

THE ELECTRON AND INFRARED SPECTRA
OF HYDROXYBENZO[*a*]PHENAZINES

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The UV spectra of thirteen and IR spectra of fourteen substituted 5-hydroxybenzo[*a*]phenazines have been measured and some of the bands have been assigned. By the use of UV spectroscopy the tautomerism of these compounds in aqueous-ethanolic solutions have been studied and the effects of protonization and deprotonization on their spectra have been investigated.

Whereas hydroxyphenazines have been studied by IR (ref.¹) and UV (ref.^{1,2}) spectroscopy, little attention^{2,3} has been given to hydroxybenzo[*a*]phenazines. Badger and coworkers² studied the UV spectra of hydroxyphenazines and have arrived at the conclusion that 2-hydroxyphenazine in aqueous-ethanolic solutions exists in two tautomeric forms, lactim and lactam, whereas 1-hydroxyphenazine exists in a lactim form only.

This paper describes the UV and the IR spectra of substituted 5-hydroxybenzo[*a*]phenazines, *I*–*XIV*. The lactim–lactam tautomerism (its vinyl analogy) in these compounds is discussed.

EXPERIMENTAL

The melting points were corrected. The samples for analysis were dried over P₄O₁₀ at 110°C and a pressure of 1 Torr for 1 h. Chromatographic separation was carried out on silica gel L 140/100 μ (Lachema) or on Al₂O₃ Reanal (activity II).

Chemicals. 5-Hydroxybenzo[*a*]phenazine (*I*), orange needles, m.p. 265°C (decomposition); reported⁴ m.p. 260°C, and 5-hydroxy-6-chlorobenzo[*a*]phenazine (*VI*), red crystals decomposing above 260°C, reported³ decomposition starting at 268°C, were prepared by condensation of *o*-phenylenediamine with 2-hydroxy-1,4-naphthoquinone or 2,3-dichloro-1,4-naphthoquinone in ethanol^{5,6}. Analogously prepared from 3,4-dimethyl-1,2-diaminobenzene and 2-hydroxy-1,4-naphthoquinone or 2,3-dichloro-1,4-naphthoquinone were: 5-hydroxy-9,10-dimethylbenzo[*a*]phenazine (*X*) m.p. 211–212°C, for C₁₈H₁₄N₂O (274.3) calculated: 78.80% C, 5.11% H, 10.22% N; found: 78.52% C, 5.28% H, 10.12% N; 5-hydroxy-6-chloro-9,10-dimethylbenzo[*a*]phenazine (*XII*), m.p. 257°C (decomp.), for C₁₈H₁₃ClN₂O (308.7) calculated: 70.04% C, 4.24% H, 9.08% N; found: 69.71% C, 4.40% H, 8.91% N. 6-Bromo-5-hydroxybenzo[*a*]phenazine (*VIII*), red crystals decomposing at 235°C, reported⁷ start of decomposition 230°C, was prepared by bromination of *I* in ethanol and chromatographic isolation on silica gel in an elution system benzene–acetone (10 : 1), see⁸. 5,6-Dihydroxybenzo[*a*]phenazine (*IV*), violet crystals melting at 268 to 270°C with decomposition, reported² m.p. 270°C, was prepared according to Zincke⁹.

Acetoxyphenazines III, V, VII, IX, XI, and XIII were prepared by acetylation of hydroxybenzo[*a*]phenazines I, IV, VI, VIII, X and XII with a mixture of acetic anhydride and pyridine (1 : 1) at room temperature. Thus we obtained: 5-acetoxybenzo[*a*]phenazine (III), m.p. 217–219°C, reported¹⁰ 217°C; 5,6-diacetoxybenzo[*a*]phenazine (V), m.p. 215–217°C, ref.² 214–216°C; 5-acetoxy-6-chlorobenzo[*a*]phenazine (VII), m.p. 233–235°C (decomp.), ref.¹¹ 230–232°C; 5-acetoxy-6-bromobenzo[*a*]phenazine (IX) m.p. 221–223°C, ref.⁷ 221°C; 5-acetoxy-9,10-dimethylbenzo[*a*]phenazine (XI), m.p. 211–212°C; for C₂₀H₁₆N₂O₂ (316.3) calculated: 8.87% N, found: 8.72% N; 5-acetoxy-6-chloro-9,10-dimethylbenzo[*a*]phenazine (XIII), m.p. 245°C (decomp.); for C₂₀H₁₅ClN₂O₂ (350.7) calculated: 7.98% N; found: 7.96% N.

