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SPECTROPHOTOMETRIC STUDIES OF MULTIDENTATE DIANILS

by

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SPECTROPHOTOMETRIC STUDIES OF MULTIDENTATE DIANILS

I. Schiff Bases derived from 2-hydroxy-1-naphthaldehyde and phenylene diamines or Benzidenes

By

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ABSTRACT

The electronic absorption spectra of some Schiff bases derived from 2-hydroxy-l-naphthaldehyde and phenylenediamines or Benzidenes are studied in organic solvents of different polarities. The absorption bands are assigned to corresponding electronic transitions and molecular structure. The main bands in the ir-spectra and signals in the nmr spectra are assigned and discussed in relation to the molecular structure.

INTRODUCTION

Azomethines have acquired wide interest in applications to biological systems and dyes, thus their structure in solution is scientifically important. Spectrophotometric studies of the solvent effect on Keto-enol equilibrium in Schiff bases were reported by some authors [1–4]. The absorption spectra of the Schiff bases salicylidene-2-amino pyridine was characterised [5] mainly by two absorption bands in the 275–400 nm region. The longer wavelength was due to π—π^* within the C=N bands influenced by CT interaction [3].

The infrared spectra of Schiff bases and anils were the subject of several investigations among which the most interesting ones seems to be those of Nakamura [6], Kraus and Issa [8].

Although the work on Schiff bases drew the attention of many workers, yet it seems that little attention has been payed for the spectral behaviour of dianils [8]. Accordingly in the present series of investigations, the electronic absorption, ir and ^{1}Hnmr spectra of some dianils are considered. The present article includes the results of the spectral study of the dianils based on phenylene diamine and benzidenes with 2-hydroxy-l-nephthaldehyde.

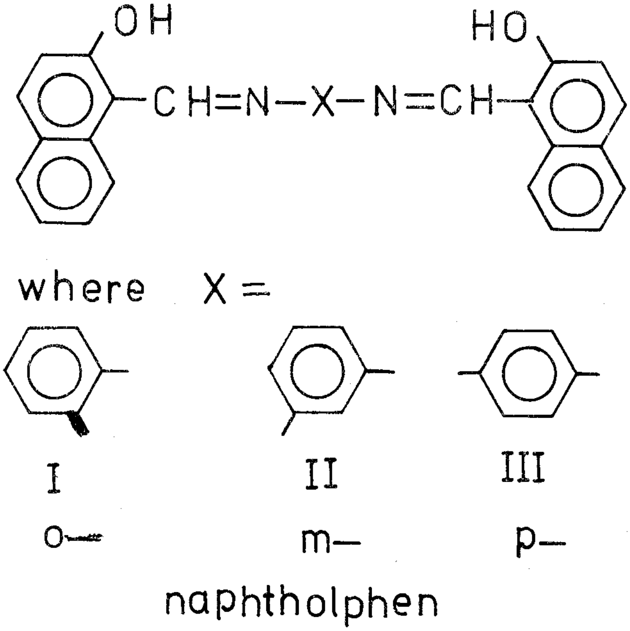
EXPERIMENTAL

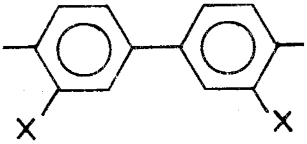
The dianils included in the present investigation were prepared by condensation of purified commerically available diamine (0 .01 mole) with the necessary amount (0 .02 mole) of - 2 -hydroxy-l-naphthaldehyde following known procedure [9]. The compounds obtained were purified by repeated crystallisation from the appropriate solvents till constant melting point.

The electronic absorption spectra were recorded by the aid of a Pye Unicam SP 8000 spectrophotometer using 1 cm matched silica cells. The ir-spectra were recorded in the solid state on a Perkin Elmer infrared spectrophotometer 598 using the KBr disc technique. The ^{1}Hnmr spectra were recorded on a Perkin Elmer R 34 220 Hz nmr spectrometer using d^6 DMSO as solvent and tetramethyl silane (TMS) as an internal standard.

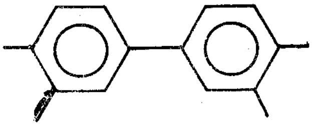
RESULTS AND DICSUSSIONS

The compounds included in the study have the general structural formula.





