ELECTRON SPECTRA OF 1-TETRALONE, HOMOPHTHALIDE, 3,4-DIHYDROISOQUINOLINE, AND 3,4-DIHYDROISOQUINOLINIUM COMPOUNDS*

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The electron spectra of 1-indanone (*I*), 1-tetralone (*II*), phthalide (*III*), homophthalide (*IV*) 3,4-dihydroisoquinoline (*VII*), and 3,4-dihydroisoquinolinium (*VIII*) compounds, substituted by electron donating groups (hydroxy, methoxy or methylenedioxy groups) on the aromatic nucleus, resemble when the electron donors are at the same distance from the electron accepting substituent. In the compounds *VII* and *VIII*, the electron spectra were measured in ethanol at acidic and alkaline pH, and the change in the spectra of the compounds *VIII* in alkaline medium was clarified.

In the previous papers of this series we reported on the electron spectroscopy of aromatic and heterocyclic compounds (particularly alkaloids) substituted by hydroxy, methoxy, and methylenedioxy groups[1-7]. Some rules have been inferred which can be made good use of when so far unknown compounds are studied[2-4]. In simple aromatic, 1-indanone (*I*) and phthalide (*III*) compounds, the position and the intensity of the *A* and *B* bands of the electron spectrum are affected particularly by electron donating substituents in the *ortho* or *para* positions to the electron accepting substituent of the aromatic nucleus (summarizingly[1]). The alkyl substituents of the aromatic nucleus have no significant effect as long as they are not in the *ortho-ortho*-position (positions 2 and 6) to the electron donating or electron accepting substituents[1,7,8]. When the aromatic nucleus of the compound is substituted by two electron donating oxygen substituents, the resulting electron spectrum consists of the spectra of both monosubstituted compounds. The determination of the effect of the position of the methoxy/methylenedioxy groups in the 1-tetralone (*II*), homophthalide (*IV*), 3,4-dihydroisoquinoline (*VII*), and 3,4-dihydroisoquinolinium (*VIII*) compounds could not be brought to an end because the quantity of the material for comparison was too small[2].

The purpose of our paper has been to study the effect on the UV spectra of the following:

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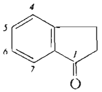
* Part X in the series Ultraviolet Spectra, Methoxy, and Methylenedioxy Groups of Some Aromatic Compounds and Alkaloids; Part IX: Acta Univ. Palacki Olomuc., Fac. Med. *90*, 45 (1979).

a) the widening of the ring B in 1-indanone (*I*) and phthalide (*III*) compounds on 1-tetralone (*II*), and homophthalide (*IV*) compounds, respectively;

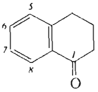
b) whether even the 1-tetralone and homophthalide compounds substituted by two *ortho* methoxy/methylenedioxy groups are subject to the same rules as indanone and phthalide compounds;

c) whether even the UV spectra of the disubstituted compounds *II*, *IV*, *VII*, and *VIII* are a superposition of those of monosubstituted compounds with electron donating oxygen groups;

d) in 3,4-dihydroisoquinoline (*VII*) and 3,4-dihydroisoquinolinium (*VIII*) compounds we attempted to verify the validity of the assumption regarding the pH effect on the UV spectra.



I



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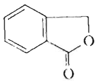

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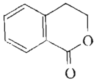

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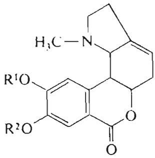
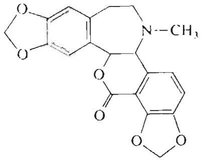
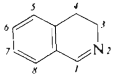


V

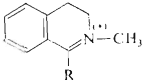


VI

Va, $R^1 = R^2 =$ Ma
Vb, $R^1 + R^2 = CH_2$
Vc, $R^1 + R^2 = CH_2$, hydroxyl group at C(5)