Methylation. Reaction of I with dimethyl sulphate at 80°, followed by chromatography on Al₂O₃ in a system benzene–acetone (14 : 6), afforded yellow 5-methoxybenzo[*a*]phenazine (II) m.p. 178–180°C, ref.¹² 176–177°C, and red 7-methyl-5-oxo-5,7-dihydrobenzo[*a*]phenazine (XIV), m.p. 261–263°C, ref. 257°C.

Spectroscopy. The UV spectra were measured with a spectrophotometer Specord UR VIS (Zeiss, Jena) in 96% ethanol and 1-cm cells, the sample concentration being 10⁻⁴M. In the same way we measured spectra in 80% aqueous ethanol, the solutions being 0.1M in respect to HCl or NaOH. The spectra of compounds III, V, VII, IX, XI and XIII in ethanol and compounds I, VI and VIII in 50–80% aqueous ethanol were measured in 10-cm cells, the concentration of the samples being 10⁻⁵M. The infrared spectra were measured in KBr on a spectrophotometer UR-20 (Zeiss, Jena); the apparatus was calibrated with polystyrene.

RESULTS AND DISCUSSION

Electron Spectra

In studying the tautomerism of 2-hydroxyphenazine Badger and coworkers² observed that the lactim–lactam equilibrium was affected by the dielectric constant of the solvent, polar media favouring the lactam form. With substituted 2-hydroxyphenazines bulky substituents adjacent to the OH group may prevent the formation of hydrogen bonds, thus impeding the formation of the lactim form¹. These general rules were observed even with hydroxybenzo[*a*]phenazines, studied in this work.

On comparing the UV spectrum of 5-hydroxybenzo[*a*]phenazine (I) with the spectrum of 5-methoxybenzo[*a*]phenazine (II), having a fixed lactim structure, and with the spectrum of 7-methyl-5-oxo-5,7-dihydrobenzo[*a*]phenazine (XIV), having a fixed lactam structure, it is seen that the spectrum of compound I is more similar to the spectrum of compound II, but exhibits an additional marked absorption at 515 nm. This absorption corresponds to an absorption band of compound XIV and testifies to the presence of a small part of the lactam form (Fig. 1). Whereas the spectra of the compounds II and XIV are not affected by an increased content of water in ethanol, the spectrum of compound I exhibits a lowered intensity of the absorption band at 427 nm, which indicates a decrease in the concentration of lactim form, and a higher absorption at 515 nm, so that the tautomeric equilibrium $A \rightleftharpoons B$ shifts to the lactam form (B). The presence of two isosbestic points proves that the conversion

TABLE I
Last Long-Wave Bands of UV Spectra of Hydroxybenzo[*a*]phenazines

Compound	Lactim			Lactam ethanol
	ethanol	0.1M-HCl ^a	0.1M-NaOH ^a	
<i>I</i>	427 (4.0)	457 (4.1)	480 (4.0)	515 (3.1)
<i>II</i>	413 (4.1)	438 (4.1)	—	—
<i>III</i>	404 (4.1)	—	—	—
<i>V</i>	403 (4.1)	—	—	—
<i>VI</i>	429 (3.8)	481 (3.9) ^b	485 (4.0)	517 (3.8)
<i>VII</i>	403 (4.1)	—	—	—
<i>VIII</i>	427 (3.7)	481 (3.9) ^b	482 (4.0)	514 (3.8)
<i>IX</i>	402 (4.1)	—	—	—
<i>X</i>	426 (4.0)	459 (4.1)	480 (4.0)	513 (3.1)
<i>XI</i>	404 (4.1)	—	—	—
<i>XII</i>	428 (3.8)	480 (3.9) ^b	482 (4.0)	515 (3.8)
<i>XIII</i>	402 (4.1)	—	—	—
<i>XIV</i>	—	482 (4.1)	—	493 (4.1)

^aIn 80% aqueous ethanol, ^b in 3M-HCl and 70% aqueous ethanol.