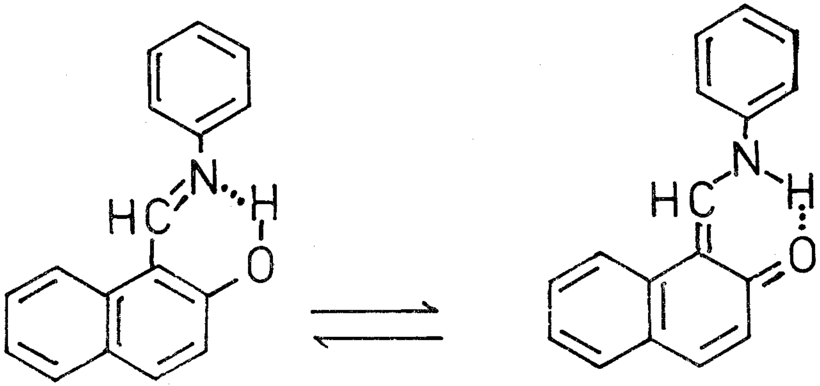
IV (X = H)
V (X = OCH_3)



VI

A. **The electronic absorption spectra:**

The spectra of the compounds display mainly five bands. The first two bands (A,B) within the range 215–265 nm can be assigned to π—π^* transitions of the aromatic rings (naphthyl aldehyde and arylamine rings). The third band (C) appears near 325 nm which can be assigned to a transition within the chelate ring formed through intramolecular hydrogen bonding [10]. The band (D) is located within the range 370–410 nm. This band can be assigned to the π—π^* transition of the naphthyl ring ($1L_b$ — ^1A). The last band (E) is splitted and can be assigned to an intramolecular charge transfer within the whole molecule.



This splitting indicates the possibility of keto-enol tautomerism due to strong conjugative contribution of the naphthyl residue leading to an increase of the charge density of the nitrogen atom and consequently makes the keto - enol tautomerism thermodynamically feasible.

The position of the various bands is influenced by changing the solvent used. The bands due to the π—π^* transition of the aromatic rings as well as the band due to the intramolecular hydrogen, hounding show no regular shifts with changing the polarity of the solvent. On the contrary the CT band display a progressive shift to red with increased polarity of the medium. The application of the dielectric relations given by Gati and Szalay [11] or Suppan [12] did not give any linear relationship. This reveals that the dielectric constant of the medium is not the only factor influencing the band shift and the so called specific solute solvent interaction plays an important role in determining the band position. The latter factor would involve changes in the solvation energies of the ground and excited states as well as solute-solvent hydrogen bonding. Further more the plots of λ_{max} as a function of E_T [13] and Z-values [14] display the same deviation from the linear relations. These results reveal that the solvent shift observed is due to some specific solute solvent interaction leading to the formation of some sort of molecular complex. This would possibly results from intermolecular hydrogen bonding association.

B . The infrared spectra:

The ir-spectra of all compounds show a broad band near 3430 cm^{-1}, which can be assigned to the υ_{OH} stretching vibration of the OH-bond. A medium band appears near 3050 cm^{-1}; which can be attributed to asymmetric streching vibration of the aromatic C—H bands. On the other hand the symmetrical stretching vibration appears as a shoulder or medium band within the range 9218 –3030 cm^{-1}. The spectra exhibit a medium intensity band around 1620 cm^{-1}, this band corresponds to the $\upsilon_{C=N}$ strectching vibration. The relative lcw frequency of $\upsilon_{C=N}$ is a support for the formation of an intramolecular hydrogen bond between the azomethine nitrogen and the OH group. The medium band located near 1180 cm^{-1} is assigned to the aromatic C—H in plane deformation vibration. Also the spectra exhibit strong bands within the range 825–860 cm^{-1}. This band can be assigned to the out of plane deformation frequency of the naphthyl ring. The out of plane deformation vibrations of the aromatic C—H groups lead to the bands within 740–820 cm^{-1}. Also, the spectra display a strong band due to the deformation vibration of the OH group near 855 cm^{-1}.

The medium to strong bands at 1600–1620, 1580–1595, and 1548–1560 cm^{-1} correspond to the skeletal stretching vibrations of the aromatic system. The two bands at 1450–1472 and 1348–1372 cm^{-1} are possibly due to the asymmetric and symmetric δ_{CH} of the azomethine hydrogen. The stretching vibration of the C—N band leads to the band at 1400–1415 cm^{-1}. The band at 1320–1370 cm^{-1} corresponds to δ_{OH} whereas the υ_{C-OH} stretching mode of the OH—group is observed within the 1244–1263 cm^{-1} range.

Table 1. Results for some dianils in different solvents.

Comp.	Solvent	Wavelength (nm)				
		A	B	C	D	E
I	ethanol	230	—	315	370,390	450,470
	Cyclohexane	215	230	320	370	475
II	Ethanol	230	255	330	365,390	422,465
	Cyclohexane	250	265	320	385	445
III	Ethanol	216	235	325	370,390	430,487
	cyclohexane	—	230	330	410	475
IV	ethanol	230	275	375	455	475
	cyclohexane	—	276	—	385	—
V	Ethanol	—	265	355	416	480
	cyclohexane	—	275	315	356	370
VI	Ethanol	—	265	318	365,420	480
	cyclohexane	—	259	310	356	375

Table 2. The assignment of the important bands in the ir - spectra.

