

## ANALYTICAL UTILIZATION OF UV SPECTRA OF AROMATIC COMPOUNDS WITH OXYGEN ELECTRON DONATING AND ELECTRON ACCEPTING GROUPS\*

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Studies of the UV spectra of simple aromatic compounds, carrying oxygen electron donating and electron accepting groups, have shown some dependence between the structure (position and type of the substituent) and the position of the first primary and the secondary band. These two bands are shifted by ionization of electron donating (hydroxyl) and electron accepting (carboxyl) groups. An attempt has been made to plot empirically the position of the first primary and the secondary band of tri- and tetrasubstituted compounds.

Recently, we have published several papers<sup>1-5</sup> dealing with the UV spectroscopy of simple aromatic compounds containing oxygen electron donating groups (hydroxyl, methoxyl and methylenedioxy groups) and one electron accepting group (aldehyde, keto, carboxyl, ethylenecarboxyl, vinyl, and propenyl groups). In addition, the spectra of substituted 1-indanones, phthalides, phthalic acid, phthalanhydride, and N-ethylphthalimide have been examined. In the studied compounds, the electron donating groups were in positions 2-6 (in phthalides and in 1-indanone in positions 4-7) *vs* the electron accepting group. In the spectra of compounds containing a carboxyl or hydroxyl group, the effect of ionization of these groups in alkaline medium on the position of the individual bands has also been determined.

In the present work, the evaluation of the shifts was carried out. An attempt was made to infer the rules which might hold with respect to the position of the electron donating substituents and the position of the first primary and the secondary band in the spectra. The results obtained were used for analytical purposes.

The UV spectra of aromatic compounds were usually studied only in the region of the longer wavelengths. Doub and Vandenberg<sup>6-8</sup> were the first who carried out a more detailed study of disubstituted as well as of trisubstituted benzene derivatives containing electron donating or electron accepting substituents. They confirmed the earlier findings made by Morton and coworkers<sup>9</sup> who found a considerable difference between the spectra of *ortho/meta*-disubstituted

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derivatives and those of *para*-disubstituted derivatives. The quantum-chemical explanation of this phenomenon was given by Tanaka and Nagakura<sup>10</sup>.

Other authors<sup>11-13</sup> studied the spectra of aromatic compounds containing substituents in the *ortho*-position. They interpreted these spectra qualitatively on the basis of steric interactions. Moser and Kohlenberg<sup>14</sup> postulated that, after introduction of various electron donating substituents into the *ortho*-position *vs* the carboxyl group, the position of the UV absorption bands of benzoic acid is dependent on the character and bulkiness of these substituents. The spectra of 2-hydroxybenzaldehyde and 2-hydroxyacetophenone and the shifts of bands (particularly of the secondary band) due to ionization and esterification of the hydroxyl group have served as material for comparison for the determination of the constitution of oxytetracycline<sup>15,16</sup>. Aulin-Erdtman and coworkers<sup>18</sup> published a comprehensive paper on the UV spectroscopy of 41 aromatic compounds which are of significance for the investigation of lignines and tanines. They also studied the effect of methylation and ionization on the position of the individual bands of the described compounds.

## EXPERIMENTAL

The UV spectra were measured in the same manner as carried out earlier<sup>2</sup>. Thus, 152 compounds were studied and the data of other thirty compounds were taken over from the literature. In the papers<sup>2,4,5</sup>, the experimental data taken over from the literature were given with the pertaining reference numbers.

## RESULTS

### *The Effect of Substitution*

The substitution of the benzene nucleus with one electron accepting oxygen group results in a red shift of all the absorption bands of unsubstituted benzene as already described by Doub and Vandenberg<sup>7</sup>. The size of this shift depends on the electron accepting ability of the substituents (Table I), which results in an increase in the positions of the first primary and the secondary band in the order benzene < benzoic acid < methyl benzoate < acetophenone < benzaldehyde < propenylbenzene = styrene < *trans*-cinnamic acid. The position of the band of *trans*-cinnamic acid is given by the conjugation of the —CH=CH— group with a benzene nucleus. Substitution of a hydrogen atom in the CH<sub>2</sub> group of styrene for a carboxyl group shifts the first primary band by c. 30 nm to the red and the secondary band by c. 8 nm, which are values comparable with those obtained on substitution of benzene with one carboxyl group. Substitution of the CH<sub>3</sub> group of propenylbenzene with a carboxyl group causes a red shift by c. 30 nm of the first primary band and by c. 20–25 nm of the secondary band (Table II). The introduction of yet another carboxyl group in the *ortho*-position to the already present carboxyl group (phthalic acid) does not lead to fundamental changes in the position of the two bands. Closure of the five-membered ring of phthalide and 1-indanone does not considerably affect the position

of the two bands similarly to the observation made in analogous compounds without such a ring (methyl benzoate or benzaldehyde – Table I).

