

SPECTROSCOPIC STUDIES OF SOME SCHIFF'S BASES
DERIVED FROM ANTHANILIC ACID.

BY

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ABSTRACT

The electronic absorption spectra some Schiff's bases derived from anthranilic acid been recorded in organic solvents of varying polarities. The solvent shift is discussed in the light of possible formation of solute-solvent molecular complexes. The application of potentiometric titrations have been utilized in calculating pK_a of the COOH and enolic OH groups of the compounds under investigation. The important bands in the I R spectra and the main 1H NMR signals are assigned and discussed in relation to molecular structures of the compounds .

INTRODUCTION

Schiff's bases compounds have application as catalysts in various chemical and photochemical reaction as well as in biological systems [1 - 4] . A clear understanding

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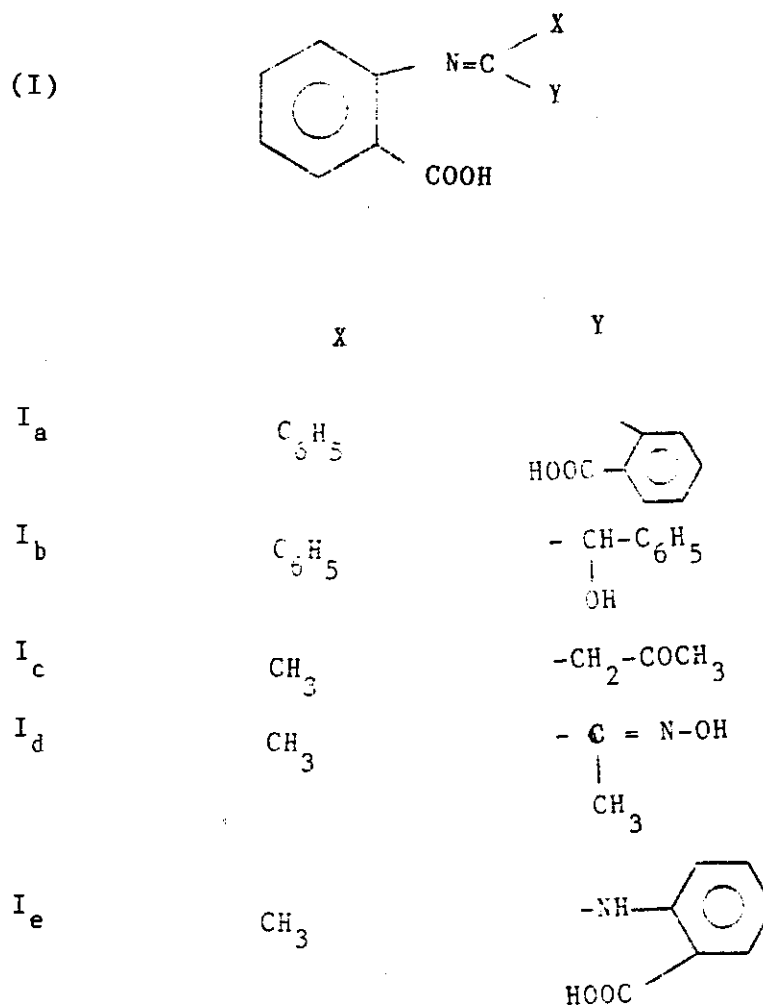
of the Schiff's bases derived from anthranilic acid can be obtained if the spectral characteristics of the compounds are known. The present paper is devoted to an investigation of the absorption spectra of some Schiff's bases derived from anthranilic acid in the UV, visible and IR regions . Also, the important signals in the ^1H NMR spectra are assigned. The spectral characteristics are discussed in relation to molecular structure.

EXPERIMENTAL

All the chemicals used in the present investigation were BDH products.

The compounds under investigation were prepared according to the method described previously [5] . The compounds included in the present investigation have the general structure formula (I):

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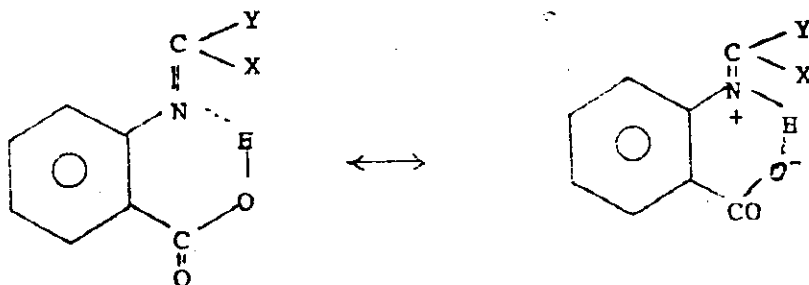
The solvents used were purified by recommended procedures [6].

