		n^*	$r \pm \delta r$	p	ν_0	t_α (α=0,999)	
X axis	Y axis					calculated	tabulated
I	II	8	0,977±0,015	0,414	82	198,15	5,405
I	III	5	0,969±0,024	0,275	45	95,80	8,610
II	III	5	0,999±0,001	0,702	14	3746,90	8,610

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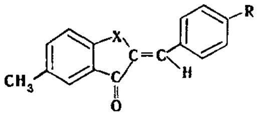
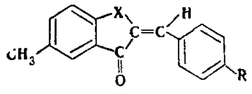
*The nitro derivatives are excluded.

Since the shift of the first band on passing from I to II (and III) reaches 3739 cm^{-1} (and 4324 cm^{-1}) but is only 1589 cm^{-1} (and 2319 cm^{-1}) for the second band, it may be assumed that the first band is associated to a greater degree than the second with charge redistribution on the heteroatom during excitation of the molecule. The shift of the first band of II (and III) under the influence of substituents does not exceed 1489 cm^{-1} (and 1035 cm^{-1}), whereas the second band is shifted by 3467 cm^{-1} (and 4008 cm^{-1}) to the long-wave region. This makes it possible to assume that the first band of derivatives II and III is associated to a lesser extent than in the second with charge redistribution on the cinnamoyl fragment of the molecule during excitation. In the I series the introduction of a substituent leads to approximately identical shifts of the first and second absorption bands (If constitutes and exception to this). Both the first and second bands of aurones are evidently associated to an identical extent with charge distribution in the cinnamoyl portion of the molecule.



Z isomer



E isomer

I X = O, II X = S, III X = Se

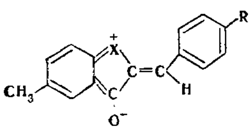
a R = H, b R = CH_3, c R = OCH_3, d R = OH, e R = NH_2, f R = $N(CH_3)_2$, g R = F, h R = Cl, i R = NO_2

The magnitude of the bathochromic shift of the first band on introduction of substituents R decreases as the donor properties of the heteroatom increases: a hydroxy or dimethylamino group in aurone I gives rise to a shift to the long-wave region of 622 cm^{-1} (or 3713 cm^{-1}), respectively, whereas the introduction of the same substituents in thioindogenide II leads to a shift of only 105 cm^{-1} (or 1489 cm^{-1}).

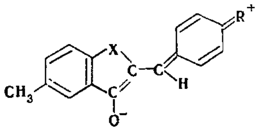
A comparison of the $\Delta\nu_{max}$ values of the first bands of I and II, I and III, and II and III leads to good proportional response [4] (Table 5). It hence follows that the long-wave bands of I-III have identical natures. The correlation coefficient (r) are considerably lower when the $\Delta\nu_{max}$ values of the first bands are compared with the $\Delta\nu_{max}$ values of the second band. This provides evidence for substantial differences in the natures of the first and second bands for I-III.

The coefficients of sensitivity of proportional response are linearly dependent on the electronegativities of the O, S, and Se heteroatoms. The low sensitivity of the ν_{max} values of the first bands of III to the introduction of substituents can be explained by the fact that the interaction of the $2\pi p_z$ electrons of selenium with the π-electron system of the molecule leads to a structure that is resistant to the effect of substituents because of the peculiar effect of saturation of the acceptor center (carbonyl group) of the molecules by electrons drawn away from the heteroatom.

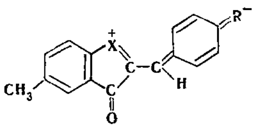
Using the terminology of the valence-bond method one can state that structures with separated charges (A and B), the ratio between which changes as a function of the nature of the heteroatom and the nature of the substituents – an increase in the donor character of the heteroatom leads to an increase in the fraction of structure A, and an increase in the donor character of the substituent leads to an increase in the fraction of structure B – have the greatest weight in the first excited state.