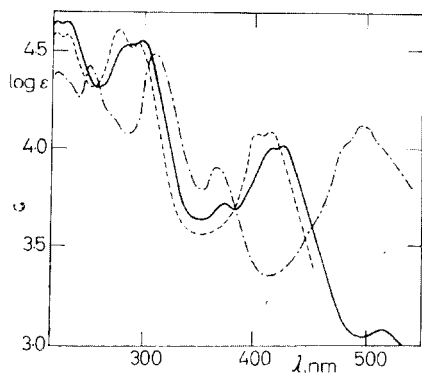


FIG. 1
UV Spectra of Hydroxybenzo[*a*]phenazines in Ethanol

— 5-Hydroxybenzo[*b*]phenazine (*I*),
 - - - 5-methoxybenzo[*a*]phenazine (*II*),
 - · - · 7-methyl-5-oxo-5,7-dihydrodibenzo-
 [a]phenazine (*XIV*).

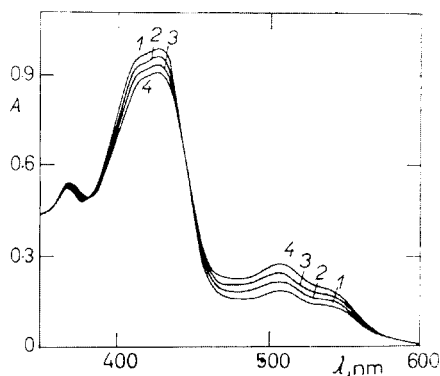
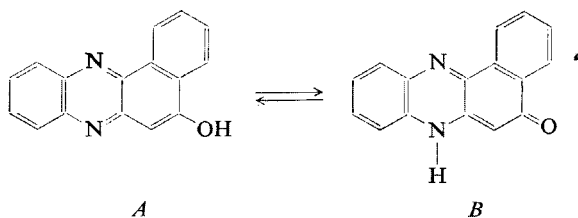
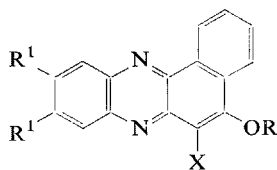


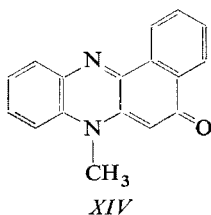
FIG. 2
Effect of Polarity of Medium on the UV Spectrum of 5-Hydroxybenzo[*a*]phenazine (10^{-4} M) in 90% (1), 75% (2), 60% (3) and 50% (4) Aqueous Ethanol
1 cm cells.



was complete (Fig. 2). Comparison of the spectra of 5-hydroxy-6-chlorobenzo[*a*]phenazine(VII) and 6-bromo-5-hydroxybenzo[*a*]phenazine(VIII) with the spectra of compounds II and XIV reveals that in ethanol the two forms were present in equal parts. The effect of polarity of the solvent was analogous to that observed with compound I.



- | | |
|---|---|
| I, R ¹ = H; R = H; X = H | VIII, R ¹ = H; R = H; X = Br |
| II, R ¹ = H; R = CH ₃ ; X = H | IX, R ¹ = H; R = Ac; X = Br |
| III, R ¹ = H; R = Ac; X = H | X, R ¹ = CH ₃ ; R = H; X = H |
| IV, R ¹ = H; R = H; X = OH | XI, R ¹ = CH ₃ ; R = Ac; X = H |
| V, R ¹ = H; R = Ac; X = OAc | XII, R ¹ = CH ₃ ; R = H; X = Cl |
| VI, R ¹ = H; R = H; X = Cl | XIII, R ¹ = CH ₃ ; R = Ac; X = Cl |
| VII, R ¹ = H; R = Ac; X = Cl | |



