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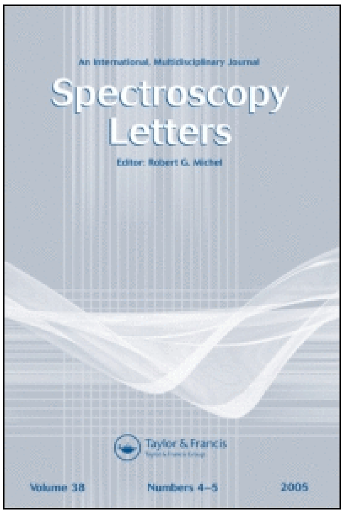

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Spectral Studies On Some 2-Quinolones

M. S. Masoud[a]; Y. S. Mohammed[b]; F. F. Abdel-latif[b]; E. M. A. Soliman[b]
[a] Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, EGYPT [b] Department of Chemistry Faculty of Science, Minia University, Minia, EGYPT

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Spectral Studies On Some 2-Quinolones

M.S.Masoud*
Department of Chemistry,Faculty of Science,Alexandria University, Alexandria, EGYPT
Y.S.Mohammed,F.F.Abdel-Latif and E.M.A.Soliman
Department of Chemistry,Faculty of Science, Minia University, Minia, EGYPT

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Spectral properties of some 2-Quinolones were investigated. IR and ^{1}H NMR were applied to characterize the ligands. The hydrogen bond property is of important parameter for controlling the behaviour of the compounds. The N-H, O-H, C=O, C-H,and C-N fundamental functional groups are characterized. The electronic transitions are assigned. The data are explained on the basis of molecular structure and substituents effects. The acid-base equilibria and the phenomena of tautomerism for these compounds are explained and discussed. The acid exponents (pK_{OH} and pK_{NH}) are evaluated.

INTRODUCTION

The quinoline nucleus has long been known to play an important role in the field of chemotherapy. An important group of quinoline compounds were isolated from Pencillia[1,2] and were found to exhibit antibacterial activity[3]. The structure of these compounds was worked out and elucidated through synthesis[4,5] to be 4-phenyl-3-hydroxy-2-quinolone and 4-(m-hydroxyphenyl)-3-hydroxy-2-quinolone. However, it is of interest to throught light on the spectral properties of such class of compounds (4-substituted-3-hydroxy-2-quinolone). The studies were achieved from electronic spectra, infrared and ^{1}H NMR measurements. The acid exponents (pK_{OH},pK_{NH}) are aimed to be evaluated. The phenomena of tautomerism is discussed.

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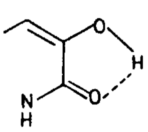
EXPERIMENTAL

The ligands under investigation : 3-hydroxy-2-quinolone I, 4-methyl-3-hydroxy-2-quinolone II, 4-phenyl-3-hydroxy-2-quinolone III, N-methyl-4-phenyl-3-hydroxy-2-quinolone IV, 4-(p-nitrophenyl)-3-hydroxy-2-quinolone V, 4-(p-cholrophenyl)-3-hydroxy-2-quinolone VI, 4-(p-hydroxyphenyl)-3-hydroxy-2-quinolone VII, 4-(p-methoxyphenyl)-3-hydroxy-2-quinolone VIII, 4-(3,4-dihydroxyphenyl)-3-hydroxy-2-quinolone IX, 4-(3,4-dimethoxyphenyl)-3-hydroxy-2-quinolone X , 4-(2,5-dihydroxyphenyl)-3-hydroxy-2-quinolone XI and 4-(2,5-dimethoxyphenyl)-3-hydroxy-2-quinolone XII were prepared by the method described by Eistert[6] and developed by Mohammed etal[7]. The solvents used for measurements were of BDH grades. The universal buffer solutions (pH 2-12) were prepared as usual[8]. Shimadzu 408 spectrophotometer was used for recording the IR spectra over the range 4000-650 cm^{-1} using KBr disc. The ^{1}H NMR spectra have been measured using a EM-360,60 MHz NMR spectrophotometer. Beckman spectrophotometer model 26 was used for measuring the electronic spectra.

