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INFLUENCE OF SOLVENTS ON THE ABSORPTION SPECTRA OF HYDROXYANTHRAQUINONES*

by

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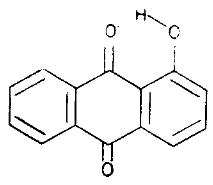
INTRODUCTION

The absorption (ultraviolet and visible) spectra of hydroxyanthraquinones have been investigated by a number of authors (1—6), but the solvent effects have not received much attention, except in the early work of Lauer and Horio (1) in which instrumental limitations have affected the accuracy of the measurements. We, therefore, undertook this re-investigation of the absorption spectra of a group of hydroxyanthraquinones, using a set of solvents which included: *n*-hexane, dioxane, carbon tetrachloride, benzene, diethyl ether, chloroform, pyridine, acetone, ethanol, methanol, acetonitrile and 0.1 *N* solution of *NaOH*. 1-Hydroxyanthraquinone (1-HA) (I) and several dihydroxyanthraquinones (DHA), namely: 1,2-DHA (II), 1,4-DHA (III), 1,5-DHA (IV), 1,8-DHA (V) and 2,6-DHA (VI) were investigated.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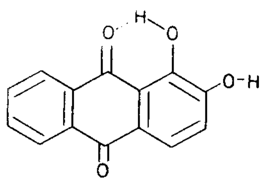
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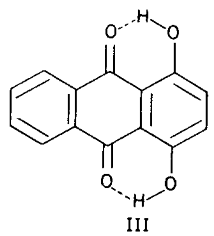
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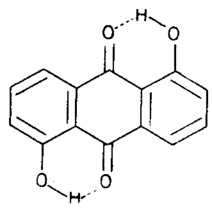
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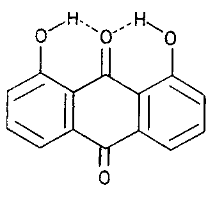
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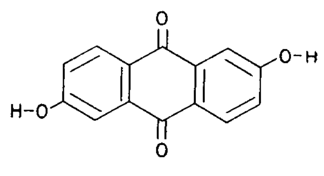
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[1] Communication presented at the XI Colloquium Spectroscopicum Internationale, Beograd, 1963.

EXPERIMENTAL

The hydroxyanthraquinones were commercial products, purified by repeated recrystallization from suitable solvents (usually ethanol or acetic acid). The solvents were of spectroscopic purity or purified before use.

The spectra were obtained initially using a Jobin-Yvon Spectrophotomètre électronique and have later been re-run on a Perkin-Elmer 137 UV recording instrument.

RESULTS AND DISCUSSION

Departing from the usual practice (to tabulate only the values of the maxima of the absorption bands), we list the wavelengths (in $m\mu$) of the absorption maxima and sub-maxima and of some of the shoulders in the absorption spectra in Tables 1—6.

The results presented in these tables show that the absorption spectra of the examined hydroxyanthraquinones are rather complex, although several common regions of absorption can be found. Three such regions are present for all hydroxyanthraquinones having α-hydroxyl groups: 210—230 $m\mu$ (this band is undetectable in most solvents, since they are not transparent that far), around 250 $m\mu$ (the most intense band in all abovementioned hydroxyanthraquinones) and between 400 and 500 $m\mu$. One or two additional bands (appearing sometimes as shoulders) are seen throughout the series of hydroxyanthraquinones in the region 275—285 $m\mu$ and sometimes a band, around 265 $m\mu$ may also appear. These latter bands have been characterized by Peters and Sumner (4) as "quinonoid", as compared with the "benzenoid" bands around 250 and 320—330 $m\mu$. In the spectra of 1,5-DHA and 1,8-DHA the band around 320—330 $m\mu$ could not be detected.

Five main bands (around 215, 240, 270, 300 and 350 $m\mu$) are found in the spectrum of 2,6-DHA. The differences between the spectrum of this compound and those of the hydroxyanthraquinones having α-hydroxyl groups is not unexpected, since the conjugation is different in the two cases, owing to the existence or non-existence of intramolecular hydrogen bonds. The spectra of the ionized form (that is, those in $NaOH$ solution) are quite different from those of the unionized form of all studied hydroxyanthraquinones. This is especially true for the longest-wavelength band which has been considerably shifted towards longer wavelengths (lower frequencies).