From the facts described above it follows that the UV spectra of compounds I, VI, VIII, as well as X and XII, should be regarded as overlapped spectra of two compounds, *i.e.* the lactim and the lactam forms. The lactim form in ethanol can be characterized by its last long-wave peak in the region 400–430 nm. An analogous absorption in the UV spectra of 2-hydroxyphenazines is considered by Corbett¹ to be due to an $n \rightarrow \pi^*$ transition. However, in the case of lactims, *i.e.* phenazine derivatives with hydroxy and methoxy substituents, no $n \rightarrow \pi^*$ transition is principally possible, because one electron pair on the oxygen atom has the π -character, lies in the plane of the other π electrons, is conjugated with them and, consequently, is

TABLE II
IR Spectra of Benzo[*a*]phenazines in the region 1800—700 cm^{-1}

Benzo[<i>a</i>]phenazine		Wave number, cm^{-1}									
<i>I</i>	—	1 634 m	1 598 s	—	1 537 s	1 503 m	1 468 sh	—	1 411 s		
<i>II</i>	—	1 633 m	1 599 s	1 582 w	1 540 w	1 497 m	1 469 m	1 427 w	1 407 m		
<i>III</i>	1 757 s	1 633 m	1 605 m	—	1 535 w	1 491 m	1 468 w	1 429 w	1 408 w		
<i>IV</i>	—	1 650 s	1 583 s	1 550 s	1 537 sh	1 500 w	1 469 sh	1 435 s	—		
<i>V</i>	1 775 s	1 638 m	1 605 w	—	—	1 469 w	1 477 w	1 430 w	—		
<i>VI</i>	—	1 614 m	1 605 m	1 551 s	1 531 s	1 503 s	1 466 w	1 452 w	1 413 m		
<i>VII</i>	1 770 s	1 621 m	1 595 m	—	1 540 w	1 491 m	1 469 m	1 432 w	1 401 w		
<i>VIII</i>	—	1 604 sh	1 593 s	1 554 s	1 534 s	1 504 s	1 463 w	—	1 408 m		
<i>IX</i>	1 765 s	1 627 w	1 593 m	1 568 w	—	1 490 w	1 473 w	1 435 w	—		
<i>X</i>	—	1 619 w	1 598 s	—	1 537 m	1 502 sh	1 479 w	1 459 m	1 408 m		
<i>XI</i>	1 770 s	1 634 w	1 604 s	—	1 532 w	1 491 m	1 469 m	1 450 m	1 510 w		
<i>XII</i>	—	1 602 sh	1 591 s	1 550 s	1 532 m	1 503 sh	1 461 m	1 443 m	—		
<i>XIII</i>	1 760 s	1 636 w	1 601 m	—	—	1 491 w	1 471 m	1 457 m	1 431 w		
<i>XIV</i>	—	1 620 sh	1 598 s	1 552 s	1 542 sh	1 520 sh	1 485 m	1 438 w	—		
<i>I</i>	1 368 sh	1 355 m	1 333 m	1 297 w	1 285 m	1 233 m	1 225 s	1 165 w	1 145 s		
<i>II</i>	1 392 m	1 357 m	1 337 m	1 297 m	—	1 227 s	1 209 s	1 163 w	1 142 w	1 102 s	
<i>III</i>	1 382 w	1 368 m	1 353 m	1 327 w	1 278 w	—	1 211 s	1 180 s	1 160 m	1 128 s	
<i>IV</i>	1 393 m	1 351 m	1 320 m	1 307 w	1 266 m	1 241 m	1 205 m	1 163 m	1 128 w	1 106 w	
<i>V</i>	1 369 m	1 350 w	1 332 m	1 306 w	1 291 m	—	1 203 s	—	1 151 m	1 100 m	
<i>VI</i>	1 377 m	1 331 m	1 319 s	1 307 m	—	1 249 m	1 209 w	1 155 m	1 127 m	1 108 m	