VII



VIII

EXPERIMENTAL

The spectra were measured on a Unicam SP 700, spectral slit width 0·45 nm at 230 nm, 0·65 nm at 300 nm, 0·8 nm at 400 nm, and 0·9 nm at 500 nm. The substance (0·5 mg, weighed with an accuracy of 0·01 mg) was dissolved in 96% ethanol to a concentration of 10^{-4}M. The ethanolic solution (2·5 ml) of some of the compounds was acidified or made alkaline with 0·1M-HCl or 0·1M-NaOH (0·4 ml). The solutions were measured in 1·00 cm silica cells; for higher ε-values than 17 000, cells of 0·20 cm length were used or the solution was diluted to a concentration of 10^{-5}M and measured in 1·00 cm cells.

The results obtained from the measurements are given in Tables I and II. The values taken from the literature were quoted with the designation of the compounds and with reference to the original papers.

RESULTS

There were studied the spectra of six 1-tetralones (Group II) (Tables I and II)[1,11–14,20]. The spectrum of 5,6-dimethoxy-1-tetralone[14] (*IIf*) was similar to that of 4,5-dimethoxy-1-indanone[3] (*If*). Furthermore, the spectrum of 5,8-dimethoxy-1-tetralone[11] (*IIh*) did not resemble that of 4,7-dimethoxy-1-indanone[22] (*Ih*). A comparison of the spectrum of the substance *Ih* with the spectra of the other compounds in this paper showed, however, that the UV spectrum of the compound *IIh* which has been taken over from the literature[11] was incorrect (the solvent had not been given).

The position and the intensity of the *A* and *B* bands in the spectra of 6,7-, 6,8-dimethoxy-, 6,7-methylenedioxy-, and 7,8-methylenedioxy-1-homophthalides (Group IV) greatly resembled those of the corresponding phthalides (Group III)[1,3]. In compounds disubstituted in the positions 6,7 and 7,8 either with methoxy or methylenedioxy groups, the two above mentioned bands were shifted by c. 10 nm bathochromically *vs* the phthalides *III* (Table II). The spectra of these compounds resembled those of the alkaloids homolycorine (*Va*), masonine (*Vb*), and hippeastrine[9] (*Vc*). The electron spectrum of oxyrhoeagenine[10] (*VI*) with the methylenedioxy group in the *ortho*-position to the carbonyl group was conform to that of the corresponding homophthalide. Even in these compounds the effect of the methylenedioxy groups *vs* the *ortho*-methoxy groups was the same as that observed in other aromatic compounds (summarizingly[1]).

The spectra of 3,4-dihydroisoquinoline (Group VII) and 3,4-dihydroisoquinolinium (Group VIII) compounds (in acidic medium) were analyzed by using those of ten compounds (Table II), four of which (6,7-, 7,8-dimethoxy-, 6,7-methylenedioxy-, and 6,7-methylenedioxy-8-methoxy derivatives) were measured in our laboratories and in those abroad[2,15,16]. The spectra of the other compounds were taken over from the literature. A comparison of the spectra of these 3,4-dihydroisoquinoline compounds with those of 1-indanone, 1-tetralone, phthalide, and homophthalide compounds and the well known structures of the compounds *VIIc*, *VIIf*, *VIIIa*–*VIIId* allowed to draw the following conclusions. All the spectra given in Table II were characterized particularly by the position of the substituents in the *ortho* and the *para* position to the double bond of the ring B, and we could make them up of the spectra of monosubstituted compounds. In the 5,6- and 6,7-disubstituted compounds, the band *A* was shifted *vs* that of indanone (*I*) compounds by about 45 nm bathochromically. In compounds carrying an oxygen electron donating substituent in the position 8, we noticed a large bathochromic shift of the *A* band the intensity of which was comparatively low (Table II, Figs 1 and 3).