Substitution of the aromatic nucleus with one electron donating group results in a red shift of all the bands which is of the same size as that of the hydroxyl and the methoxyl group (Table III). In disubstituted compounds, the greatest shifts are

TABLE I

UV Bands ( $\lambda$ , nm) of Benzene Derivatives Containing Electron Accepting Oxygen Substituents (in ethanol) and Their Shifts ( $\Delta\lambda$ , nm) vs Those of Analogous Bands of Benzene

Compounds	First primary band		Secondary band	
	$\lambda$	$\Delta\lambda$	$\lambda$	$\Delta\lambda$
Benzene	207	—	255	—
Benzaldehyde	246	39	281	26
Acetophenone	242	35	280	25
Benzoic acid	228	21	272	17
Methyl benzoate	228	21	276	21
Propenylbenzene	246	39	287	32
Styrene	244	37	288	33
<i>trans</i> -Cinnamic acid	274	67	296	41
Phthalide	227	20	277	22
1-Indanone	244	37	288	33
Phthalic acid	225	18	282	27
Phthalanhydride	246	39	286	31

TABLE II

Shift ( $\Delta\lambda$ , nm) of the First Primary and the Secondary Band (in ethanol) of Derivatives of *trans*-Cinnamic Acid and Propenylbenzene

Substituent	Band	<i>trans</i> -Cinnamic acid	Propenylbenzene	$\Delta\lambda$
4-OCH <sub>3</sub>	1st primary	293	259	34
	secondary	308	289	19
3,4-(OCH <sub>3</sub> ) <sub>2</sub>	1st primary	287	260	27
	secondary	318	293	25
3,4-OCH <sub>2</sub> O	1st primary	289	260	29
	secondary	324	304	20

TABLE III  
UV Bands ( $\lambda$ , nm) of Benzene Derivatives Containing Electron Donating Oxygen Substituents and Their Shifts ( $\Delta\lambda$ , nm) vs Those of Analogous Bands of Benzene

Substituents	Ethanol				Ethanol-0.1M-NaOH	
	first primary		secondary		first primary	secondary
	$\lambda$	$\Delta\lambda$	$\lambda$	$\Delta\lambda$	$\lambda$	$\lambda$
H	207	—	255	—	—	—
1-OH	219	12	273	18	239	290
1,2-(OH) <sub>2</sub>	218	11	287	23	241	292
1,3-(OH) <sub>2</sub>	219	12	276	21	239	288
1,4-(OH) <sub>2</sub>	225	18	295	40	245	273
1-OCH <sub>3</sub>	219	12	273	18	—	—
1,3-(OCH <sub>3</sub> ) <sub>2</sub>	225	18	275	20	—	—
1,3-(OCH <sub>3</sub> ) <sub>2</sub>	221	14	275	20	—	—
1,4-(OCH <sub>3</sub> ) <sub>2</sub>	226	19	290	35	—	—
1,2-OCH <sub>2</sub> O	232	25	282	27	—	—

observed in 1,4-isomers. The shifts of the bands of variously substituted benzene derivatives increase in the order  $1 < 1,3 < 1,2 < 1,4$ . This sequence holds good for both bands of the methoxy derivatives and for the secondary band of the hydroxy compounds. The shift of the first primary band of hydroxy derivatives increases in the order  $1,2 < 1 < 1,3 < 1,4$ . Substitution of the couple of *ortho*-methoxy groups for a methylenedioxy group results in a red shift of the two bands by c. 7 nm.

Substitution of the aromatic nucleus containing already one electron accepting group ( $-\text{CHO}$ ,  $-\text{COCH}_3$ ,  $-\text{COOH}$ ,  $-\text{COOCH}_3$ ,  $-\text{CH}=\text{CH}-\text{COOH}$ ) with an electron donating group (hydroxyl or methoxyl) causes another red shift of all the originally unsubstituted oxo compounds (Table IV). Contrary to other derivatives, the compounds with one electron donating substituent in the *para*-position vs the electron accepting group exhibit only a red shift of the first primary band. The position of the secondary band does not practically change. The resulting spectrum is then formed by one broad band which has arisen by overlapping of the first primary and the secondary band which in the bands of some compounds appear as shoulders<sup>17</sup>. The characteristic course of the absorption spectra of *para*-disubstituted compounds allows their differentiation from those of other isomers.

In derivatives substituted with one electron donating group, the red shift of the first primary band increases in dependence on the position of the substituent in the order *ortho* = *meta* < *para*. The shift of the secondary band increases in reverse order. The distance between the two bands, on the basis of which the position of the

TABLE IV

Shift ( $\Delta\lambda$ , nm) of UV Bands of Aromatic Oxo Compounds Due to Substitution with Electron Donating Groups