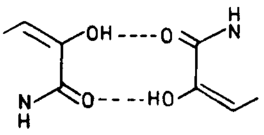
RESULTS AND DISCUSSION

IR and ^{1}H NMR spectra

Table (1) collects the fundamental infrared bands with their assignments for the compounds under investigation. The stretching vibration of the hydroxyl group in position 3 of the quinoline nucleus was found to have absorption bands (broad in most cases) lied between 3460-3250 cm^{-1}. This is shifted from its normal position[9] for the free phenolic hydroxyl group to be at 3650 cm^{-1}. Such finding introduces the probable formation of a hydrogen bond in the form of chelate (intramolecular) or dimer (intermolecular) as follows:



Chelate



Dimer

The 4-(p-hydroxyphenyl)-3-hydroxy-2-quinolone showed two vibration bands one at 3655 cm^{-1} (strong) revealed to free phenolic -OH group while the other at 3460 cm^{-1} (broad) was argued to hydrogen bonded hydroxyl group in position 3. It is important to add that the compounds which have dihydroxyphenyl substituents as IX and XI showed broadness in the ν(O-H) region, while their methoxy analogous X and XII showed broad-

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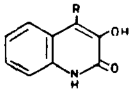

R=H	R=-CH$_3$	R=-ph	R=-ph, NCH$_3$	R=p-NO$_2$-ph	R=p-Cl-ph	R=p-OH-ph	R=p-OCH$_3$-ph	R= 3,4-(OH)$_2$-ph	R= 3,4-(OCH$_3$)$_2$-ph	R= 2,5-(OH)$_2$-ph	R= 2,5-(OCH$_3$)$_2$-ph	Assignment
3250(b)	3300(s)	3365(m)	3400(b)	3380(b)	3355(s)	3655(s) 3460(b)	3375(m)	3380(m)	3400(s)	3375(b)	3440(s)	ν_{O-H}
3100-	3000-	3000-	3000-	3000-	3000-	3280(m)	3000-	3220(m)	3200(s)	-	3000-	ν_{N-H}, C—H aromatic,
2950(b)	2850(b)	2850(b)	2850(b)	2850(b)	2850(b)	3180(b)	2800(b)	-	-	-	2850(b)	alkyl -CH$_3$
1650(s)	1655(s)	1650(s)	1660(s)	1665(s)	1655(s)	1660(s)	1650(s)	1645(s)	1650(s)	1645(s)	1655(s)	$\nu_{C=O}$
1605(w)	1635(w)	1635(sh)	-	1635(vw)	1630(sh)	1630(sh	1610(sh)	1600(m)	1630(vw)	1610(vw)	1638(w)	$\nu_{C=N}$
1570(m)	1574(s)	1570(sh)	1600(w) 1554(m)	1595(m) 1570(w)	1575(s)	1575(m)	1575(m)	1575(s)	1595(sh) 1578(s)	1570(w)	1575(s)	N-H deformation
-	1504(s)	1500(b)	-	1520(s)	-	1514(s)	1514(s)	1520(m)	1506(s)	-	1500(s)	quinoline nucleus
1496(m)	-	-	1495(m)	-	1490(s)	1498(s)	1465(w)	1455(m)	1455(m)	1490(s)	1470(b)	and phenyl sub-
1440(m)	1435(sh)	1444(sh)	1430(m)	1445(vw)	1436(w)	1430(b)	1440(w)	1435(m)	1440(w)	1460(w)	1420(m)	stituent
-	1408(s)	1406(s)	1405(w)	1410(sh)	1410(s)	-	1405(m)	1400(s)	1400(s)	-	1405(w)	C— H bending
1395(vw)	1380(w)	-	1375(s)	1395(sh)	1395(s)	1395(s)	-	-	-	1385(vs)	-	
1345(s)	1354(m)	1350(m)	1350(w)	1350(s)	-	1348(s)	1350(m)	1350(m)	1345(sh)	1350(sh)	1356(w)	
-	-	1305(sh)	1315(m)	-	-	-	-	-	1312(m)	-	1310(sh)	
-	-	1290(sh)	-	1290(m)	1290(vs)	1292(sh	1294(s)	1288(sh)	1288(sh)	1294(s)	1294(b)	ν_{C-O}
1286(s)	1285(s)	-	1282(s)	-	-	-	-	1280(m)	-	-	1282(sh)	
-	-	-	-		-	1264(w)	-	1264(sh)	1275(sh)	1268(vw)	1260(w)	
1245(m)	1250(b)	-	-	1250(vw)	-	-	1248(s)	1240(m)	1248(s)	1250(w)	-	
-	1218(s)	1224(m)	1220(s)	1220(w)	1228(m)	1215(m)	-	-	1228(s)	1215(b)	1220(s)	ν_{C-N}
1180(m)	-	-	-	-	-	1174(s)	1180(s)	1195(m)	1170(w)	-	1180(m)	δ_{C-H}
-	1155(m)	1152(s)	1146(s)	-	1160(m)	1158(m)	-	1164(s)		1160(vw)	1160(m)	
1120(sh)	1126(sh)	1115(w)	1122(m)	-	-	-	1140(vw)	-	1150(vw)	1140(vw)	1130(vw)	
							1115(w)	1114(s)	-	1120(vw)	1108(w)	
-	1072(s)	1072(w)	1072(w)	1105(m)	1090(vs)	1104(m)	1090(m)	-	-	1100(s)	-	δ_{C-H} of substituent in position 4
-	1025(s)	1026(w)	1035(sh) 1008(s)	1035(vw)	1020(s)	1015(w)	1035(s)	1045(vw)	1020(s)	1045(vw)	1040(vs)	
-	960(vw)	-	-	-	960(m)	955(s)	955(m)	995(m)	965(sh)	990(s)	-	
931(m)	-	948(s)	940(s)	940(s)	940(m)	942(w)	930(m)	945(s)	940(s)	950(vs)	945(s)	dimeric associated hydrogen bonding
900(m)	-	-	-	-	-	928(w)	-	917(m)	918(sh)	910(s)	900(s)	
855(b)	872(s)	878(s)	870(b)	850(s)	865(m)	855(w)	-	860(m)	858(s)	880(s)	865(sh)	ρ O-H
-	-	832(vw)	830(vw)	-	838(s)	838(s)	830(w)	805(s)	-	820(b)	810(sh)	
748(s)	742(vs)	752(vs)	750(vs)	750(s)	750(s)	750(s)	760(s)	770(b)	750(s)	755(s)	764(s)	ρ_{C-H} in benzo-quinoline-ring
730(sh)	712(s)	712(s)	-	715(s)	716(m)	705(m)	720(s)	710(s)	705(s)	712(s)	714(s)	