TABLE I

UV-Spectra of Unsubstituted and Monomethoxy Substituted Compounds (λ_{max} in nm, ε values are given in parentheses)

Position of substituents: Indanone Phthalide (Tetralone)	1-Indanone *I*	1-Tetralone *II*	Phthalide *III*
—	*Ia* (ref.[19])	*IIa* (ref.[20])	*IIIa* (ref.[21])
	244 (14 500)	248 (12 500)	227 (10 000)
	286 (3 000)	291 (1 600)	273 (1 700)
	291 (3 100)	325 (600) s	280 (1 700)
	Ib (ref.[22])	*IIb* (ref.[12])	*IIIb*
	225 (26 000)[a]	257 (12 600)	214 (32 400)
4	258 (8 700)		229 (7 000)
(5)	313 (2 700)		292 (2 900)
	Ic (ref.[23])	*IIc* (ref.[13])	*IIIc*
5	266 (2 100)[b]	225 (12 300)	210 (15 900)
(6)	287 (1 550)	274 (15 100)	215 (12 800) s
			256 (11 000)
			276 (3 600) s
			287 (1 600)
	Id	*IId* (ref.[13])	*IIId*
6	219 (19 700)	225 (19 500)	211 (31 600)
(7)[c]	248 (8 900)	252 (10 200)	226 (7 250) s
	320 (4 100)	320 (2 300)	298 (3 600)
	Ie (ref.[24])		*IIIe* (ref.[26])
7	240 (6 300)[a]	—	209 (33 000)
(8)	295 (2 000)		234 (8 100)
			296 (4 700)

[a] Hydroxy derivative; [b] solvent not given; [c] 1-homophthalide *IVd* (ref.[25]) 248 nm (ε = 1 500) and 276 nm (ε = 1 350).

TABLE II

UV-Spectra of Di- and Trisubstituted Compounds

Position of substituents		1-Indanone (*I*)	1-Tetralone (*II*)	Phthalide (*III*)	Homo-pthalide (*IV*)	3,4-Dihydroisoquinoline (*VII*)		N-Methyl-3,4-dihydro-isoquinolinium (*VIII*)	
Indanone Phthalide	tetralone homo-phthalide 3,4-dihydro-isoquinoline derivatives					$C_2H_5OH.HCl$	C_2H_5OH. 0·1M-NaOH	C_2H_5OH. HCl	C_2H_5OH. 0·1M-NaOH
		If	*IIf* (ref.[14])	*IIIf*		*VIIa* (ref.[16])	*VIIa* (ref.[16])		
4,5- $-(CH_3O)_2$	5,6- $-(CH_3O)_2$	230 (22 900) 281 (13 800)	232 (18 200) 281 (13 200)	221 (26 300) 260 (11 000) 291 (1 500) s	—	210 (15 400) 238 (5 800) 279 (5 500) s 327 (13 600)	215 (15 200) 262 (13 700)	—	—
		Ig		*IIIg* (ref.[9])					
4,5- $-CH_2O_2$	5,6- $-CH_2O_2$	236 (23 400) 286 (6 300) 307 (4 900) s	—	24 (28 200) 269 (6 200) 294 (4 900)	—	—	—	—	—
		Ih (ref.[22])	*IIh* (ref.[11])			*VIIb* (ref.[16])	*VIIb* (ref.[16])		
4,7- $-(CH_3O)_2$	5,8- $-(CH_3O)_2$	220 (17 400)[a] 230 (17 000) 278 (17 400)	228 (20 000)[b] 253 (7 200) 338 (4 200)	—	—	215 (18 300)[c] 235 (8 550) s 298 (12 100) 408 (6 000)	225 (14 500) s[c] 263 (9 600) 333 (5 300)	—	—
		Ii		*IIIi* (ref.[28])	*Va* (ref.[9])	*VIIc* (ref.[15])	*VIIc*	*VIIIa*	*VIIIa*
5,6- $-(CH_3O)_2$	6,7- $-(CH_3O)_2$	210 (16 600) 229 (17 800) 268 (11 200) 312 (10 000)	—	220 (24 100) 258 (9 400) 294 (7 200)	226 (26 300) 267 (9 300) 302 (5 600)	244 (17 800) 306 (10 000) 355 (8 500)	230 (16 200) 272 (9 600) 303 (8 200)	244 (22 400) 308 (10 800) 358 (10 000)	222 (18 200) 285 (3 500)

