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Spectroscopic and Conductometric Studies on some *Schiff* Bases

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Summary. The electronic absorption spectra of some *Schiff* bases derived from 3-amino-1,2,4-triazole have been investigated in organic solvents of different polarities. Assignment of the absorption bands, solvent effects, and spectral structure correlations are considered. The fundamental IR bands and the main signals in the ¹H NMR spectra are assigned and discussed with respect to the effect of substituents on the phenyl ring. A change of the electrical conductance of the compounds with increasing temperature is observed for the solid samples.

Keywords. Spectroscopy; Conductometric studies; Schiff bases.

Spektroskopische und konduktometrische Untersuchungen einiger Schiffscher Basen

Zusammenfassung. Die UV/Vis-Spektren einiger von 3-Amino-1,2,4-triazol abgeleiteter Schiffscher Basen wurden in Lösungsmitteln unterschiedlicher Polarität bezüglich Zuordnung der Banden, Lösungsmitteleffekten und Spektrum-Struktur – Korrelationen untersucht. Die wesentlichen IR- und ¹H-NMR – Signale wurden zugeordnet und werden mit Substituenteneffekten in Beziehung gesetzt. Im Festzustand zeigen die Proben eine Änderung der elektrischen Leitfähigkeit mit steigender Temperatur.

Introduction

Schiff bases have found many applications as catalysts in various chemical and photochemical reactions and in biological systems [1-3]. The biological activity of the compounds is mainly dependent on their molecular structure. It is known that the spectral behaviour of an organic molecule is strongly related to its structure both in the ground and excited states. Based on this knowledge, the spectral behaviour of the Schiff bases has been the subject of several investigations [4-8].

The electrical conductivity of solid organic compounds is a property which is covered by a very wide range of studies [9]. The enthusiasm for discovery and research of organic compounds which conduct the electric current owes to Szent-Gyorgy [10] who speculated about the conducting properties of proteins. This plays an important role in the life process. Recently, *Schiff* bases were shown to have semiconducting properties in an attempt for their use in solar energy storage [11].

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The present article is devoted to an investigation of the absorption spectra of some *Schiff* bases derived from 3-amino-1,2,4-triazole in the UV/Vis and IR regions; their ¹H NMR spectra are considered as well. The spectral characteristics are discussed in relation to molecular structure. In addition, the electrical conductance properties of the relevant compounds have been studied.

Results and Discussion

Electronic Absorption Spectra

The electronic absorption spectra of the entitled compounds were studied in some organic solvents (ethanol, methanol, formamide, DMF, $CHCl_3$, CCl_4 , and cyclohexane). The data are listed in Table 1 and are represented in Fig. 1. The spectra exhibit mainly four absorption bands within the 200–350 nm region. The first two bands (A, B), appearing within the 210–265 nm region, can be assigned to the $\pi - \pi^*$ transition of the aromatic rings. The third band (C) appears at 275–318 nm and can be assigned to the transition of the triazole ring. The band D, located within the 300–340 nm range, corresponds to the electronic transition involving charge transfer within the entire molecule [14]. The data for compounds 1, 7, and 8 indicate a weak

		Band A		Band B		Band C		Band D	
Compound	Solvent	λ	$\varepsilon \times 10^{-5}$	λ	$\epsilon \times 10^{-5}$	λ	$\epsilon \times 10^{-5}$	λ	$\epsilon \times 10^{-5}$
1	Ethanol	225	0.53	242	0.73	300sh	0.70	338	3.0
	Cyclohexane	232		240	_	318	_	325	_
2	Ethanol	232	0.93		_	295	2.07	315	2.5
	Cyclohexane	220	_	266	_	285	-	-	_
3	Ethanol	230	0.11	283	0.28	293	0.28	318	0.28
	Cyclohexane	218		265		290sh		320	
4	Ethanol	232	6.6	255	6.1	275	5.8	310	4.4
	Cyclohexane	217		252		302		310sh	
5	Ethanol	232	0.32	260sh	0.34	284	0.47	300	0.4ª
6	Ethanol	235	0.78	253	0.45	315sh	0.29	330	0.35 ^b
	Cyclohexane	213	_	245	-	_		320	_
7	Ethanol	232		242	_	275		_	_
	Cyclohexane	210		240	_	286	_	310	_
8	Ethanol	225	0.26	265	0.53	_	_	340sh	0.14
	Cyclohexane	213	_	258	_	_	_	330	_
9	Ethanol	232	_	260	_	_	_	320	<u> </u>
	Cyclohexane	225		260	_	285		_	-
10	Ethanol	238	_	260	_	_		310	_
	Cyclohexane	212	_	250	_	280	_	310	-
11	Ethanol	230	0.31	265	0.56	280	0.58	310	_
	Cyclohexane	215	_	256	-	288	-	325	