Substituent	First primary band				Secondary band			
	benzaldehyde	acetophenone	benzoic acid	<i>trans</i> -cinnamic acid	benzaldehyde	acetophenone	benzoic acid	<i>trans</i> -cinnamic acid
2-OH	9	9	6	0	46	45	30	30
3-OH	9	9	6	3	36	31	24	17
4-OH	40	35	26	18	5	-3	-18	15
2,3-(OH) <sub>2</sub>	<sup>a</sup>	<sup>a</sup>	18	14	<sup>a</sup>	<sup>a</sup>	42	39
2,4-(OH) <sub>2</sub>	35	35	27	12	33	35	23	28
2,5-(OH) <sub>2</sub>	13	15	6	4	86	87	60	59
2,6-(OH) <sub>2</sub>	<sup>a</sup>	28	21	<sup>a</sup>	<sup>a</sup>	64	32	<sup>a</sup>
3,4-(OH) <sub>2</sub>	35	34	26	25	34	27	21	30
3,5-(OH) <sub>2</sub>	9	23	23	<sup>a</sup>	53	41	38	<sup>a</sup>
2-OCH <sub>3</sub>	8	7	4	1	39	30	19	24
3-OCH <sub>3</sub>	8	7	3	2	32	26	22	13
4-OCH <sub>3</sub>	31	29	26	19	2	-9	-18	12
2,3-(OCH <sub>3</sub> ) <sub>2</sub>	14	9	7	5	42	26	22	24
2,4-(OCH <sub>3</sub> ) <sub>2</sub>	28	25	26	16	33	23	18	28
2,5-(OCH <sub>3</sub> ) <sub>2</sub>	11	8	<sup>a</sup>	1	74	56	<sup>a</sup>	50
2,6-(OCH <sub>3</sub> ) <sub>2</sub>	<sup>a</sup>	17	13	<sup>a</sup>	<sup>a</sup>	-21	8	<sup>a</sup>
3,4-(OCH <sub>3</sub> ) <sub>2</sub>	29	30	30	13	28	23	18	22
3,5-(OCH <sub>3</sub> ) <sub>2</sub>	29	21	21	<sup>a</sup>	44	38	29	<sup>a</sup>
2-OH, 3-OCH <sub>3</sub>	21	<sup>a</sup>	14	4	63	<sup>a</sup>	39	29
2-OH, 4-OCH <sub>3</sub>	31	31	25	18	33	34	22	32
2-OH, 5-OCH <sub>3</sub>	11	13	8	2	79	77	59	58
2-OH, 6-OCH <sub>3</sub>	<sup>a</sup>	30	23	23	<sup>a</sup>	60	39	1
3-OH, 4-OCH <sub>3</sub>	30	32	30	18	33	30	23	26
3-OH, 5-OCH <sub>3</sub>	<sup>a</sup>	<sup>a</sup>	17	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	26	<sup>a</sup>
2-OCH <sub>3</sub> , 5-OH	<sup>a</sup>	8	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	60	<sup>a</sup>	<sup>a</sup>
2-OCH <sub>3</sub> , 4-OH	<sup>a</sup>	34	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	24	<sup>a</sup>	<sup>a</sup>
3-OCH <sub>3</sub> , 4-OH	34	36	32	22	28	25	19	27
2,3-OCH <sub>2</sub> O	12	<sup>a</sup>	5	1	61	<sup>a</sup>	43	33
3,4-OCH <sub>2</sub> O	27	32	31	15	33	28	23	28

<sup>a</sup> The spectral data were unavailable to us.

substituents on the aromatic nucleus can be determined, amounts to c. 60 nm in *ortho*-disubstituted compounds, to c. 70 nm in *meta*-derivatives, and in *para*-derivatives it varies in the range from 0 to 10 nm.

In aromatic oxo compounds, the electron donating ability of the hydroxyl differs from that of the methoxyl group. Substitution with a hydroxyl group causes a greater shift of all three bands to the red than that observed after substitution with a methoxyl group. The same effect is also present in all oxo compounds containing two electron donating substituents; an exception is 3,4-dihydroxybenzoic acid whose first primary and the secondary band are shifted less to the red than those of 3,4-dimethoxybenzoic acid. In derivatives containing one of the electron donating groups in the position 4 (2,4- and 3,4-dihydroxy/dimethoxy derivatives), the shifts of the first primary band (similarly to those of the 4-hydroxy/methoxy derivatives) are significantly greater than those of the bands of 2,3, 2,5, 2,6, or 3,5 derivatives. In oxo compounds disubstituted by electron donating groups in various positions, the red

TABLE V

Shifts ( $\Delta\lambda$ , nm) of UV Bands of Phthalic Acid and Related Substances Due to Substitution with Electron Donating Groups

Substituent	First primary band			Secondary band		
	phthalide	1-inda- none	phthalic acid	phthalide	1-inda- none	phthalic acid
4-OH	<sup>a</sup>	13	31	<sup>a</sup>	24	15
5-OH	<sup>a</sup>	26	—	<sup>a</sup>	4	—
7-OH	5	9	—	22	27	—
3-OCH <sub>3</sub>	—	—	13	—	—	15
4-OCH <sub>3</sub>	2	<sup>a</sup>	29	15	<sup>a</sup>	3
5-OCH <sub>3</sub>	29	22	—	10	-1	—
6-OCH <sub>3</sub>	-1	4	—	21	38	—
7-OCH <sub>3</sub>	7	-4	—	19	7	—
3,4-(OCH <sub>3</sub> ) <sub>2</sub>	—	—	30	—	—	1
4,5-(OCH <sub>3</sub> ) <sub>2</sub>	33	37	45	14	-7	-12
5,6-(OCH <sub>3</sub> ) <sub>2</sub>	31	24	—	17	24	—
5,7-(OCH <sub>3</sub> ) <sub>2</sub>	29	31	—	13	10	—
6,7-(OCH <sub>3</sub> ) <sub>2</sub>	11	11	—	33	37	—
3,4-OCH <sub>2</sub> O	—	—	36	—	—	23
4,5-OCH <sub>2</sub> O	42	42	46	17	17	11
5,6-OCH <sub>2</sub> O	29	23	—	21	28	—
6,7-OCH <sub>2</sub> O	7	7	—	45	59	—

<sup>a</sup> The spectral data were unavailable to us.