VII	1 370 s	1 348 m	1 330 sh	1 311 sh	1 281 m	1 225 m	1 205 s	1 160 m	1 134 s
VIII	1 386 w	1 369 w	1 316 s			1 224 sh	1 210 w	1 157 w	1 149 m
IX	1 368 s		1 352 sh	1 278 m		1 227 s	1 202 s	1 168 m	1 139 m
X	1 362 s	—	1 329 w	1 297 m			1 208 m	1 157 m	1 137 m
XI	1 389 m	1 377 m	1 356 m	1 298 w	1 276 w		1 207 s	1 193 s	1 152 s
XII	1 398 w	1 352 s	1 316 w	1 298 m	1 276 m	1 250 w	1 201 w	1 159 w	1 139 m
XIII	1 388 m	1 378 m	1 357 m	1 298 w	1 277 w		1 209 s	1 197 s	1 156 m
XIV	1 370 m	1 342 sh	1 322 s	1 278 w	1 248 s	1 232 sh		1 172 w	1 148 m
I	1 090 m	1 021 m	967 w	922 m	893 w	861 m	840 w	778 m	768 s
II	1 060 w	1 041 w	986 m	960 w	852 m	828 m	802 m	767 m	749 s
III	1 071 s	1 049 w	963 w		905 m	864 m	837 w	767 m	758 s
IV	1 071 s	1 026 w	949 m	936 m	890 w	856 w	802 w	770 s	760 m
V	1 065 s	1 048 sh	988 m	945 w	902 m	859 w	814 w	766 s	742 w
VI	1 051 w	1 032 w	1 018 m	944 w	858 m		814 m	789 m	770 s
VII	1 079 s	1 048 m	967 w	943 m	902 s	866 m	816 w	768 s	727 m
VIII	1 049 w	1 032 w	945 m	937 m	819 w		802 w	779 s	772 m
IX	1 078 s	1 052 m	938 m	900 w	859 m	836 m	776 s	761 s	724 w
X	1 087 w	1 041 w	961 w	882 w	868 m	841 sh	783 m	769 m	735 m
XI	1 071 s	1 041 w	960 w		905 m	879 m	870 m	773 s	748 w
XII	1 094 w	1 049 m	932 m	880 m	858 m	832 m	784 m	770 sh	764 w
XIII	1 073 s	1 041 w	960 w	906 m	880 m	866 m	818 w	774 s	746 w
XIV	1 097 w	1 062 m	967 m	921 w		877 w	853 m	826 m	772 s

localized. The energy of the other localized electron pair is so low that its excitation in the long-wave region of the UV spectrum can be ruled out, so that the considered absorption is more likely a $\pi \rightarrow \pi^*$ transition. Also the last long-wave peaks of the lactam forms at 490 to 520 nm should be regarded as rather a $\pi \rightarrow \pi^*$ than an $n \rightarrow \pi^*$ transition, although in this case the $n \rightarrow \pi^*$ transition is theoretically possible owing to the presence of a carbonyl group; this has two electron pairs on the oxygen atom and the energy level of one of them permits excitation in the long-wave region of the UV spectrum. This transition, however, is generally forbidden, so that the relatively high values of the absorptivities (for $XIV \epsilon > 10000$) is more indicative of a $\pi \rightarrow \pi^*$ transition.

The effects of protonization and deprotonization on the UV spectra (Table I) have also been studied. The last long-wave bands of the individual forms are in the following order according to their wave lengths: lactam > anion > cation > lactim. Quite analogous orders were observed with a number of simpler compounds exhibiting the lactim–lactam tautomerism¹³.