 Table 1. Electronic absorption spectra of Schiff bases derived from 3-amino-1,2,4-triazole

 $^{a}\lambda_{max} = 340$ nm, $\varepsilon_{max} = 0.32 \times 10^{5}$; $^{b}\lambda_{max} = 375$ nm, $\varepsilon_{max} = 0.37 \times 10^{5}$; sh: shoulder





solvent shift for the transition of the aromatic system. The CT band displays a red shift with increasing polarity of the medium. The application of the *Gati* and *Szalay* [15] equation and the dielectric functions given by *Suppan* [16] did not yield a linear relationship between λ_{max} and the dielectric constant functions, indicating that the dielectric constant is not the main controlling factor in solvent shifts. However, the specific solute-solvent interaction plays an important role in determining the band position. This involves changes in the solvation energies of the ground and excited states as well as solute-solvent hydrogen bonding. Furthermore, the plots of λ_{max} as a function of E_T [17] and Z-values [18] show the same deviation from a linear relationship.

 λ_{max} of the CT bands is correlated to *Hammett*'s σ -values of the substituents in a linear way indicating that the position of the CT band is affected by the electronic requirements:

$$\lambda_{\mathbf{R}} = \lambda_{\mathbf{H}} - \rho \sigma_{\mathbf{R}} \ (\rho = 10 \ \mathrm{nm})$$

Infrared Spectra

The IR spectra of all compounds (Table 2) show a band in the range $3100-3300 \text{ cm}^{-1}$ which can be assigned to v_{NH} (stretching) of the NH group. The bands located at $1590-1627 \text{ cm}^{-1}$ and $970-1025 \text{ cm}^{-1}$ are due to $v_{\text{C=N}}$ and v_{CH} , respectively. These bands are affected by the electronic properties of the substitutents.

The variation of $v_{C=N}$ and v_{CH} with σ (Fig. 2) shows a good linear relation. The ρ values amount to 9.2 and 23 for $v_{C=N}$ and v_{CH} , respectively. The positive slopes (Fig. 2) indicate that the band position is shifted to lower wavenumbers for electron donor groups. This may be due to the increase of the electron density on the C=H group and *vice versa*.

	IR (cr				¹ H NMR (ppm)				
Compound	v _{NH}	v _{CH=N}	V _{CH=N}	v _{OH}	v _{с-он}	$\delta_{\rm NH}$	$\delta_{\rm CH}$	$\delta_{a romatic}$	$\delta_{_{ ext{other signals}}}$
1	3100	1590	987	_		9.1	8.1	6.8-7.93	3.1 (CH ₃) ₂
2	3200	1595	970		_	9.2	8.25	7.0-8.1	3.85 (OCH ₃)
3	3180	1600	1010	1250	1172	9.05ª	7.87	6.7-7.8	8.12 (OH)
4	3300	1610	1030	1285	1180	9.91ª	8.27	6.9–7.4	9.1 (OH)
5	3150	1620	982	1280	1155		—	-	_
6	3100	1627	1015	1250	1190	_	-	_	_
7	3260	1600	1010	-	_	9.3	8.3	7.5-8.1	
8	3180	1605	1015	-		9.3	8.37	7.9-8.2	_
9	3300	1605	1025	_	_	9.4	8.83	7.7-8.5	_
10	3260	1600	1015	-	_	9.2	8.3	7.4–7.9	-
11	3180	1592	1010	-		-	-		-

Table 2. IR and ¹H NMR spectra of Schiff bases derived from 3-amino-1,2,4-triazole

 $^{a}NH + OH$



Fig. 2. Correlation of IR parameters of 3-amino-1,2,4-triazole Schiff bases with Hammett's σ -constants

¹H NMR Spectra

The main signals in the ¹H NMR spectra of compounds 1–4 and 6–9 are given in Table 2. The signals are within the range 9.05-9.91 ppm with an integration corresponding to one proton and can be assigned to the proton of NH group, whereas that of the CH=N group appears at 7.87–8.83 ppm. The multiplets of the aromatic protons appear within the range of 6.4–8.5 ppm.

A plot of the NH and CH=N chemical shifts as a function of σ yields a fairly well linear relation (Fig. 2). The ρ values are 0.12 (NH) and 0.18 (-CH=N-). The signals shift to higher δ values as the acceptor character increases as a result of the

increasing deshielding effect of the substituent, whereas donor substituents that increase the shielding of the protons shift the signals to lower δ values.