shift of the first primary band increases in the order  $2,5 < 2,3 < 2,6 < 3,5 < 2,4 < 3,4$ . The red shift of the secondary band of dihydroxy derivatives increases in an almost reverse order  $3,4 = 2,4 < 2,6 < 3,5 < 2,3 < 2,5$ . The shift of the secondary

TABLE VI

Shifts ( $\Delta\lambda$ , nm) of UV Bands of Aromatic Oxo Compounds Substituted with Electron Donating Groups Due to Ionization

Substituent	First primary band				Secondary band			
	benzaldehyde	acetophenone	benzoic acid	<i>trans</i> -cinnamic acid	benzaldehyde	acetophenone	benzoic acid	<i>trans</i> -cinnamic acid
2-OH	11	5	-6	0	55	40	-5	39
3-OH	12	12	8	0	48	46	18	17
4-OH	50	52	25	21	50	52	25	25
2,3-(OH) <sub>2</sub>	<sup>a</sup>	<sup>a</sup>	4	1	<sup>a</sup>	<sup>a</sup>	15	107
2,4-(OH) <sub>2</sub>	55	58	17	<sup>a</sup>	22	20	4	<sup>a</sup>
2,5-(OH) <sub>2</sub>	9	16	2	27	50	40	-12	72
2,6-(OH) <sub>2</sub>	<sup>a</sup>	16	-3	<sup>a</sup>	<sup>a</sup>	48	-1	<sup>a</sup>
3,4-(OH) <sub>2</sub>	72	38	19	3	38	56	3	22
3,5-(OH) <sub>2</sub>	<sup>a</sup>	<sup>a</sup>	14	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	10	<sup>a</sup>
2-OCH <sub>3</sub> <sup>b</sup>	-	-	-5	-6	-	-	-12	-8
3-OCH <sub>3</sub>	-	-	-3	-6	-	-	-7	-4
4-OCH <sub>3</sub>	-	-	-9	-15	-	-	-9	-8
2,3-(OCH <sub>3</sub> ) <sub>2</sub>	-	-	-12	-6	-	-	-15	-9
2,4-(OCH <sub>3</sub> ) <sub>2</sub>	-	-	-9	-5	-	-	-8	-15
2,5-(OCH <sub>3</sub> ) <sub>2</sub>	-	-	<sup>a</sup>	-10	-	-	<sup>a</sup>	-18
2,6-(OCH <sub>3</sub> ) <sub>2</sub>	-	-	-14	<sup>a</sup>	-	-	-3	<sup>a</sup>
3,4-(OCH <sub>3</sub> ) <sub>2</sub>	-	-	-9	-4	-	-	-7	-7
3,5-(OCH <sub>3</sub> ) <sub>2</sub>	-	-	-6	<sup>a</sup>	-	-	-7	<sup>a</sup>
2-OH, 3-OCH <sub>3</sub>	15	<sup>a</sup>	-12	<sup>a</sup>	52	<sup>a</sup>	-7	<sup>a</sup>
2-OH, 4-OCH <sub>3</sub>	5	<sup>a</sup>	-5	-13	54	<sup>a</sup>	-1	17
2-OH, 5-OCH <sub>3</sub>	6	<sup>a</sup>	-6	-1	54	<sup>a</sup>	-11	31
2-OH, 6-OCH <sub>3</sub>	<sup>a</sup>	3	-5	-2	<sup>a</sup>	0	-11	<sup>a</sup>
3-OH, 4-OCH <sub>3</sub>	16	<sup>a</sup>	1	-3	51	<sup>a</sup>	16	24
3-OH, 5-OCH <sub>3</sub>	<sup>a</sup>	<sup>a</sup>	0	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	17	<sup>a</sup>
3-OCH <sub>3</sub> , 4-OH	14	17	26	10	45	43	6	25
3,4-OCH <sub>2</sub> O	-	-	-6	-7	-	-	-4	-10

<sup>a</sup> The spectral data were not available. <sup>b</sup> The methoxy and the methylenedioxy derivatives of benzaldehyde and acetophenone were not ionized under the conditions employed.

band in dimethoxy derivatives increases in the order  $2,6 < 3,4 = 2,4 < 2,3 < 3,5 < 2,5$ . In compounds with a methylenedioxy group, the secondary band is shifted to longer wavelengths *vs* those of the corresponding dimethoxy derivatives. The shift depends on the position of the methylenedioxy group. It is greater in 2,3-methylenedioxy than in 3,4-methylenedioxy derivatives.

The position of the bands depends on the strength of the conjugation of the electron accepting group with the  $\pi$ -electron system of the aromatic nucleus. In derivatives substituted both with electron donating and electron accepting groups the shifts of the bands increase in the order  $\text{COOH} < \text{COOCH}_3 < \text{COCH}_3 < \text{CHO} < \text{CH}=\text{CH}-\text{COOH}(\textit{trans})$  in the same manner as in the case of the benzene ring which does not carry any electron donating oxygen substituent (p. 2451). An exception is observed in the case of the first primary band of 2,5-dihydroxy, 2,5-dimethoxy, 3,4-dimethoxy, and 3,5-dihydroxy derivatives. A guide for the estimation of the position of the electron donating substituents *vs* the oxo group might be the distance between the first primary and the secondary band. In 2,3-derivatives, it is 60–80 nm, in 2,4-derivatives 36–40 nm, in 2,5-derivatives 80–100 nm, in 2,6-derivatives 60–70 nm, in 3,4-derivatives 30–35 nm, and in 3,5-derivatives 50–60 nm.