Apparants and physical measurements are the same as previously described [7,8].

RESULTS AND DISCUSSION

A] Electronic absorption spectra:

The UV spectra of the Schiff's bases in organic solvents (Table I and Fig. 1) display mainly two bands in the regions 220 - 240 (A) and 280 - 320 (B) nm with a broad shoulder (C) 360 - 440 nm, on the longer wavelength side of band (B) . The Band A can be assigned to a $\pi - \pi^*$ transition ($^1L_a - ^1L_A$) of the phenyl group while the band (B) can be assigned to the $\pi - \pi^*$ transitions within the $N = C$ bond ; the broad shoulder may be assigned to an intramolecular charge transfer involving possibly the following resonance forms:



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The red shift of the bands (A) and (B) with increased solvent polarity is of low magnitude compared to that of (C) . The red shift of (C) is in agreement with the observations of Bayliss [9] and Schubert [10] who proposed that the polar solvent molecules are oriented in the solvation layer in such a way as to solvate more the excited state causing more solvent stabilization of the excited state than that of the ground state. The higher shifts in DMF can be ascribed to the ability of this solvent to act as proton acceptor in addition to ability to act as π -electron donor towards the solute molecules. In case of ethanol, CHCl_3 or dioxane the solvent molecules can behave as proton donors or electron acceptors [11].

The application of the dielectric function of Gati and Szalay [12] revealed that the dielectric constant of the medium is not the main factor governing the band shifts. This is further substantiated by various solvent parameters, the plots of λ_{max} versus the dielectric functions $f(D)$ and $\epsilon(D)$ given by Suppan [13] , the Kosower [14] Z-solvent parameter and the E_T (acidity function) given by Reichardt [15], where nonlinear relations are obtained. The main role seemed to be played by the formation of some sort of molecular compounds through solute-solvent hydrogen bonding or electron transfer interactions.

Based on these results, the shift in band position

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would be attributed to combined effect of the dielectric constant, change in the solvation energies of the ground and excited states as well as the probable formation of hydrogen bond solvent molecular complexes. Another possible factor is the changes in the strength of the intramolecular hydrogen bonding governed by proton donor acceptor interaction. The hydrogen bonding governed by proton donor and acceptor interaction between solute and solvent molecules.

C] Acid dissociation

The acid dissociation curves of I_a and I_b are shown with increasing ν_{OH} in Fig. (1). The curves are fitted with a very good fit. The values of pK_a in all compounds under investigation are ascribed to the ionization of the COOH group and not to the phenol. The values pK_a in case of compounds (I_a and I_b) correspond to the ionization of the COOH group whereas in I_c compounds can be ascribed to the ionization of alcoholic and phenolic OH groups respectively.

The values of pK_a or pK_b as a function of the structure of the compounds are shown in Table (1). The linear relations, Fig.(2), indicate that the ionization of COOH and the OH groups of the phenyl and Schiff base are governed by the side chain structure.

C] The IR Spectra:

The IR spectra of the compounds (I_{a-e}) show ν_{OH}

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carboxylic in the range $3400-3490\text{ cm}^{-1}$ while the ν_{COO} appears at $1670-1680\text{ cm}^{-1}$. The strong to medium bands observed at $1570-1590\text{ cm}^{-1}$ are assigned to $\nu_{\text{C=N}}$ while the ν_{NH} for compound I_e is observed at 3100 cm^{-1} . The strong to medium bands observed at $1570-1590\text{ cm}^{-1}$ are assigned to $\nu_{\text{C=N}}$ while the ν_{NH} for compound I_e is observed at 3100 cm^{-1} . The spectra of I_c , I_d and I_e compounds display strong or medium sharp band at $1380-1390\text{ cm}^{-1}$ due to the in-plane deformation of the CH_3 -group. The