A



B



C

An analysis of the spectra of nitro derivatives I-IIIi shows that their first band is associated with migration of the charge from the heteroatom not only to the carbonyl group (structure A) but also to the nitro group (structure C), i.e., with the formation of a "donor–double acceptor" system [5-7]. This should lead to a bathochromic shift of the bands as compared with the corresponding unsubstituted compounds, and this is in agreement with the experimental results.

LITERATURE CITED

1. M. A. Mostoslavskii, S. I. Saenko, and V. L. Belyaev, Khim. Geterostikl. Soedin., No. 8, 1034 (1973).
2. M. A. Mostoslavskii and M. D. Kravchenko, Khim. Geterostikl. Soedin., No. 1, 58 (1968).
3. G. A. Yugai, M. A. Mostoslavskii, and T. V. Denisova, Khim. Geterostikl. Soedin., No. 10, 1326 (1970).

4. M. A. Mostoslavskii, Reakts. Sposobn. Org. Soedin., 1, No. 2, 72 (1964).
5. E. E. Milliaresi, V. I. Danilova, B. F. Minaev, and G. D. Barabasheva, Opt. Spektrosk., 30, 882 (1971).
6. V. A. Izmail'skii and O. I. Lobova, Dokl. Akad. Nauk SSSR, 205, 1100 (1972).
7. V. A. Izmail'skii and E. A. Smirnov, Zh. Obshch. Khim., 7, 535 (1937).

SUBSTITUTED 2-ARYLIMINONAPHTHO[1,8-bc]THIOPHENE

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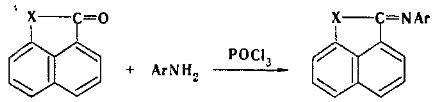
The first dyes based on naphtho[1,8-bc]thiophen-3-(2H)-one were synthesized. The carbonyl group of these compounds has lower reactivity than the carbonyl group of naphthostyryl in condensation with arylamines.

Naphtho[1,8-bc]thiophen-3(2H)-one (I) is isoelectronic with respect to naphthostyryl (II) and 1-phenalenone. Approximately 100 patents on dyes from naphthostyryl have been granted in the last 15 years. On the other hand, although the methods for the preparation of and the physical and chemical properties of I have been studied (for example, see [1-3]), not one specific dye based on it has been described.

We have synthesized yellow disperse dyes of the general formula IV (see Table 1) that include a naphtho[1,8-bc]thiophene fragment by condensation of naphthothiophenone I with aromatic amines III, containing a nitro group, in the presence of phosphorus oxychloride.

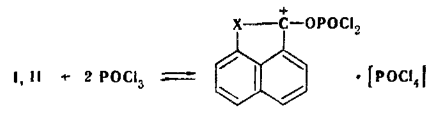


I, II III IVa-f, V

IVa-f, I X=S; II, V X=NH

The dyes on lavsan have good light fastness but unsatisfactory resistance to sublimation at 200° (Table 1).

In contrast to naphthostyryl [4], I does not give Schiff bases (V) with aniline and other amines that do not contain a nitro group (o-bromoaniline, aminoacenaphthene, p-aminobenzoic acid, etc.). The mechanism of the condensation of carbonyl-containing substances with amines in the presence of phosphorus oxychloride has usually not been considered [5, 6].



(1)

VI X=S; VII X=NH

$$ArNH_2 + 2\,POCl_3 \rightleftharpoons (ArNH_2 \cdot \overset{+}{POCl_2}) \cdot \overset{-}{POCl_4} \qquad (2)$$

$$VI, VII + ArNH_2 \longrightarrow IV, V + HPOCl_4 + PO(OH)Cl_2 \qquad (3)$$

If phosphorus oxychloride is capable (see [7]) of undergoing reactions (1) and (2), it may be assumed (see [8]) that nitroanilines, retaining sufficient nucleophilicity for reaction (3) with carbonium ion VI, have relatively low basicities that insure the presence in solution of the necessary concentration of the free amine, not deactivated by reaction with phosphorus oxychloride. Basic amines (aniline, etc.) react with phosphorus oxychloride

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