The dependence of the position of the bands on the position of the electron donating substituents *vs* the electron accepting group manifests itself in the derivatives

TABLE VII

Increments ( $\Delta\lambda$ ) Introduced into the Equation (I)–(9) for Plotting the Position of the Maxima of UV Bands of Compounds Containing Electron Accepting and Electron Donating Substituents

Electron accepting substituent X	Electron donating substituent Y, Z					
	2-OH	3-OH	4-OH	2-OCH <sub>3</sub>	3-OCH <sub>3</sub>	4-OCH <sub>3</sub>
First primary band						
H	12	—	—	12	—	—
CHO	9	9	40	8	8	31
COCH <sub>3</sub>	9	9	35	7	7	29
COOH	6	6	26	4	3	26
<i>trans</i> -CH=CH-COOH	0	3	18	1	2	19
Secondary band						
H	18	—	—	18	—	—
CHO	46	36	5	39	32	2
COCH <sub>3</sub>	45	31	—3	30	26	—9
COOH	30	24	—18	19	22	—18
<i>trans</i> -CH=CH-COOH	30	17	15	24	13	12



TABLE VIII

The Position of the First Primary Band ( $\lambda_{\text{exp}}$ ) and the Deviations ( $\delta$ ) of the Values Plotted According to the Equations (1)–(9)

Substituents	Benzaldehyde		Acetophenone		Benzoic acid		<i>trans</i> -Cinnamic acid	
	$\lambda_{\text{exp}}$	$\delta$	$\lambda_{\text{exp}}$	$\delta$	$\lambda_{\text{exp}}$	$\delta$	$\lambda_{\text{exp}}$	$\delta$
2,3-OH	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	246	-9	288	-8
2,4-OH	281	-1	277	-1	255	-1	286	+9
2,5-OH	259	+5	257	+3	234	+6	278	-1
2,6-OH	<i>a</i>	<i>a</i>	270	+2	249	+3	<i>a</i>	<i>a</i>
3,4-OH	281	+1	276	0	254	+2	299	-2
3,5-OH	255	+12	265	-2	251	-5	<i>a</i>	<i>a</i>
2,3-OCH <sub>3</sub>	260	-1	251	+3	235	+4	279	+4
2,4-OCH <sub>3</sub>	274	+3	267	+5	254	+1	290	+6
2,5-OCH <sub>3</sub>	257	+5	250	+6	<i>a</i>	<i>a</i>	275	+2
2,6-OCH <sub>3</sub>	<i>a</i>	<i>a</i>	259	+11	241	+9	<i>a</i>	<i>a</i>
3,4-OCH <sub>3</sub>	275	+2	272	0	258	+3	287	+9
3,5-OCH <sub>3</sub>	269	-1	263	0	249	-4	<i>a</i>	<i>a</i>
2-OH, 3-OCH <sub>3</sub>	267	-2	<i>a</i>	<i>a</i>	242	-4	278	+3
2-OH, 4-OCH <sub>3</sub>	277	+1	273	0	253	+3	292	+3
2-OH, 5-OCH <sub>3</sub>	257	+6	255	+3	236	+1	276	0
2-OH, 6-OCH <sub>3</sub>	<i>a</i>	<i>a</i>	272	-1	251	0	297	-9
3-OH, 4-OCH <sub>3</sub>	276	+2	274	-1	258	-2	292	+5
3-OH, 5-OCH <sub>3</sub>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	245	+2	<i>a</i>	<i>a</i>
2-OCH <sub>3</sub> , 4-OH	<i>a</i>	<i>a</i>	276	-1	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
2-OCH <sub>3</sub> , 5-OH	<i>a</i>	<i>a</i>	250	+8	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
3-OCH <sub>3</sub> , 4-OH	280	+2	278	-3	260	-5	296	0

*a* The spectral data were unavailable to us.

of 1-indanone and of the phthalide in a similar manner as in the compounds listed in the Tables I, III, and IV. Substitution with a methoxyl group in the position 5 (*para*-position in respect to the oxo group) leads to a shift of the first primary band of 1-indanone and of that of the phthalide which is similar to the shift of the band of benzoic acid containing a substituent in the position 4. The substituent in the position 7, *i.e.* in the *ortho*-position to the oxo group, exhibits a similar shift (Table V) as the substituents in the position 2 or 3 in benzaldehydes and in benzoic acid, respectively. The secondary band of phthalides and that of 1-indanones substituted with one electron donating group shows, similarly to that of benzaldehyde or benzoic acid, the smallest shift on substitution in the *para*-position in respect to the oxo group (position 5). The greatest red shift is observed in 6-substituted 1-indanones and phthalides.

In derivatives of 1-indanone and phthalide substituted with a pair of *ortho*-methoxyl groups, the red shift of the first primary band increases in the order  $6,7 < 5,6 < 4,5$ , the shifts of the secondary band change in the reverse order. A similar dependence of band shifts is also observed in phthalides and in 1-indanones, substituted with a methylenedioxy group in the positions 4,5 or 5,6 or 6,7.