δ_{CH_2} band for compound I_c is observed at 1455 cm^{-1} . The alcoholic ν_{OH} in the spectra of I_c and I_b appear at $2890-2910\text{ cm}^{-1}$. Also, the spectra display the bands due to the δ_{OH} and $\delta_{\text{C-OH}}$ at $1260-1275$ and $1155-1170\text{ cm}^{-1}$ respectively. The bands near 1000 cm^{-1} can be assigned to the δ_{CH} of the phenyl ring while the out-of plane deformation of the phenyl ring appears at $750-770\text{ cm}^{-1}$. Most of the IR bands are affected by changes in molecular structure but most prominent changes occur in ν_{COOH} and $\nu_{\text{C=N}}$. The plots of ν_{COOH} and $\nu_{\text{C=N}}$ against σ^* (Taft constant) are linear relations with slope (-0.38) . This reveals the charge migration from N to the CXY part over the C=N linkage acting as a bridge.

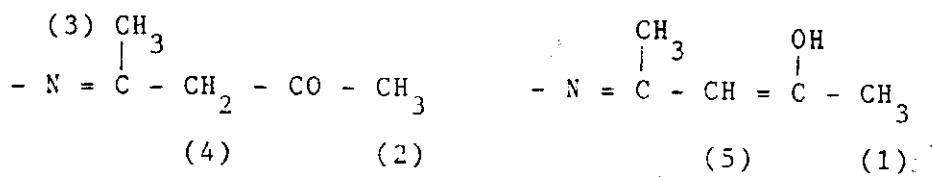
D] The ^1H NMR Spectra :

The ^1H NMR spectra of some compounds under investigation were recorded in DMSO (d_6) using TMS as internal standard. The COOH group gives a broad signal at $11.0-12.0$

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ppm . Compounds I_b and I_c show a signal at 5.66 and 15.6 ppm respectively corresponding to alcoholic and enolic OH , resulting from a tautomeric shift in compound I_c .



A support of this idea is the appearance in the ^1H -NMR spectra of compound I_c of five signals with integration equivalent to three, three, six, two, and one proton at 1.8, 2.3, 2.5, 4.2 and 6.2 ppm . which can be assigned to $\text{CH}_3(1)$, $\text{CH}_3(2)$, $\text{CH}_3(3)$, $\text{CH}_2(4)$ and $\text{CH}(5)$ respectively. In all the compounds under investigation the broad signal at 6.7-7.8 ppm. can be assigned to the aromatic protons,

The plot of δ_{COOH} as a function of the σ^* -(Taft constant) is also linear as in the case of IR spectra indicating that the strength of the intramolecular hydrogen bonding occurring between the carboxylic OH and C=H groups is governed by the electron density on the azomethine nitrogen atom as influenced by the side chain structure.

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Table (1)

Assignment of the Electronic Spectral,Bands of the Schiff's
Bases Derived from Anthranilic Acid in Organic Solvents.

Compound	$\pi-\pi^*$ phenyl		$\pi-\pi^*$ C=N		CT band	
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
IN ETHANOL						
I _a			290	2920	380	1112
I _b			295	3245	385	1615
I _c	235	5673	300	3725	395	1820
I _d	230	6783	305	4623	405	1720
I _e	225	5783	315	4155	415	1965
IN CHCl ₃						
I _a			280	2115	360	1009
I _b			285	2512	370	1112
I _c	240	2215	285	3112	380	1617
I _d	235	4215	290	3985	390	1512
I _e	235	4112	300	3776	400	1617
IN DIOXANE						
I _a			290	2916	370	1212
I _b			295	3101	380	1413
I _c	240	3450	300	3212	385	1612
I _d	225	4600	310	4121	395	1573
I _e	220	4312	315	3125	405	1628
IN DMP						
I _a	230	3617	290	2899	380	2115
I _b	235	3619	295	4167	390	2412
I _c	230	6118	295	4869	400	2615
I _d	240	9117	300	5617	420	2780
I _e	240	8413	320	4216	440	3019