In this work we attempted to classify the absorbtion bands according to their origin; it has been proposed (7) that the change of solvents from hexane to polar solvents, shifts the bands originating from $\pi \rightarrow \pi^*$ transitions towards the longer wavelengths (red shift) and those originating from $n \rightarrow \pi^*$. transitions towards shorter wavelengths (blue shift). For the so called $n \rightarrow \pi^*$ blue shift phenomenon various explanations have been proposed. It was considered that this phenomenon is caused by the solvation (7), solvent polarization, various dipole-dipole interactions, hydrogen-bonding forces (8) etc. In the opinion of Mc Rae (9) the dispersion forces between the solvent and solute molecules, dipole-dipole interactions and the quadratic Stark effect should be taken into consideration and he gave an expression which correlates the band shifts with the macroscopic properties of the solvents. Brealey and Kasha (10), Pimentel (11) and other investigators (12—18) have pointed out that hydrogen bonding, when pre-

TABLE I ТАБЛИЦА

Absorption spectrum of 1-hydroxyanthraquinone[1]

*Апсорпциони спектар 1-хидроксиантрахинона**

n-Hexane *n*-Хексан	Dioxane Диоксан	Carbon tetrachloride Угљен-тетрахлорид	Benzene Бензол	Diethyl ether Диетил етер	Chloroform Хлороформ
220				218	
224.5				221.5	
244.5				246 sh	
250	252.5			250	253
264.5	265.5 sh	264.5 sh		263.5 sh	269 sh
276	274.5 sh	278		274.5 sh	279.5
322.5	327	322.5	328.5	324.5	332.5
336		335		332	
362 sh					
390 sh		392 sh	397 sh	388 sh	
403	401	406	407	401	408
417 sh		416 sh	422 sh	425 sh	

Pyridine Пиридин	Acetone Ацетон	Ethanol Етанол	Methanol Метанол	Acetonitrile Ацетонитрил	*NaOH* 0.1 *N*
		218.5	217.5		
					233 sh
					246.5 sh
		251.5	251.5	252 ?	
		264.5 sh	264.5 sh	265 sh	270
		276	276.5 sh	278	
333		329.5	330	330	312
406.5	401	403	402	402	486

[1] The abbreviations used in this and in the following tables are: sh: shoulder; i.s.: insoluble; v.s.s.: very slightly soluble.

When more than one maximum or shoulder are observed in a complex band, the main maximum is underlined.

* У овој и следећим таблицама употребљене скраћенице значе: sh: превој; i.s.: нерастворно; v.s.s.: веома слабо растворно.

Кад се у некој комплексној траци виде више максимума или превоја, главни максимум је подвучен.

TABLE II ТАБЛИЦА

Absorption spectrum of *1,2-dihydroxyanthraquinone*

Апсорпциони спектар 1,2-дихидроксиантрахинона

n-Hexane *n*-Хексан	Dioxane Диоксан	Carbon tetrachloride Угљен-тетрахлорид	Benzene Бензол	Diethyl ether Диетил етер	Chloroform Хлороформ
i.s.		i.s.	v.s.s.	226 ?	i.s.
	251			249	
	266 sh				
	279 sh				
				285 ?	
	322 sh			321	
	428		420	416	
			436	434	

Pyridine Пиридин	Acetone Ацетон	Ethanol Етанол	Methanol Метанол	Acetonitrile Ацетонитрил	*NaOH* 0. . *N*
			235.5 sh		
		249	249.5	251	
		256 sh	256 sh	261 sh	265.5
		264 sh	263 sh	266 sh	
		279 sh	278 sh	278 sh	
		323 ? sh	326 ? sh	329? sh	
335					
439	431	427	423	425	
					555
					590 sh

sent, would be the most important effect to be considered. The observed shifts have also been correlated with some empirical quantities, such as Kosower's (19—21) *Z*-values or the *F*-values of Dubois and co-workers (22, 23).