Abbreviations : w=weak ; m=medium ; s=strong ; sh=shoulder ; b=broad

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ness in the alkyl ν(C-H) region. The next absorption band located mainly between 3280-2850 cm^{-1} was argued to the stretching vibrations of aromatic (N-H,C-H) and aliphatic C-H of both methyl and methoxy substituents. The compounds VII, IX and X showed their aromatic -NH stretching vibration frequency at 3280 cm^{-1} (strong), 3220 cm^{-1} (medium) and 3200 cm^{-1} (strong) respectively, shifted from the normal position of the free aromatic -NH which give rise to the probable formation of chelated hydrogen bond with the adjacent carbonyl group in position 2. The strong band of the region (1665-1645 cm^{-1}) was assigned to the ν(C=O) overlapped with ν(C=N) at (1665-1638 cm^{-1}) possibly arises due to a high degree of conjugation in the ligands[10]. The higher frequency (1665 cm^{-1}) was observed for the nitro compound V owing to increasing the single bond character of the carbonyl group arised by the negative mesomeric effect of the nitro group. Furthermore, it showed two absorption bands at 1520 and 1410 cm^{-1} which were revealed to the antisymmetric and symmetric vibrations of the nitro group respectively. The frequency region from (1600-1400 cm^{-1}) revealed the fundamental frequency of the quinoline nucleus beside the phenyl substituent. The common band around 1570 cm^{-1} was due to the -NH deformation,since this band was absent on methylation (compound IV). The (C-H) deformation of both alkyl and methoxy groups were observed in the frequency region (1400-1300 cm^{-1}). The region from (1300-1200 cm^{-1}) was assigned to the stretching vibration of C-O overlapped with C-N. It was remarkable that the number of spectral bands in such region was related to some extent to the number of hydroxy and methoxy groups present in the molecule. For example 4-(p-hydroxyphenyl)-3-hydroxy-2-quinolone VII gave three vibration bands, one at 1215 cm^{-1} assigned to ν(C-N) and the other two at 1264 and 1292 cm^{-1} were due to ν(C-O) of the two hydroxyl groups. The in-plane C-H deformation in the frequency range 1100-1000 cm^{-1} was highly influenced by the incorporation of a substituent in position 4 of the quinoline nucleus. The unsubstituted compound I gave no absorption bands in this region but, when a methyl group was introduced in position 4 (compound II) two strong bands were borned at 1072 and 1025 cm^{-1}. The frequency region from (1000-600 cm^{-1}) was assigned to the out-of-plane aromatic (C-H) deformation where a strong band lied between 770 and 742 cm^{-1} was apparent and could be attributed to the (C-H) deformation of the four adjacent H atoms in the benzo-ring of the quinoline nucleus[11]. The characteristic band located in the frequency range (950-928 cm^{-1}) in a strong feature pin-pointed to that these compounds were probably present in an associated picture through hydrogen bond. Regarding the ^1H NMR spectra for such compounds, the multiplet signals lied between 6.7-8.5 ppm were argued to the aromatic protons for both the quinoline system and the phenyl substituents. The 4-methyl compound II gave a singlet signal at $\delta = 9.0$ ppm attributed to the aromatic -NH proton[12,13]. This conclusion was strengthened by the disappearance of such signal in the case of N-methyl compound IV, where a singlet signal was appeared at $\delta = 3.2$ ppm due to the protons of the $N-CH_3$ group[13]. The 4-(p-hydroxyphenyl) VII and 4-(3,4-dihydroxy-phenyl) IX showed a singlet signal of broadness feature at $\delta = 9.5$ and 9.0 ppm respectively. The data denoted to the -NH signal beside the probable existence of hydroxylic hydrogen bonds where their signals located at the same position for the -NH proton[14]. The aromatic -NH signal for the p-nitro compound V appeared at a lower field of 12.6 ppm reflecting the deshielding effect of the nitro group.