λ_{\max} in nm ϵ_{\max} in lit.mol.⁻¹ cm.⁻¹

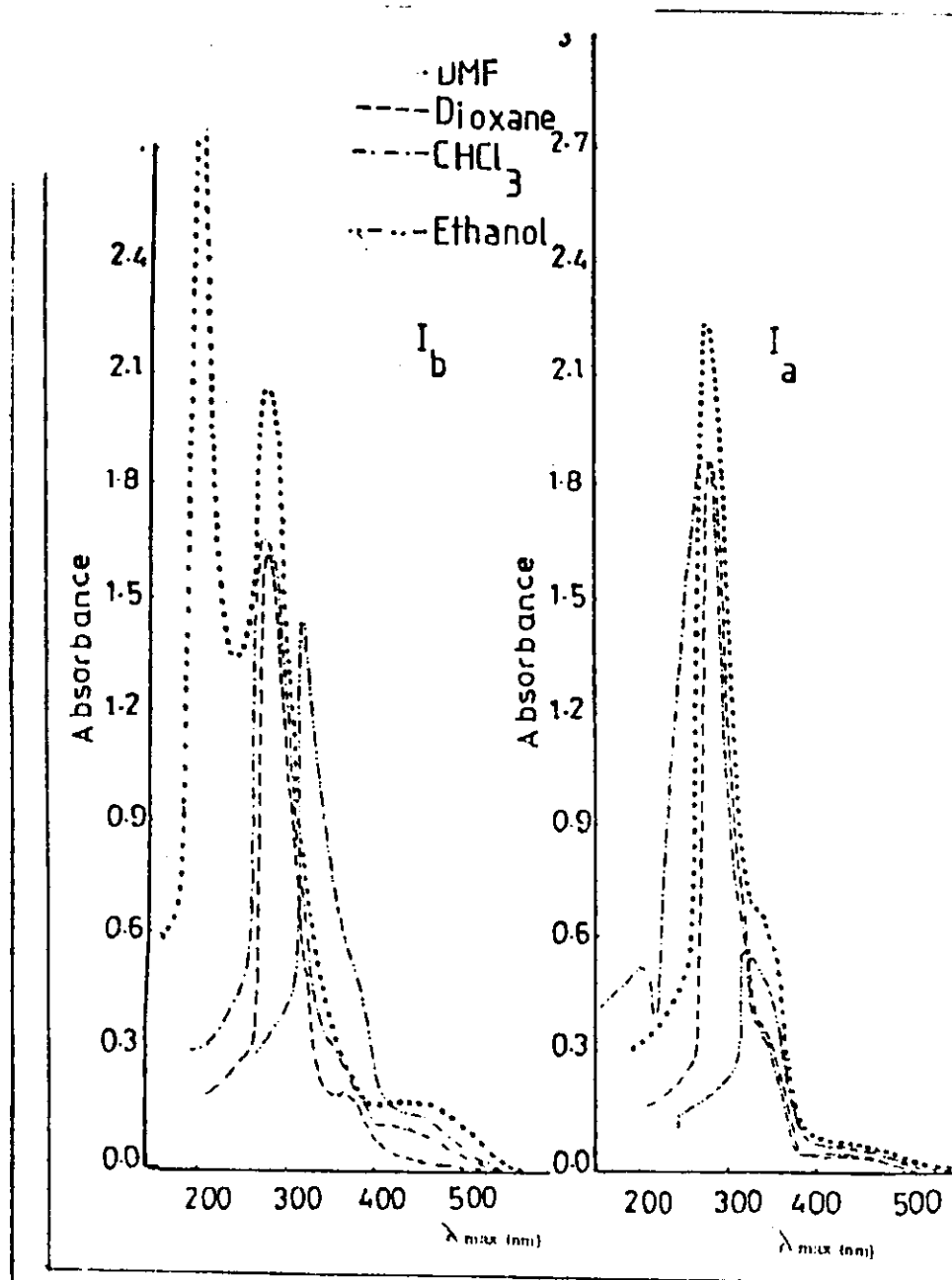


Fig. (1): Electronic absorption spectra of Schiff base compounds in different organic solvents.