5,6- $-CH_2O_2$	6,7- $-CH_2O_2$	*Ij* 231 (15 900) 267 (7 100) 316 (8 900)	—	*IIIj* (ref.[28]) 220 (21 900) 256 (5 400) 298 (7 300)	*Vb* (ref.[9]) 226 (22 900) 268 (5 600) 307 (5 750)	—	—	*VIIIb* 244 (17 800) 306 (10 000) 355 (8 500)	*VIIIb* 234 (4 550) 293 (4 700)
5,7- $-(CH_3O)_2$	6,8- $-(CH_3O)_2$	*Ik* 226 (22 400) 275 (18 600) 298 (6 400)	—	*IIIk* (ref.[30]) 216 (37 000) 256 (15 900) 290 (5 250)	*IVf* (ref.[31]) 216 (23 000)[d] 267 (14 800) 302 (6 050)	*VIIe* (ref.[16]) 223 (15 800) 306 (8 100) 385 (1 700)	—	—	—
6,7- $-(CH_3O)_2$	7,8- $-(CH_3O)_2$	*Il* 219 (22 900) 255 (9 550) 325 (3 550)	—	*IIIl* (ref.[29]) 238 (7 950) s 310 (4 000)	*VI* 223 (22 900) 243 (10 900) s 292 (6 900) 325 (4 400)	*VIIf* (ref.[2,16]) 237 (11 500) 293 (9 550) 374 (2 200)	*VIIf* (ref.[16]) 224 (24 000) 260 (7 400) 322 (2 100)	*VIIIc* 219 (26 900) 244 (10 700) 300 (10 700) 380 (2 400)	*VIIIc* 223 (20 800) s254 (2 700) 287 (2 700)
6,7- $-CH_2O_2$	7,8- $-CH_2O_2$	*Im* 232 (20 000) 247 (10 300) 256 (10 400) 347 (3 550)	—	*IIIm* 221 (24 600) 234 (7 950) 322 (4 600)	—	—	—	—	—
	6,7- $-CH_2O_2$ 8-CH_3O	—	—	—	—	*VIIg* (ref.[15]) 252 (12 400) 330 (13 900) 370 (4 100) s	—	*VIIId* (ref.[2,15]) 252 (9 600) 334 (12 000) 375 (3 600) s	*VIIId* (ref.[2,15]) 219 (16 600) 230 (7 250) s 287 (1 900)

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[a] Dihydroxy compounds; [b] solvent not given; [c] 2-propanol; [d] hydroxy-methoxyhomophthalide-3-methyl.

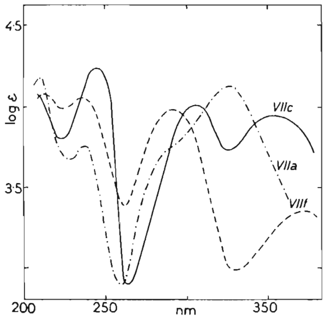

FIG. 1

UV Spectra of 5,6- (*VIIa*); 6,7- (*VIIc*) and 7,8-Dimethoxy-3,4-dihydroisoquinolines (*VIIf*) (hydrochlorides in ethanol)

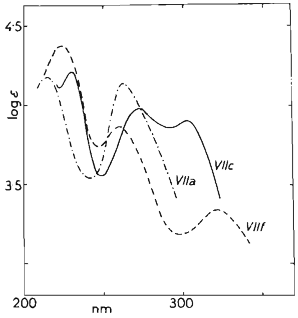

FIG. 2

UV Spectra of 5,6- (*VIIa*); 6,7- (*VIIc*) and 7,8-Dimethoxy-3,4-dihydroisoquinoline (*VIIf*) in Ethanol Containing 0·1M-NaOH