Electronic spectral studies

The ultrviolet absorption spectra of 4×10^{-5}M of the quinolines under investigation in dioxane solvent exhibited in most cases seven absorption bands, their position along with their log ϵ values were collected in Table (2). The bands were located within the wavelength ranges 221-225 , 234-264 , 273-276 , 280-287 , 303-307 , 313-323 and 327-336 nm. The first four absorption bands were probably due to the allowed $\pi-\pi^*$ type electronic transition arising from the local excitation of the π-system. The next three bands characterized by low intensity were argued to the forbidden $n-\pi^*$ electronic transition of an electron from a lone pair orbital of quinoline nitrogen or carbonyl oxygen to the π - orbital of the ring system. The longest absorption band for the N-methyl compound IV exhibited a bathochromic shift regard to the parent non methylated one III. So one can say that methylation leads to decrease the number of resonating structures participating in the stabilization of the molecule[15]. The intensity of the electronic spectral band was greatly influenced by introducing a substituent in position 4. This phenomenon was apparent with respect to the first absorption band of the $\pi-\pi^*$ electronic transition which

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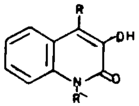
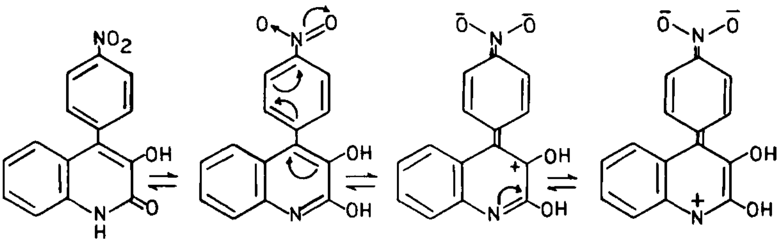


Table (2) : λmax - logε relationship for 4 x 10^{-5}M of 4-substituted-3-hydroxy-2-quinolone in dioxane solvent.

	Ligand R	R`	λmax. log(ε)	λmax. log(ε)	λmax. log(ε)	λmax. log(ε)	λmax. log(ε)	λmax. log(ε)	λmax. log(ε)	λmax. log(ε)
I	H	,H	221(s) (4.56)	-	264(b) (3.76)	274(s) (3.89)	284(s) (3.86)	304(b) (3.88)	315(s) (4.00)	327(m) (3.87)
II	CH_3	,H	224(s) (4.57)	-	263(b) (3.76)	273(s) (3.87)	283(s) (3.86)	303(b) (3.89)	315(s) (4.04)	327(s) (3.93)
III	C_6H_5	,H	224(s) (4.62)	244(b) (4.27)	-	275(b) (3.90)	285(b) (3.93)	305(b) (3.92)	315(s) (4.02)	328(m) (3.89)
IV	C_6H_5	,CH_3	225(s) (4.59)	-	-	-	280(b) (3.89)	312(b) (3.88)	323(b) (3.93)	336(b) (3.74)
V	p-NO_2-C_6H_5	,H	223(s) (4.64)	-	-	274(b) (4.20)	285(b) (4.10)	304(b) (4.06)	316(s) (4.11)	330(b) (3.98)
VI	p-Cl-C_6H_5	,H	224(s) (4.55)	246(b) (4.22)	-	276(b) (3.99)	286(b) (4.06)	307(b) (4.12)	315(m) (4.15)	332(b) (3.94)
VII	p-OH-C_6H_5	,H	225(s) (4.62)	246(m) (4.30)	-	275(b) (4.02)	285(b) (4.06)	304(b) (4.04)	316(s) (4.09)	328(m) (3.97)
VIII	p-OCH_3-C_6H_5	,H	225(s) (4.56)	246(m) (4.24)	-	276(b) (3.97)	284(b) (3.98)	303(b) (3.96)	316(s) (4.01)	330(m) (3.88)
IX	3,4$(OH)_2$-C_6H_5	,H	222(s) (4.58)	224(m) (4.22)	-	276(b) (3.95)	285(b) (4.00)	304(b) (4.03)	315(s) (4.07)	330(m) (3.90)
X	3,4$(OCH_3)_2$-C_6H_5	,H	223(s) (4.60)	243(m) (4.28)	-	276(b) (3.98)	284(b) (4.01)	304(b) (4.03)	316(s) (4.08)	330(m) (3.93)
XI	2,5$(OH)_2$-C_6H_5	,H	223(s) (4.63)	-	-	275(b) (3.93)	286(b) (3.98)	304(b) (4.06)	315(s) (4.11)	328(m) (3.95)
XII	2,5$(OCH_3)_2$-C_6H_5	,H	223(s) (4.64)	-	-	275(b) (3.92)	287(b) (3.99)	304(s) (4.04)	316(s) (4.08)	330(m) (3.90)