In phthalic acid, the displacement of the first primary band is greater on substitution with a methoxyl group in the position 4 (in the *para*-position *vs* one of the carboxyl groups) than that observed on substitution in the position 3 (in the *ortho*-position *vs* the carboxyl group). The dependence of the position of the secondary band on the position of the methoxyl group increases in the reverse order  $4 < 3$ . In derivatives disubstituted with methoxyl or methylenedioxy groups, the red shift of the first primary band changes in the order  $3,4 < 4,5$ , whereas the shift of the secondary band in the reverse order.

### *The Effect of Ionization*

Ionization of 1-, 1,2-, and 1,3-hydroxybenzenes (without an electron accepting group) in ethanolic alkaline medium also leads to red shifts of the absorption bands: the first primary band shifts by c. 20 nm, the secondary band by c. 15 nm. Ionization of 1,4-dihydroxy derivatives results in a blue shift of the secondary band (Table III).

The effect of ionization of the hydroxyl group in ethanolic alkaline medium on the UV spectra of aromatic compounds was observed for the first time in hydroxy derivatives of benzaldehyde, acetophenone, and in methyl benzoates (Table VI). Ionization of the hydroxyl group, due to an increase in the conjugation of nonbonded electrons of the oxygen anion with  $\pi$ -electrons of the aromatic system, results in a considerable red shift of all the bands in comparison with the shifts in the spectra of the same non-ionized compounds. The shift of the first primary and the secondary band depends on the position of the substituents on the nucleus and on the type of the electron accepting group similarly to that in non-ionized compounds. In 4-hydroxy derivatives, in alkaline medium, the complete broad band (the first primary and the secondary band) is displaced and it does not come to its splitting. In disubstituted derivatives with a hydroxyl group in the position 4, the two longer wavelength bands are overlapping thus giving rise to an intensive band of similar pattern as that of 4-hydroxy derivatives.

The effect produced by ionization of the carboxyl group on the UV absorption bands was studied in unsubstituted benzoic acid, in *trans*-cinnamic acid, and their methoxy derivatives. Ionization of the carboxyl group leads to a blue shift of the first primary and the secondary band. In unsubstituted acids, the value of this shift is lower than that in derivatives with one or two methoxyl groups. In ethanolic alkaline medium, the presence of a hydroxyl and a carboxyl group on the aromatic nucleus results in a combination of the effects of these two groups. Since the red

shift, which is due to the effect of ionization of the hydroxyl group, is greater than the blue shift caused by ionization of the carboxyl group, the spectra of hydroxy acids are shifted somewhat to higher wavelengths if compared with those of non-ionized acids. An exception are the absorption bands of 2-hydroxybenzoic and 2,6-dihydroxybenzoic acids which undergo a blue shift in ethanolic alkaline medium. In 2-hydroxy derivatives of *trans*-cinnamic acid, only a blue shift of the first primary band is observed.

*An Attempt to Plot Empirically the Position of the First Primary and the Secondary Band*

So far, the empirical plotting of the position of the absorption bands of benzene derivatives has been tackled by many authors<sup>16</sup>. However, they did not succeed to establish the rule on the basis of which the position of the absorption maxima could be predicted in the larger scope of aromatic compounds.

Scott<sup>16</sup> described the plotting of the position of the first primary band of substituted benzaldehydes and acetophenones by adding the increments of the corresponding electron donating substituents to the value corresponding to the position of the absorption maxima of unsubstituted oxo-compounds. In the sterically hindered derivatives, the deviations of the plotted and measured values reached up to  $\pm 20$  nm. The additive principle was also made use of for the plotting of the position of the secondary band of some aromatic compounds with methoxyl and methylenedioxy groups where the benzene nucleus was not conjugated with another  $\pi$ -electron system<sup>19</sup>. Doub and Vandenberg<sup>6</sup> derived the equation for the plotting of the position of the first primary band of substituted benzene derivatives. These authors could, however, confirm the validity of this equation only for the *para*-disubstituted derivatives containing one electron accepting and one electron donating group.

On the basis of the already published<sup>1-5</sup> UV data, we undertook to plot empirically the position of the first primary and the secondary band of aromatic compounds substituted with hydroxyl and methoxyl groups. For the plotting, use was made of the position of the maximum of the band of the unsubstituted oxo compound ( $\lambda_{\max}$ ) and the increments of the hydroxyl and the methoxyl groups ( $\Delta\lambda$ ). In derivatives of benzaldehyde, acetophenone, benzoic and *trans*-cinnamic acid, it is possible to plot the resulting position of the bands of the disubstituted oxo compound by combination of these values according to the equations (1)–(9)

$$\lambda(X_1Y_2Z_3)_I = \lambda(X_1)_I + \frac{1}{2}[\Delta\lambda(X_1Y_2)_I + \Delta\lambda(Y_1Z_2)_I], \quad (1)$$

$$\lambda(X_1Y_2Z_3)_{II} = \lambda(X_1)_{II} + \Delta\lambda(X_1Y_2)_{II}, \quad (2)$$

$$\lambda(X_1Y_2Z_4)_{I,II} = \lambda(X_1)_{I,II} + \frac{1}{2}[\Delta\lambda(X_1Y_2)_{I,II} + \Delta\lambda(X_1Y_4)_{I,II} + \Delta\lambda(Y_1)_{I,II} + \Delta\lambda(Z_1)_{I,II}], \quad (3)$$