Ligant assignment	I	II	III	IV	V	VI
ν_{OH}	3440	3430	3440	3440	3440	3440
ν_{CH}	3055	3050	3050	3040	3040	3050
	3030	2918	2920	2920w	2920s	2920m
$\nu_{C=N}$	1621	1625	1620	1625	1620	1620
ring vib.	1595	1590	1585sh	1545	1445	1545
ring vib.	1468	1484	1490	1492	1483	1485
$\nu\varnothing_{-O}$	1288	—	—	1310	1312	1312
δ_{OH}	1244	1248	1250	1245w	1250	1245
$\nu\varnothing_{-OH}$	1140	1140	1142	1138	1140	1140
ν_{c-OH}	1080	1085	1090	1085	1087	1082
γ_{OH}	855	856	855	855	855	860
γ_{naph}	825	825	860	815	835	822
γ_{CH} benz.	745	745	820	745	750	745

sh = shoulder w = weak m = medium s = sharp.

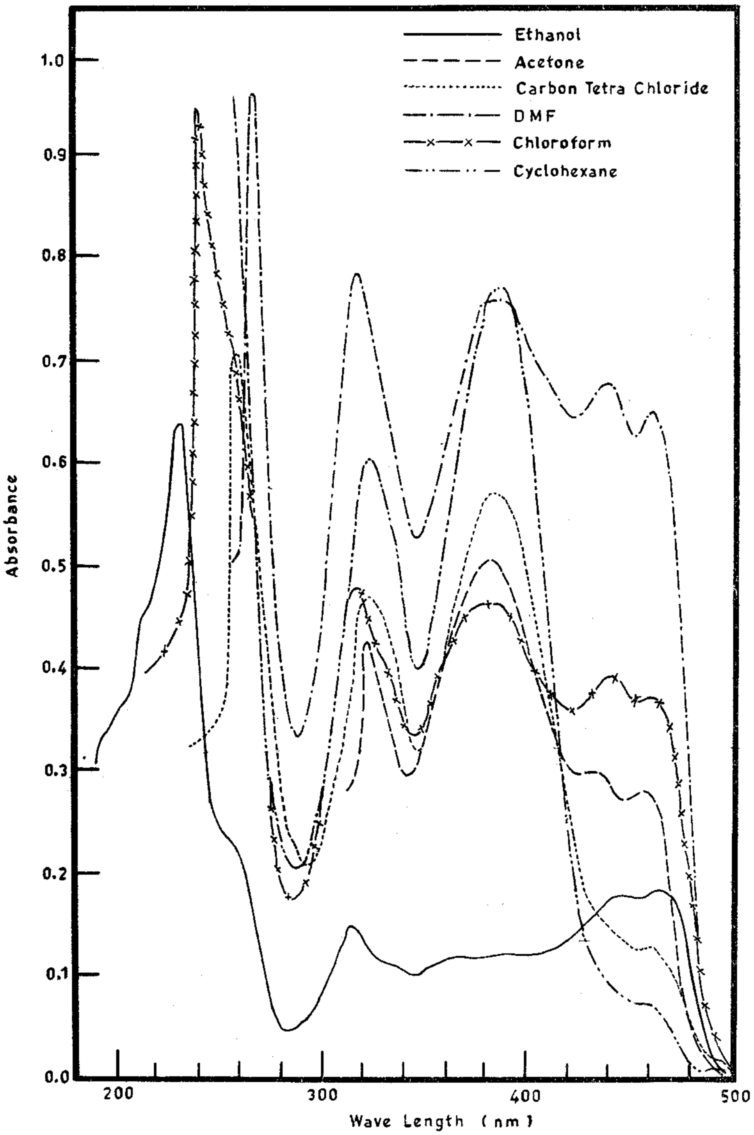


Fig.(2).The Electronic Absorption Spectra of (II)
In Different Organic Solvents .

C—The ^{1}Hnmr spectra

The OH—group leads to a signal at 15 .15 and 9 .38 ppm for I and II respectively. The position of this signal can be taken as an argument for the contribution of the OH groups in an intramolecular hydrogen bonding. The higher value of I denotes a stronger hydrogen bond. The signals at 9 .5 and 8 .15 ppm, with integration equivalent to two protons can be assigned to the proton of the =CH— group for compounds I and II respectively. The multisignals of the aromatic protons appear at 7 .08–8 .20 ppm.

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