Abbreviations : (s) strong ; (m) medium ; (b) broad lied in the wavelength range 221-225 nm with log ε values in the range 36,750-43,750 . So the unsubstituted compound I gave the lowest absorption value while the p-nitrophenyl substituent gave the highest absorption values which may be due to the greatest distance between the hetero-nitrogen and the nitro group oxygen. It is apparent that the area under a peak is a function of the dipole strength of the chromophore and therefore approximately proportional to the square of the distance between the ends of the absorbing system[16]. This explained that the p-nitro compound V probably exists in the following resonating structures :



Effect of pH on the electronic spectra

The absorption - pH profile of 4 x 10^{-5}M of 3-hydroxy -2-quinolone I at different pH's (2.71-11.98) gave interesting observations. In acidic to neutral solutions five absorption bands can easly traced at 217,275,304,315 and 330 nm. The first band due to $\pi-\pi^*$ type electronic transition decreased in intensity as the pH increased in contrast to that observed for the band at 330 nm which showed increasing in intensity with increasing pH. The former band at 217 nm could be ascribed to the formation of a protonized species where a proton derived from the medium takes a position on the carbonyl oxygen. The spectra of this compound in basic solutions (pH $\geqslant$ 9.45) gave a new band at 250 nm. Such band represented the shift of the tautomeric equilibria towards the enol form in moderate basic solutions. Furthermore, the red shift of the band at 330 nm in acidic to neutral solutions to be at 340 nm in pH $\geqslant$ 9.45 denoted to the ionization of the hydroxyl group in position 3. This equilibrium was represented as follows :

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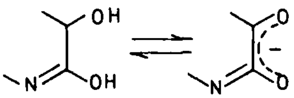
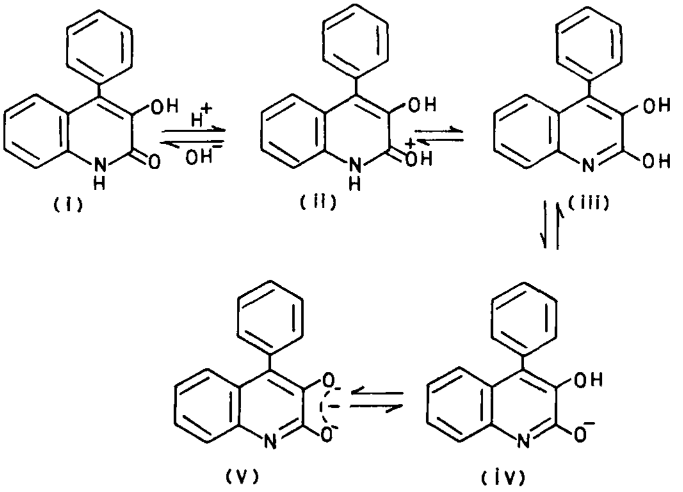


The electronic spectra of 4 x 10^{-5}M 4-methyl-3-hydroxy-2-quinolone II in pH range (2.67-8.47) showed five characteristic absorption bands at 220,272,303,313 and 326 nm. In solutions with pH's (9.65-11.61), the three bands located at 220,313 and 326 nm undergo a bathochromic shift to be at 226, 327 and 340 nm respectively. The two bands at 272 and 303 nm were disappeared in solutions of pH 9.65 with the formation of a new absorption band at 248 nm which showed a steady increase in intensity with the increase of pH. The longer wavelength band in the spectra of such compound at 340 nm goes parallel with compound I. The presence of well defined isobestic points at 265 and 320 nm explained the presence of analogous equilibria to the previously discussed compound I. Similar trend was observed for 4 x 10^{-5}M 4-phenyl-3-hydroxy-2-quinolone III.Fig. 1, at different pH's (2.55-12.02). Furthermore, four isobestic points were located at 230,244,274 and 320 nm. The formation of an isobestic point has been taken as a proof of the existence of two and only two absorbing species in a given system usually in equilibrium with each other[17]. The presence of these points could explain the equilibria for such compound to proceed in the following :