$$\lambda(X_1 Y_2 Z_5)_{I,II} = \lambda(X_1)_{I,II} + \Delta\lambda(X_1 Y_2)_{I,II} + \Delta\lambda(X_1 Z_3)_{I,II}, \quad (4)$$

$$\lambda(X_1 Y_2 Z_6)_I = \lambda(X_1)_I + \Delta\lambda(X_1 Y_2)_I + \Delta\lambda(X_1 Z_2)_I + \Delta\lambda(Y_1 Z_3)_I, \quad (5)$$

$$\lambda(X_1 Y_2 Z_6)_{II} = \lambda(X_1)_{II} + \Delta\lambda(X_1 Y_2)_{II}, \quad (6)$$

$$\lambda(X_1 Y_3 Z_4)_{I,II} = \lambda(X_1)_{I,II} + \frac{1}{2}[\Delta\lambda(X_1 Y_3)_{I,II} + \Delta\lambda(X_1 Z_4)_{I,II} + \Delta\lambda(Y_1)_{I,II} + \Delta\lambda(Z_1)_{I,II}], \quad (7)$$

$$\lambda(X_1 Y_3 Z_5)_I = \lambda(X_1)_I + \Delta\lambda(X_1 Y_3)_I + \Delta\lambda(Y_1 Z_3)_I, \quad (8)$$

$$\lambda(X_1 Y_3 Z_5)_{II} = \lambda(X_1)_{II} + \Delta\lambda(X_1 Y_3)_{II} + \frac{1}{2} \Delta\lambda(Y_1 Z_3)_{II}, \quad (9)$$

TABLE IX

The Position of the Secondary Band ( $\lambda_{exp}$ ) and the Deviations ( $\delta$ ) of the Values Plotted According to the Equations (4)–(9)

Substituents	Benzaldehyde		Acetophenone		Benzoic acid		<i>trans</i> -Cinnamic acid	
	$\lambda_{exp}$	$\delta$	$\lambda_{exp}$	$\delta$	$\lambda_{exp}$	$\delta$	$\lambda_{exp}$	$\delta$
2,3-OH	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	314	-12	335	-9
2,4-OH	314	+10	315	+4	295	+1	324	+12
2,5-OH	367	-4	367	-11	332	-6	355	-12
2,6-OH	<sup>a</sup>	<sup>a</sup>	344	-19	304	-2	<sup>a</sup>	<sup>a</sup>
3,4-OH	315	+4	307	+5	293	0	326	+4
3,5-OH	334	-6	321	0	310	-3	<sup>a</sup>	<sup>a</sup>
2,3-OCH <sub>3</sub>	323	-3	306	+4	294	-3	320	0
2,4-OCH <sub>3</sub>	314	+5	303	+5	290	0	324	+8
2,5-OCH <sub>3</sub>	355	-3	336	0	<sup>a</sup>	<sup>a</sup>	346	-13
2,6-OCH <sub>3</sub>	<sup>a</sup>	<sup>a</sup>	270	+50	280	+11	<sup>a</sup>	<sup>a</sup>
3,4-OCH <sub>3</sub>	309	+7	303	+3	290	+2	318	+8
3,5-OCH <sub>3</sub>	325	-2	318	-2	301	+3	<sup>a</sup>	<sup>a</sup>
2-OH, 3-OCH <sub>3</sub>	344	-17	<sup>a</sup>	<sup>a</sup>	311	-9	325	+1
2-OH, 4-OCH <sub>3</sub>	314	+9	314	+2	294	+2	328	+7
2-OH, 5-OCH <sub>3</sub>	360	-1	357	-6	331	-7	339	-15
2-OH, 6-OCH <sub>3</sub>	<sup>a</sup>	<sup>a</sup>	340	-15	311	-9	297	-29
3-OH, 4-OCH <sub>3</sub>	314	+4	310	-1	295	-2	322	+6
3-OH, 5-OCH <sub>3</sub>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	298	+7	<sup>a</sup>	<sup>a</sup>
2-OCH <sub>3</sub> , 4-OH	<sup>a</sup>	<sup>a</sup>	304	+7	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
2-OCH <sub>3</sub> , 5-OH	<sup>a</sup>	<sup>a</sup>	340	+1	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>
3-OCH <sub>3</sub> , 4-OH	309	+8	305	+4	291	+1	323	+5

<sup>a</sup> The spectral data were unavailable to us.

TABLE X  
Plotting of the Position of the First Primary and the Secondary Bands of Phthalide and 1-Indanone