Infrared Spectra

In evaluating the IR spectra we proceeded from the work by Corbett¹, analysing the spectra of a number of solid hydroxyphenazines and their solutions in CCl_4 . By comparing the spectra in the region 3600 to 3100 cm^{-1} the author was able to decide whether a compound was in the lactim or the lactam form. In the region 1650–1500 cm^{-1} , where either form exhibits a greater number of vibrations of aromatic bonds, it was not possible to assign unequivocally the band corresponding to the stretching vibration of the carbonyl; according to Corbett this band occurs in the region 1631–1622 cm^{-1} . Owing to the poor solubility of 5-hydroxybenzo[*a*]phenazine(I) and its derivatives IV, VI, VIII, X and XII in carbon disulphide, chloroform and acetonitrile the region 3600–3100 cm^{-1} could not be used to distinguish the possible tautomers in the solutions. For this reason we proceeded from comparison of the spectra of hydroxyphenazines (Table II) with the spectra of compounds II and XIV.

In the region 1800–1500 cm^{-1} the spectra of compounds II and XIV are markedly different only in the region 1560–1510 cm^{-1} . Compound II has a very intense band at 1552 cm^{-1} with shoulders at 1542 and 1520 cm^{-1} . Compound II exhibits a band of small intensity at 1540 cm^{-1} . Comparison with the spectra of the other compounds reveals that all the acetates absorb insignificantly in this region, whereas the hydroxy derivatives exhibit one intense broad band. It would be difficult to assign it unequivocally and the same is true of the other bands in the region 1800–1500 cm^{-1} , except for the $\nu(C=O)$ bands of the acetoxy group around 1770 cm^{-1} . In the "fingerprint" region the $\nu(C-O)$ band can be identified; in the case of hydroxyphenazines this band occurs¹ between 1220 and 1190 cm^{-1} . With compound II it was an intense band in

this region and with all the acetates it was the most intense band of the spectrum. With compound *XIV*, lacking a C—O bond, and with the hydroxy derivatives *VI*, *VIII* and *XII* the absorption was not marked. Compounds *I* and *X* exhibited a band of medium intensity at 1225 and 1227 cm^{-1} , respectively. The medium intensity band of compound *IV* at 1205 cm^{-1} was probably due to $\nu_{(\text{C}-\text{O})}$ on the carbon atom at position 6. In the region of out-of-plane deformation vibrations of aromatic C—H bonds the results we obtained confirm Corbett's conclusions¹. All the compounds studied had at least one band in the region 770–735 cm^{-1} , associated with the four adjacent hydrogen atoms of the benzo[*a*]phenazine ring. With the non-methylated compounds the absorption was stronger than with the dimethyl derivatives *X–XIII*. A marked absorption in the region 900–840 cm^{-1} was observed only with compounds containing an isolated hydrogen atom. Compounds *VI* and *VII* have no such atom, but they still exhibited a medium-intensity band at 858 and 866 cm^{-1} , respectively. This can evidently be ascribed to $\nu(\text{C}-\text{Cl})$. With compounds *XII* and *XIII* these bands had the same positions as with *VI* and *VII*. The band $\nu(\text{C}-\text{Br})$, occurring among the deformation vibrations of the aromatic C—H bonds, has not been identified. From comparison of the spectra of compounds *VI* and *VIII* it follows that it might be the band at 819 cm^{-1} or the band at 802 cm^{-1} .

REFERENCES

1. Corbett J.: Spectrochim. Acta 20, 1665 (1964).
2. Badger G. M., Pearce R. S., Pettit R.: J. Chem. Soc. 1951, 3204.
3. Van Allan J. A., Reynolds G. A.: J. Org. Chem. 28, 1019 (1963).
4. Kehrman F.: Ber. 23, 2446 (1890).
5. Zincke T., Schmidt M.: Ann. Chem. 268, 257 (1891).
6. Ott R., Lachnit R.: Monatsh. Chem. 104, 15 (1973).
7. Lindenbaum K.: Ber. 34, 1054 (1901).
8. Juřina J., Kandrnál J.: This Journal, in press.
9. Zincke T., Wiegand P.: Ann. Chem. 286, 76 (1895).
10. Zincke T.: Ber. 26, 622 (1893).
11. Badger G. M., Pettit R.: J. Chem. Soc. 1952, 1877.
12. Kehrman F., Messinger J.: Ber. 24, 2167 (1891).
13. Masson S. F.: J. Chem. Soc. 1959, 1253.

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