Although the blue shift of bands in polar solvents has been widely used to assign the absorptions to $n \rightarrow \pi^*$ transitions, exceptions from such a behaviour have also been reported (24, 25).

An inspection of our results shows that no drastic change in the position of maxima is encountered in the spectra of hydroxyanthraquinones. The 250 $m\mu$ band is shifted slightly to higher wavelengths in 1-HA when passing from hexane to etanol or methanol, whereas the shift is difficult to be observed in the case of dihydroxyanthraquinones, because of the intensity redistribution which takes place within the band. Thus, although

TABLE III ТАБЛИЦА

Absorption spectrum of 1,4-dihydroxyanthraquinone

Апсорпциони спектар 1,4-дихидроксиантрахинона

n-Hexane *n*-Хексэн		Dioxane Диоксан		Carbon tetrachloride Угљен-тетрахлорид		Benzene Бензол		Diethyl ether Диетил етер		Chloroform Хлороформ	
225								224			
229.5								227			
241.5											
249.5		249.5						248.5		250	
256		255	sh					255.5		257	
277		280		279.5		280.5		278		272	
323											
334	sh	324		324.5		320 ?	sh	323		327.5	
458											
460		460	sh	460		460	sh	458		459	
472		468	sh	473		474		469		472	sh
483		479		484		484		480		484	
490	sh	494	sh								
504				505		500	sh	500		500	sh
516		510	sh	518		515		514		517	
526	sh										

Pyridine Пиридин		Acetone Ацетон		Ethanol Етанол		Methanol Метанол		Acetonitrile Ацетонитрил		*NaOH* 0.1 *N*	
				225.5		224.5					
				249		248		252 ?		249	
				255.5		254.5		255		255	sh
				278.5		279		277		270	sh
325	sh			325		325.5		325		297	sh
		459	sh	459	sh						
475	sh	467	sh	469		467	sh	464	sh	470	
485		480		479		478		477			
		494	sh	496	sh	493	sh				
514	sh	510	sh	513		510	sh				
								562		564	
580										595	

the maximum is shifted slightly to the blue, the whole band seems to be shifted in the opposite direction (red shift). The center of the band around 320—330 $m\mu$ in the spectra of 1-HA and 1,4-DHA lies also at longer wa-

TABLE IV ТАБЛИЦА

Absorption spectrum of 1,5-dihydroxyanthraquinone
Апсорпциони спектар 1,5-дихидроксиантрахинона

n-Hexane *n*-Хексан	Dioxane Диоксан	Carbon tetrachloride Угљен-тетрахлорид	Benzene Бензол	Diethyl ether Диетил етер	Chlorofor Хлорофор
226				225	
250 sh				250 sh	
254.5	254			253.5	255
261 sh					
274 sh	274.5 sh	274 sh		274 sh	278
286	284 sh	287	284 ? sh	285	288
		373 sh			401 sh
400 sh	400 sh	400 sh	402 sh	400 sh	420
415	415	418	422	415	435
433		435	437	433	

Pyridine Пиридин	Acetone Ацетон	Ethanol Етанол	Methanol Метанол	Acetonitrile Ацетонитрил	*NaOH* 0.1
		225	225		235
		250 sh	249 sh		
		253	253	254.5	
		275	275 sh	275 sh	276.5
		285.5	285.5	285	
405 sh	402 sh	400 sh	400 sh	400 sh	
423	418	416	415	416	
435	432	431	430	430	482

velengths in ethanol than in hexane. Therefore these bands might be assigne to $\pi \to \pi^*$ transitions, as it has been done (26) with the correspondin bands in the spectra of some hydroxynaphtaquinones.

On the other hand, the band found in the visible part of the spectru (around 400—500 $m\mu$) seems to be shifted towards shorter wavelengt when passing from hexane to alcohols. This may be an indication of a $n \to \pi^*$ transition (by all chance of the $C = O$ group). Its relatively hig intensity shows that this is an allowed transition, i.e. a $W \leftarrow A$ transitio in the Platt's (27, 28) notation.

The situation is less clear with 2,6-DHA, on account of its insolubilit in inert solvents.