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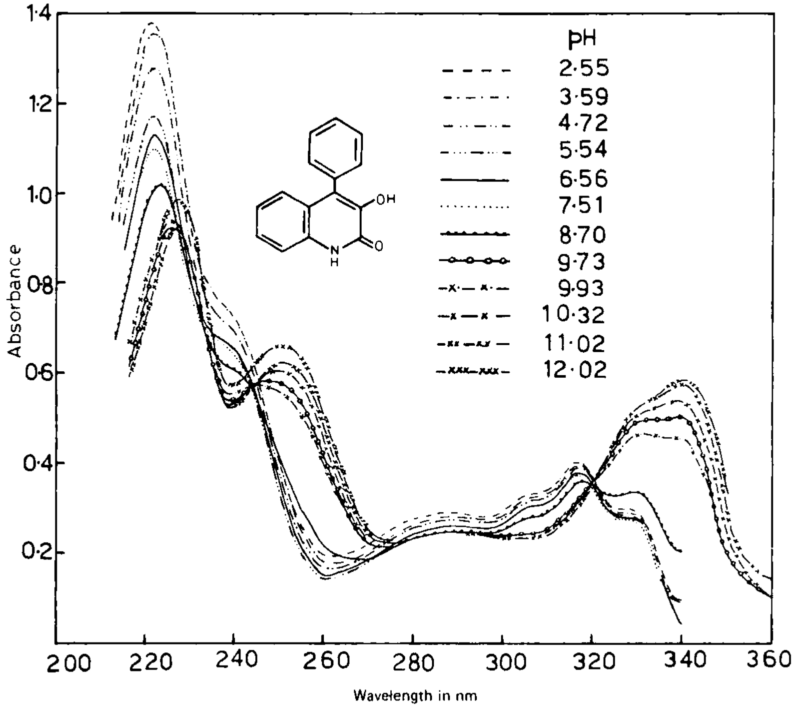

Figure (1) : Effect of pH on the electronic spectra of 4 x 10^{-5}M 4-Phenyl-3-hydroxy-2-quinolone III .

It was apparent that the phenyl group in position 4 facilitated the tracing of species (iv) compared to componud I. The assumptions given for the appearance of the new absorption band at 250, 248 and 252 nm in the spectra of the compounds I, II and III respectively, to the shift of the equilibria towards the enol form were strengthened on studying the effect of pH (2.48-11.0) on the electronic spectra of 4 x 10^{-5}M, N-methyl-4-phenyl-3-hydroxy-2-quinolone IV ,Fig. 2, This compound was of purely keto-structure. To some extent, the non existence of clear isobestic points on dealing with the spectra of 4 x 10^{-5}M 4-(p-nitrophenyl)-3-hydroxy-2-quinolone V at different pH's (2.60-12.03) interpretted the overlapping of the different absorbing species. The spectra of 4 x 10^{-5}M 4-(p-hydroxyphenyl)-3-hydroxy-2-quinolone in solutions with

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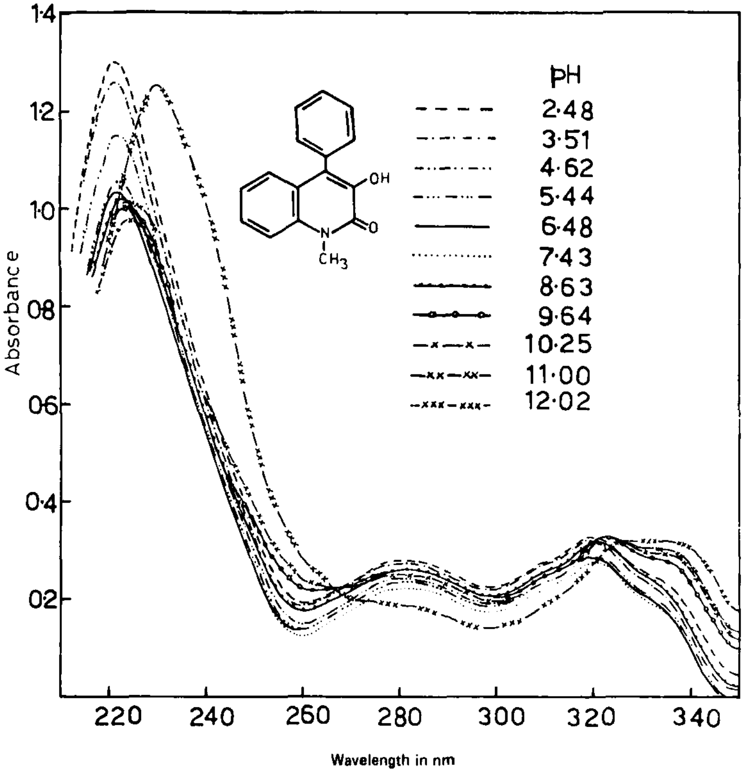