Electrical Conductivity Measurements

The electrical conductivity was measured over a relatively moderate temperature range to avoid melting of the materials. Figs. 3 and 4 represent the variation of the electrical conductivity (log σ) as a function of temperature (1000/TK⁻¹) for some of the *Schiff* bases under investigation. The following relation is applicable:

$$\sigma = \sigma_0 \cdot \exp(-\Delta E/kT)$$

The parameters have their usual meanings. The plot of the electrical conductivity as a function of reciprocal absolute temperature (Figs. 3 and 4) shows two inflections for compounds 1, 2, 7, 9, and 10. This denotes that the mode of conduction changes during the conductivity measurements. A linear behaviour is observed for compounds 8 and 5. The values of the transition temperature and the activation energies on heating and cooling rates were calculated according to equation 1 and are listed in Table 3. The activation energy of the Schiff bases decreases in the order 1 < 2 < 7 < 10 < 8. Consequently, the electrical conductivity increases in a reverse order. This is probably explained on the basis of increased electron density and polarization of the molecule as a function of the substitution inductive effect [11], facilitating the electron delocalization in the molecule. A justification for the above conclusion stems from the linear relationship observed between the activation energies under and above the transition temperature with σ_{\perp}^{+} values of substitution (Fig. 5). The electrical conductivity values for compounds of the same type of substituent at different positions (e.g. 9 and 8) increase in the order p > m position, due to the mesomeric effect of the substituent [19].



Fig. 3. Variation of electrical conductivity $(\log \sigma, \Omega^{-1} \cdot cm^{-1})$ as a function of reciprocal absolute temperature for some solid *Schiff* bases (1, 2, 10, 8)



The difference in the position of the heating and cooling curves has no essential effect on the specific conductivity level and causes only slight changes of the activation energy (Table 3). The activation energies below and above the transition temperature are large. This can be attributed to the following [20]:

- (1) As the conjugation is increased through the *Schiff* base molecule, the π -electrons are not delocalized over a corresponding greater distance, and the activation energy (ΔE) for generation of the carriers no longer falls linearly with the conjugation chain length;
- (2) The triazole and the phenyl rings are actually not coplaner. Consequently, the rotation of the two molecules against each other in a twisting motion is

	Heating	ç		Cooling			
	Activati	ion energy		Activati	on energy		
Compound	ΔE_1	ΔE_2	- Transition temperature	$\Delta E_1 \qquad \Delta E_2$		Transition temperature	
1	0.742	0.260	353.36	_	_	_	
2	1.025	0.715	436.68	1.206	0.693	429.18	
5	2.121	_	_	2.199	-	-	
7	1.23	0.990	413.22	1.24	0.778	411.52	
8	1.732	_	_	_	_		
9	2.249	1.164	409.84	2.224	1.109	414.94	
10	1.320	0.469	399.20	1.237	0.616	402.41	

Table 3. Values of activation energy for the conduction (eV) and transition temperature (K) for some of the investigated *Schiff* bases

considered which breaks the conjugation between them; hence, the atomic p-orbitals can no longer overlap.

Experimental

Preparation and spectrophotometric measurements of the Schiff bases

The anils included in the present investigation were prepared by condensation of purified 3-amino-1,2,4-triazole with the necessary amount of benzaldehyde derivatives following a known procedure [12]. The compounds obtained were purified by repeated crystallization from ethanol. The compounds included in the present study have the general structure formula given below where $R = p-N(CH_3)_2$ (1), $p-OCH_3$ (2), p-OH (3), m-OH (4), o-OH (5), 2-OH-1-naph (6), H (7), $p-NO_2$ (8), $m-NO_2$ (9), p-Cl (10), and p-Br (11). Working procedure and apparatus were as described previously [13].



Electrical Conductivity measurements

These were carried out on some of the investigated *Schiff* bases using a Super Megometer Electrometer Model RM 170. The samples had the form of discs of a diameter of 13 mm and a thickness 1 mm produced under a pressure of $\sim 300 \text{ kg} \cdot \text{cm}^{-2}$. The cross section area of the pellets was covered with silver paste to eliminate as far as possible the contact resistance between the electrodes and the discs. The temperature was measured in air using a Cu–CuNi thermocouple placed close to the sample. Measurements were carried out from room temperatures up to 460 K and then on cooling down to room temperature. The electrical conductivity control was occurate to $\pm 0.3 \Omega^{-1} \cdot \text{cm}^{-1}$.

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