TABLE V ТАБЛИЦА

Absorption spectrum of 1,8-dihydroxyanthraquinone

Апсорпциони спектар 1,8-дихидроксиантрахинона

n-Hexane *n*-Хексан	Dioxane Диоксан	Carbon tetrachloride Угљен-тетрахлорид	Benzene Бензол	Diethyl ether Диетил етер	Chloroform Хлороформ
224				224	
253	253.5			252	254.5
263					
				272.5	
273.5	272 sh	274.5			275.5
				282.5	
283.5	282.5	284.5			286
				411 sh	
411		413	415 sh		
422		424 sh			
				428	431
430	427	431	432		
				440 sh	445 sh
440 sh		445 sh	445 sh		
454		455 sh			

Pyridine Пиридин	Acetone Ацетон	Ethanol Етанол	Methanol Метанол	Acetonitrile Ацетонитрил	*NaOH* 0.1 *N*
		224	224		
		252.5	252.5	253	232
		273	273	273.5	
		283.5	283	283	280.5
					305 sh
420 sh	415 sh	413 sh			
433	428	429	427	427	
445 sh					
510					496

The correlations, difficult even when only hexane and alcohols are considered, become practically impossible with other solvents.

Table 7 lists the quantities (the refractive index, n_D, dielectric constant, D, dipole moment, μ) usually employed to describe the solvent polarity and some of their combinations which are encountered in the Mc Rae's expression (9), as well as the Kosower's (19) Z- values and the F-values of Dubois and co-workers (22, 23). The values of these constants have been taken from "Spravochnik Khimika" (29). It can be seen that the correlation of the observed shifts with any of these quantities is poor. No simple correlation could be established with the hydrogen-bonding ability of the solvents

TABLE VI ТАБЛИЦА

Absorption spectrum of 2,6-dihydroxyanthraquinone

Апсорпциони спектар 2,6-дихидроксиантрахинона

n-Hexane *n*-Хексан	Dioxane Диоксан	Carbon tetrachloride Угљен-тетрахлорид	Benzene Бензол	Diethyl ether Диетил етер	Chloroform Хлороформ
i.s.		i.s.	i.s.		
				216	
	243 sh			240	
	265 sh			262.5	
	273			270.5	275
	290 sh			288 sh	
	298			297	300.5
				335 sh	
	345.5			343	349

Pyridine Пиридин	Acetone Ацетон	Ethanol Етанол	Methanol Метанол	Acetonitrile Ацетонитрил	*NaOH* 0.1 *N*
		218	217		235
		241	240		
		268 sh	267 sh	265 sh	
		273	272	271	
				291 sh	294
		300	298	298	
346 sh	336 sh				
353	345.5	347	344	345.5	341
380 sh					
					414

either. However, it should be born in mind that, when passing from one solvent to another, more than one parameter is changed simultaneously, so that the effects might be diminished or even cancelled out. The dimensions and the shape of the solvent molecules are also changed and this could not be without consequences. In order to avoid complications of this type, mixtures of one polar and one non-polar solvent (or other suitable binary combinations) should be used. Such an investigation is presently under way.

Another known effect of polar solvents, especially those that can form hydrogen bonds, is the blurring of the substructure of the absorption bands, frequently present in hydrocarbon solvents. This substructure is due to transitions between the vibrational levels of two electronic states and, when

TABLE VII ТАБЛИЦА

Some properties of solvents used
Нека својства употребљених раствaрача

Solvent Раствaрач	n_D	D	μ	$\frac{n^2-1}{2n^2+1}$	Δ*	Z	F
n-Hexane *n*-Хексан	1.375	1.90	0	0.186	0.002		0
Dioxane Диоксан	1.422	2.21	0	0.203	0.033		0.10
Carbon tetrachloride Угљен-тетрахлорид	1.460	2.23	0	0.215	0.017		
Benzene Бензол	1.501	2.28	0	0.228	0.004		—0.05
Diethyl ether Диетил етер	1.353	4.22	1.17	0.178	0.301		0.07
Chloroform Хлороформ	1.446	4.72	1.06	0.210	0.287	63.2	0.08
Pyridine Пиридин	1.510	12.3	2.20	0.230	0.491	64.0	
Acetone Ацетон	1.359	20.74	2.85	0.180	0.648	65.7	
Ethanol Етанол	1.361	25.2	1.68	0.181	0.668	79.6	0.25
Methanol Метанол	1.329	32.65	1.71	0.169	0.710	83.6	0.34
Acetonitrile Ацетонитрил	1.344	37.4	3.94	0.175	0.712	71.3	0.16