Figure (2) : Effect of pH on the electronic spectra of 4 x 10^{-5}M N-Methyl-4-phenyl-3-hydroxy-2-quinolone IV .

pH range (2.61-8.72) showed six maximal bands at 222,242,280, 305,316 and 330 nm. A regular decrease in the band intensity at 222 nm with increasing pH was observed. The band at 242 nm not found in the previous compounds was argued to slight contribution of the enol tautomer beside the protonized species. Such finding was reinforced by the strong band located at 252 nm found in basic solutions. This was simply interpretted as due to the shift of the tautomeric equilibria towards the enol form. In the pH range (9.76-12.02) there was an apparent red shift for the bands formed in acidic and neutral solutions. Such bathochromic shifts were due to the strong contribution of the anionic species with their quinonidal

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structures arising from the hydroxyl group in position 3 beside the enolic shift of the 2-quinolone system. Furthermore, there was an additional phenoxide anion resulting from the p-hydroxyphenyl substituent in position 4 of the quinoline nucleus. Such finding reflects the appearance of an absorption band at 280 nm which became more intense with increasing pH. The electronic spectra of 4×10^{-5}M 4-(p-methoxyphenyl) -3-hydroxy-2-quinolone at different pH's (2.60-11.90) showed the following observations : In the pH range (2.60-8.32) six maximal bands were located at 223,240,280,304,316 and 330 nm. In solutions starting with pH = 9.47 all these bands were red shifted to be at 225,247,282,318,330 and 340 nm as the pH increased. This supported the stepwise acid-base equilibria for such compound which justified by the presence of clear isobestic points at 245,275,and 320 nm. The general view of the absorption-pH profile for 4×10^{-5}M of each 4-(3,4-dihydroxyphenyl) IX , 4-(2,5-dihydroxyphenyl) XI and their dimethoxy analogous 4-(3,4-dimethoxyphenyl) X , 4-(2,5-dimethoxyphenyl) XII indicated that the ionization proceeds in a similar fasion. Both the dihydroxyphenyl compounds were highly affected by the strong basic conditions pH ~ 12. Under such conditions the colour was changed from colourless to faint yellow denoting that some structural changes may be occured. Two sharp isobestic points were located at 250 and 320 nm for the 3,4-dihydroxyphenyl compound. However, such finding was not clear in the 2,5-dihydroxyphenyl compound. With regarde to their dimethoxy analogous X and XII, the most remarkable observation was the presence of two sharp isobestic points at 245, 322 nm and at 242 , 320 nm for the 3,4-dimethoxy X and 2,5-dimethoxy XII respectively.

The spectral data of the compounds in solvents with different dielectric constants showed that the bands of $\pi-\pi^*$ type electronic transition in presence of hydrogen bonding solvents (ethanol and methanol) depicted that association of the solvent molecules with the compounds probably takes place through hydrogen bond formation. The bands arised due to $n-\pi^*$ electronic transition were slightly red shifted with increasing the dielectric constant of the medium to be apparent in the DMF solvent denoting to strong solute-solvent interaction[18]. The basic property of the solvent leads to a reasonable degree of correlation with the transition energy based on its dielectric constant. The non linear plots obtained with our ligands come to the conclusion that specific

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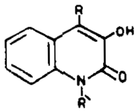

Table (3) Summary of the pK's values obtained spectrophotometrically at different wavelengths