Substituent	First primary band				Secondary band			
	phthalide		1-indanone		phthalide		1-indanone	
	$\lambda_{\text{exp}}$	$\Delta\lambda$	$\lambda_{\text{exp}}$	$\Delta\lambda$	$\lambda_{\text{exp}}$	$\Delta\lambda$	$\lambda_{\text{exp}}$	$\Delta\lambda$
4-OCH <sub>3</sub>	229	+2	256	+12	292	+15	<sup>a</sup>	<sup>a</sup>
5-OCH <sub>3</sub>	256	+29	266	+22	287	+10	287	-1
6-OCH <sub>3</sub>	226	-1	248	+4	298	+21	320	+32
7-OCH <sub>3</sub>	234	+7	240	-4	296	+19	295	=7
	$\lambda_{\text{exp}}$	$\delta$	$\lambda_{\text{exp}}$	$\delta$	$\lambda_{\text{exp}}$	$\delta$	$\lambda_{\text{exp}}$	$\delta$
4,5-(OCH <sub>3</sub> ) <sub>2</sub>	260	-2	281	-3	291	-1	<sup>a</sup>	<sup>a</sup>
5,6-(OCH <sub>3</sub> ) <sub>2</sub>	258	-3	268	+2	294	-1	312	-9
5,7-(OCH <sub>3</sub> ) <sub>2</sub>	256	+7	275	-13	290	+2	298	-7
6,7-(OCH <sub>3</sub> ) <sub>2</sub>	238	-4	255	-11	310	+7	325	+2

<sup>a</sup> In the spectrum the secondary band is not discernible.

where X is the electron accepting substituent ( $-\text{CHO}$ ,  $-\text{COCH}_3$ ,  $-\text{COOH}$ , *trans*- $\text{CH}=\text{CH}-\text{COOH}$ ), Y and Z are the electron donating substituents ( $-\text{OH}$ ) and/or  $-\text{OCH}_3$ ). The subscripts 1 to 6 denote the relative position of the corresponding substituent *vs* the substituent preceding the symbol, the subscript I refers to the first primary band, the subscript II to the secondary band;  $\Delta\lambda$  is the difference between the position of the band of a compound with a given substitution with electron donating substituents and that of a compound without this substitution, however, with the same electron accepting group. The increment shows the influence upon the band produced by a specific substitution with an electron donating substituent.

While plotting the position of the bands of disubstituted phthalides and 1-indanones, we have found that the position of the first primary band can be plotted by adding the corresponding increments ( $\Delta\lambda$ ) of the methoxyl groups to the position of the absorption maxima of the band of the unsubstituted compound. Similarly, it is possible to plot the position of the secondary band of the derivatives of 1-indanone and of phthalide containing substituents in the positions 6,7. In these compounds where the substituent is also present in the position 5, the theoretical values of the position of the secondary band is obtained according to the equation (10)

$$\lambda(W_1 Y_5 Z_{4 \text{ or } 6 \text{ or } 7})_{II} = \frac{1}{2}[\lambda(W_1 Y_5)_{II} + \lambda(W_1 Z_{4 \text{ or } 6 \text{ or } 7})_{II}] , \quad (10)$$

where W is the oxo group of the phthalide or 1-indanone.

In 5,7-dimethoxy-1-indanone<sup>20</sup>, the plotted value differs from the experimental value of the first primary band by 13 nm and in the secondary band by 7 nm. The Tables VII and X give a survey of the increments for plotting the position of the bands.

In such a manner it was possible, with a few exceptions, to obtain values which were in agreement with the experimental data (Tables VIII, IX, and X). A greater difference between the plotted and the experimental values was found in the secondary bands of some 2,5- and 2,6-disubstituted derivatives. These differences were caused by steric interaction of the electron accepting group with two electron donating groups in the *ortho*-position on both sides (2,6-disubstituted compounds) and by the *para*-position of two electron donating groups whereby to one of them an electron accepting group was added in the *ortho*-position (2,5-disubstituted compounds).

#### REFERENCES

- Hruban L., Šantavý F.: This Journal 32, 3414 (1967).
- Šantavý F., Hruban L., Šimánek V., Walterová D.: This Journal 35, 2418 (1970).
- Hruban L., Šantavý F., Hegerová S.: This Journal 35, 3240 (1970).
- Šantavý F., Walterová D., Hruban L.: This Journal 37, 1825 (1972).
- Šantavý F., Hegerová S., Hruban L., Klásek A., Němečková A., Šimánek V., Walterová D.: Acta Univ. Olomouc., Fac. Med. Suppl. XIII, 1973.
- Doub L., Vandebelt J. M.: J. Am. Chem. Soc. 69, 2741 (1947).
- Doub L., Vandebelt J. M.: J. Am. Chem. Soc. 71, 2414 (1949).
- Doub L., Vandebelt J. M.: J. Am. Chem. Soc. 77, 4535 (1955).
- Morton R. A., Sawires Z.: J. Chem. Soc. 1940, 1052.
- Tanaka J., Nagakura S.: J. Chem. Phys. 24, 1274 (1956).
- Dearden J. C., Forbes W. F.: Can. J. Chem. 36, 1362 (1958).
- Murrell J. N.: J. Chem. Soc. 1956, 3779.
- Heilbronner E., Gerdil R.: Helv. Chim. Acta 39, 1996 (1956).
- Moser C., Kohlenberg A. I.: J. Chem. Soc. 1951, 804.
- Conover L. H.: Chem. Soc. (London), Special Publications 5, 48 (1956).
- Scott A. I.: Interpretation of the Ultraviolet Spectra of Natural Products, p. 89. Pergamon Press, London 1964.
- Castille A., Klingstedt F. W.: Compt. Rend. 176, 749 (1923).
- Aulin-Erdtman G., Sandén R.: Acta Chem. Scand. 22, 1187 (1958).
- Láng L., Bárczai B. M.: Period. Polytech. 8, 261 (1964).
- Huisgen R., Seidl G., Wimmer I.: Liebigs Ann. Chem. 677, 21 (1964).

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