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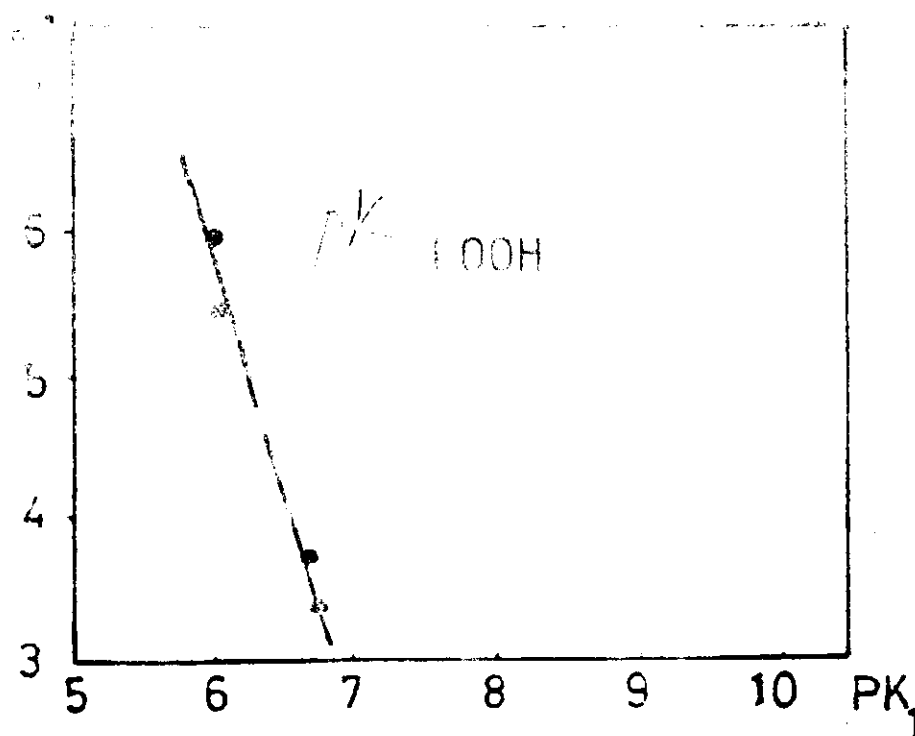


Fig. (2) - Effect of molecular structure of Schiff base on PK_1 compounds.

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REFERENCES

- 1- M.D.Cohen and S.Flavian, J.Chem.Soc. (B),317(1967).
- 2- M.D.Cohen and S.Flavian, J.Chem.Soc.(B),312(1967).
- 3- G.O.Dudek and F.P.Dudek , J.Am. Chem. Soc., 88, 2407 (1966).
- 4- B.M.Krasoviskii, B.M.Bolotin and R.N.Nurmukhametov, zh ; obshch. Khim, 34, 3786 (1964).
- 5- A.I. Vogel "Practical Organic Chemistry". Longmans, London (1962).
- 6- N.Vinogradov., Can J. Chem., 40, 2170 (1962).
- 7- M.A.El-Ries, S.M.Abu-El-Wafa, F.A. Aly and M.A. El-Behairy, Analytical letters, 18, 1905 (1985).
- 8- S.M. Abu-El-Wafa, E.A. Mohamed, R.M.Issa and M.Gaber Indian J. Chem., 24A, 407 (1985).
- 9- N. S. Bayliss and M. MacRae, J. Phys. Chem. 58. 1002, (1959).
- 10- W. M. Schubert, J.Robins and J.L. Haum, J.Am. Chem. Soc., 82, 1353 (1960).
- 11- R.Föster "Donor Acceptor Complexes " Academic Press, London N.Y. (1969).
- 12- L.Gati and L. Szalay, Acta Phys. Chim,5, 87 (1969).
- 13- P. Suppan , J. Chem. Soc.(A), 3125 (1968).
- 14- E. M. Kosower " An Introduction to physical Organic Chemistry " Willey N.Y., p.301 (1968).
- 15- C. Reichardt, Lösungsmittel Effekte in der organischen Chemie, Verlag Chemie (Weinheim Bergstr-Germany)(1973).

دراسات طيفية على بعض متراكبات شيف المنشقة من حمض الانثرائيليك

تم دراسة الأطياف الالكترونية ودون الحمراء والرنين النووي المغناطيس لبعض متراكبات شيف الشقة من حمض الانثرائيليك .
وقد تم مناقشة الازاحة فى الأطياف الالكترونية فى المذيبات مختلفة القطبية فى ضوء تكون متراكبات جزيئية مع المذيب كما تم تعيين ثوابت الاتزان لمجموعات الكربوكسيل والهيدروكسيل الانىولية للمركبات قيد الدراسة .