Ligand	pK_a			pK_b			λ
	Half height	Limiting absorbance	Colleter	Half height	Limiting absorbance	Colleter	in nm
I R=H	9.1	-	-	5.0	4.8	4.8±0.8	226
R̃=H	9.0	-	-	-	-	-	260
	8.8	8.7	8.8±0.3	-	-	-	330
II R=-CH_3	-	-	-	4.8	5.0	5.0±0.8	226
R̃=H	9.5	-	-	4.4	-	-	256
	9.5	9.1	9.4±0.2	-	-	-	330
III R=-C_6H_5	9.1	-	-	5.0	5.0	4.8±0.6	226
R̃=H	9.3	-	-	4.4	-	-	256
	9.4	9.2	9.1±0.5	-	-	-	330
IV R=-C_6H_5	8.8	8.8	8.8±0.3	4.2	3.9	4.1±0.7	260
R̃=-CH_3	8.7	8.7	-	3.7	3.7	4.1±0.8	330
V R=p-NO_2-C_6H_5	9.3	-	-	4.4	4.1	4.4±0.7	240
R̃=H	8.3	-	-	-	-	-	256
	8.1	8.0	8.0±0.2	-	-	-	330
VII R=p-OH-C_6H_5	9.2	-	-	5.0	5.1	-	226
R̃=H	9.0 10.9	-	-	5.2	-	-	240
	9.4	-	-	-	-	-	256
	9.0	-	-	4.9	-	-	310
	9.2	9.2	8.9±0.2	-	-	-	330
VIII R=p-OCH_3-	9.0	-	-	5.0	4.9	4.6±0.6	222
C_6H_5	9.5	-	-	-	-	-	260
R=H	9.4	9.4	9.3±0.2	-	-	-	330
IX R=3,4$(OH)_2$-	9.1	-	-	-	-	-	256
C_6H_5	9.8	-	-	-	-	-	304
R̃=H	9.2	9.0	9.5±0.1	-	-	-	330
X R=3,4$(OCH_3)_2$	9.1	-	-	5.0	5.0	-	226
C_6H_5	9.3	-	-	5.0	-	-	240
R̃=H	9.1	-	-	-	-	-	256
	9.0	9.0	9.4±0.3	-	-	-	330
XI R=2,5$(OH)_2$-	8.3 10.05	-	-	5.05	-	-	240
C_6H_5	8.3 10.0	-	-	-	-	-	256
R̃=H							
	8.8 10.1	8.1	8.3±0.1	-	-	-	330
XII R=2,5$(OCH_3)_2$	9.1	-	-	4.60	4.65	-	226
C_6H_5	8.6	-	-	4.2	-	-	240
R̃=H	9.0	-	-	-	-	-	256
	9.05	9.10	8.7±0.7	-	-	-	330

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association occured between the solute and the solvent independent on the wavelength of measurements.

Evaluation of the acid exponents (pK_{OH}, pK_{NH})

The acid exponents (pK_{OH}, pK_{NH}) were determined using different spectrophotometric methods (half-height[19], modified limiting absorbance[20] and Colleter[21]). Table (3) collects the values obtained at different wavelengths. The pK_a value of 3-hydroxy-2-quinolone was found to be 8.70 higher than the value[22] for 3-hydroxy quinoline (8.06). This was explained based on the probability of hydrogen bond formation between the hydroxylic proton and the adjacent carbonyl oxygen. The relative acidity of the p-nitro compound V (8.0) was due to the strong attracting property of the nitro group by its (-I, -M) effects, leading to enhance the proton displacement. The ligands with electron donating substituents (4-methyl II , $pK_a = 9.1$; p-hydroxyphenyl VII , $pK_a = 9.2$; p-methoxyphenyl VIII , $pK_a = 9.4$) showed a decrease in the liberation of the -OH proton. The p-nitro compound V gave two pK_a,s values with nearly the same magnitude 8.3 and 8.1 at $\lambda = 256$ and $\lambda = 330$ nm respectively. When the data were plotted at $\lambda = 240$ nm another pK_a value was obtained (9.3) denoting the probable existence of other acidic species. The p-hydroxyphenyl compound VII gave two pK_a's values 9.0 and 10.9 at $\lambda = 240$ nm. The pK_2 was assumed to the dissociation of the -OH group in the phenyl substituent. The 3,4-dihydroxy compound IX showed two pK_a's values 9.1 and 9.8 . The pK_1 value was independent on the wavelength of measurements and the pK_2 was strongly comparable to catechol[23]. However, the 2,5-dihydroxy XI gave two pK_a's values (8.2 ± 0.1 and 10 ± 0.05). The pK_1 value was due to the ionization of the hydroxylic proton in position 3 of the quinoline system, while the pK_2 was related to the hydroxyl of the phenolic substituent[24]. The correlation of the pK_a versus the substituent constant σX or the polar substituent constant $\sigma^* XC_6H_4$ for the 4-(monosubstituted phenyl)-3-hydroxy-2-quinolones gave straight lines with a slope amounting to 1.13 ± 0.02 denoting that the electronic character of the substituent was a matter of importance for its behaviour. The pK_b's of the ligands under investigation lied between 3.8-5.1 . The affinity of 2- and 4-hydroxy quinoline[22] for protons (pK_b) was similar to their N-methyl (keto form) and far from their O-methyl (enol form). Our data reflected the effect of the presence of a hydroxy

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group in the position 3 of the quinoline nucleus adjacent to the carbonyl in position 2 in shifting the tautomeric equilibria towards the enol form to be near to the value of 3.17 given for 2-methoxy quinoline. The effect of the substituent on the reactivity of the hetero-nitrogen was satisfactory. The slope of the pK_b versus $(\sigma X, \sigma^{*} X\ C_6H_4)$ relationship gave a value of 0.8 .

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