* $\Delta = (D-1) \;/\; (D+2) - (n^2-1) \;/\; (n^2+2)$

a hydrogen-bonded complex is formed, many more vibrational levels are available, which could account for the blurring of the substructure. Another factor which can lead to the disappearance of the vibrational substructure is the perturbing effect of the dipolar electric fields. Such an effect has been encountered in the spectra of hydroxyanthraquinones studied, the most pronounced being probably in the case of the band of the longest-wavelength of 1,4-DHA; well-defined peaks making the vibrational substructure of this band in hexane solution were completely blurred in spectra of 1,4-DHA in the most of polar solvents. Quite similar was the case with the corresponding band of 1,8-DHA and, to a lesser extent, with most other bands. It should be noted that one of Peters and Sumner's "quinonoid" bands (the one having the longest wavelength) is always observed, regardless of the solvent used, and this may support the assumption that this band is a separate band.

One further fact deserves attention. Namely, the structure of the 483 $m\mu$ band in 1,4-DHA (similar is the case with other bands and with other compounds) is completely lost in dioxane, although this solvent can hardly be considered as polar, whichever criterion is used. Dioxane can, however, act as a proton acceptor and a hydrogen-bonding mechanism for the blurring of the substructure can be envisaged: intramolecular hydrogen bonds present in 1,4-DHA, are partly ruptured and intermolecular hydrogen bonds are formed instead. Although dioxane is not considered to be a strong proton acceptor (30), such a mechanism could, explain some unexpected shifts in dioxane and other proton-accepting solvents. The origin of very weak bands around 510 $m\mu$ in the spectrum of 1,8-DHA and around 580 $m\mu$ in the spectrum of 1,4-DHA in pyridine (the wavelengths of both bands correspond to those of ionized forms) could possibly be attributed also to such a hydrogen-bonding mechanism, since pyridine is known as a strong proton acceptor.

From all afore said, it is clear that the study of solvent effects on the absorption spectra of hydroxyanthraquinones is far from being completed and deserves further attention.

SUMMARY

The absorption (ultraviolet and visible) spectra of 1-hydroxyanthraquinone and of several dihydroxyanthraquinones were measured in solutions in *n*-hexane, dioxane, carbon tetrachloride, benzene, diethyl ether, chloroform, pyridine, acetone, ethanol, methanol, acetonitrile and 0.1 *N* solution of *NaOH*.

An attempt to classify the absorption bands according to their origin was made, and a hydrogen-bonding mechanism was thought to be the main cause of the blurring of the vibrational substructure of bands; some unexpected shifts and the appearence of new weak bands in proton-accepting solvents were also accounted for by the same mechanism.

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ИЗВОД

УТИЦАЈ РАСТВАРАЧА НА АПСОРПЦИОНЕ СПЕКТРЕ ХИДРОКСИАНТРАХИНОНА*

од

ИВАНА Н. ПЕТРОВА и БОЈАНА Т. ШОПТРАЈАНОВА

Измерени су апсорпциони (ултравиолетни и видљиви) спектри 1-хидроксиантрахинона и неколико дихидроксиантрахинона у растворима у хексану, диоксану, угљентетрахлориду, бензолу, диетилетру,

* Рад је делом саопштен на XI Colloquium Spectroscopicum Internationale, Београд, 1963.

хлороформу, пиридину, ацетону, етанолу, метанолу, ацетонитрилу и 0,1 *N* раствору *NaOH*.

Учињен је покушај да се апсорпционе траке класификују према њиховом пореклу, док је као главни узрок разливања вибрационе супструктуре, као и за нека неочекивана померања и за појаву нових слабих трака у растварачима који су протон акцептори, сматран механизам у коме су интрамолекулске водонично везе делимично разорене и уместо њих створене интермолекулске водоничне везе.

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