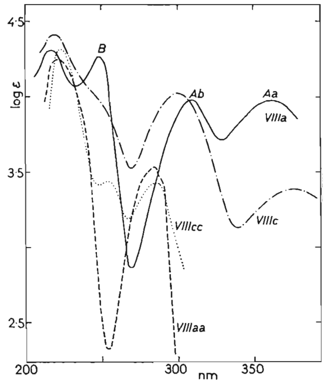

FIG. 3

UV Spectra of 6,7- and 7,8-Dimethoxy-3,4-dihydroisoquinolinium Salts in Acidic (*VIIIa* and *VIIIc*) or in Alkaline Medium (*VIIIaa* and *VIIIcc*)

There was some resemblance between the spectra of the corresponding couples of compounds with substituents in the positions 6,7- and 7,8- of 3,4-dihydroisoquinoline (*VII*) and those of N-methyl-3,4-dihydroisoquinolinium (*VIII*) compounds in acidic medium. In the spectrum of 6,7-dimethoxy-3,4-dihydroisoquinoline hydrochloride, the band *Aa* at *c.* 355 nm increased with increasing concentration of the hydrogen ions. In 3,4-dihydroisoquinoline and 3,4-dihydroisoquinolinium compounds the *Ab* band corresponded to transitions in the aromatic nucleus conjugated with the double bond of the ring B. This band remained maintained in alkaline medium even though it was shifted hypsochromically and hypochromically (Figs 1 and 2). The effect of the methylenedioxy groups *vs* the *ortho*-dimethoxy groups (hyperchromic and bathochromic shifts of the band *Aa* of methylenedioxy derivatives) manifested itself in 3,4-dihydroisoquinoline compounds with substituents in the positions 6,7 only slightly as was shown in 1-indanone (*I*) or phthalide (*III*) compounds[1,2,5].

On the basis of our analyses, the 5,7- and 6,8-dimethoxy-3,4-dihydroisoquinoline compounds[16] have the methoxy substituents in the positions 6,8- and 6,7.

The spectra of 5,6-, 6,7-, and 7,8-dimethoxy-3,4-dihydroisoquinoline compounds (in alkaline ethanolic medium) resembled those of their salts with that difference that the individual bands *A* and *B* in the spectra of the bases were hypsochromically shifted into the range from 300 to 325 nm (Table II, Figs 1 and 2). There was maintained particularly the same number of bands. From that followed that those compounds did not form carbinol forms[17,18] in alkaline ethanolic medium and the resulting spectrum corresponded to that of the analogously substituted indanone (*I*) or 1-tetralone (*II*) compounds. On the contrary, the carbinol form was formed (in alkaline ethanolic medium) by all the studied N-methyl-3,4-dihydroisoquinolinium compounds *VIII* (Table II, Fig. 3). In the spectra of those compounds, the bands *Aa* and *Ab* fused and they resembled the spectra of the similarly substituted benzene. In acidic ethanolic medium, the spectrum of 6,7-methylenedioxy-8-methoxy-N-methyl-3,4-dihydroisoquinoline (cotarnine) (*VIIId*) consisted of the spectra of 6,7- and 7,8-disubstituted compounds (Table II). The bands *Aa* and *Ab* of this compound were fused into one band, and at 375 nm a band of a considerably lower intensity appeared which corresponded to the substituent in position 8. In the disubstituted compounds *VIIIa* and *VIIIb*, the carbinol form showed the effect of the methoxy and the methylenedioxy group on the band *A*.

Widening of the ring between 1-indanone and 1-tetralone, or between phthalide and homophthalide had no significant effect on the position and the intensity of the *A* and the *B* band. In homophthalides *vs* phthalides this shift was *c.* 10 nm.

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