

Synthesis and spectral studies of Schiff bases of 2-amino-5-mercapto-1,3,4-thiadiazole

Shar S. Al-Shihry

Department of Chemistry, College of Science, King Faisal University,
Al-Hasa, Saudi Arabia

Abstract:

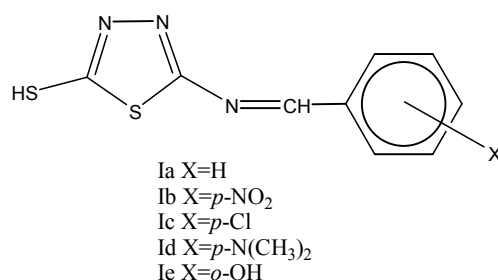
The synthesis and characterization of Schiff bases derived from 2-amino-5-mercapto-1,3,4-thiadiazole are described. The structures of the titled Schiff bases were elucidated by elemental analysis, electronic absorption, infrared, ^1H - and ^{13}C NMR spectral measurements. The electronic absorption spectra of the Schiff bases were studied in organic solvents of different polarity. The dependence of λ_{max} upon the type of the substituents and their positions was investigated using UV-Vis spectra. The observed UV-Vis absorption bands were assigned to the corresponding electronic transitions. The important bands in the IR spectra as well as the main signals of the ^1H - and ^{13}C NMR spectra were assigned.

Introduction:

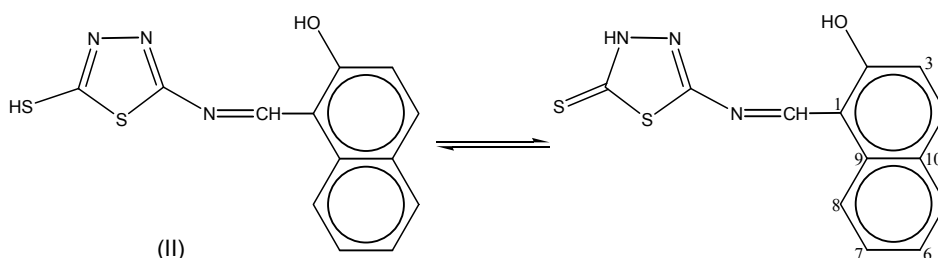
Heterocyclic moieties can be found in a large number of compounds which display biological activity. The biological activity of the compounds is mainly dependent on their molecular structures. It is also known that the spectral behaviour of an organic molecule is strongly related to its structure. Based on these knowledges, a considerable work has been reported on the spectroscopic behaviour of Schiff bases (Guha, *et al.* 2000, Dziembowska, *et al.* 2001, Zhao, *et al.* 2001, Schiff, *et al.* 2002, Issa, *et al.* 2003). In addition, many azomethine compounds are used as dyestuffs (Papic, *et al.* 1994). Recently, there has been a considerable interest in the chemistry of Schiff base compounds and their metal complexes due to their applications to biological systems (Hossain, *et al.* 1996, Jeewoth, *et al.* 1999, Gaber, *et al.* 2001). 1,3,4-thiadiazoles are very interesting compounds due to their important applications in many pharmaceutical, biological and analytical fields (Kornis, 1984, Ahmed, *et al.* 2002). So, the aim of the present work is to study the electronic absorption, infrared, ^1H - and ^{13}C -NMR spectra of some Schiff bases derived from 2-amino-5-mercapto-1,3,4-thiadiazole. The effect of solvents of different polarities was also considered. The diagnostic bands in the IR, and the signals of the ^1H - and ^{13}C -NMR spectra were assigned and discussed.

Experimental:

The used solvents were all of BDH spectral grade. The Schiff bases under investigation were synthesized in the usual way for the preparation of anils (Gaber, *et al.* 2001) by condensation of 2-amino-5-mercapto-1,3,4-thiadiazole with aldehyde derivatives in 1:1 molar proportion in ethanol. The reaction mixture was heated under reflux for about 4-6 hrs, then filtered off and washed with ethanol. The compounds were purified by repeated crystallization from pure ethanol and then dried. The purity of the compounds was checked by elemental analysis and constancy of melting points (Table 1). The Schiff bases have the general formula:



The naphthylidene derivative (II) has the following structure:



The electronic absorption spectra were recorded on a Shimadzu UV-Vis 1601 PC spectrophotometer in the wavelength range 200-700 nm using a 1 cm matched quartz cell. The IR spectra were measured with a Shimadzu 8000 FTIR spectrometer using KBr pellets. The ¹H-¹³C-NMR spectra were recorded on a JEOL 400 spectrometer using TMS as internal reference.

Table (1)
Elemental analysis and physical properties of Schiff bases (Ia-Ie and II).

No.	colour	formula	m.p. °C	Elemental analysis ^(a)		
				%C	%H	%N
Ia	Yellow	C ₉ H ₇ N ₃ S ₂	247	48.87 (48.68)	3.17 (3.01)	19.00 (18.80)
Ib	Yellow	C ₉ H ₆ N ₄ S ₂ O ₂	195	40.60 (40.43)	2.26 (2.23)	21.05 (21.00)
Ic	Yellow	C ₉ H ₆ N ₃ S ₂ Cl	206	42.27 (42.00)	2.35 (2.24)	16.44 (16.31)
Id	Orange	C ₁₁ H ₁₂ N ₄ S ₂	185	50.00 (49.80)	4.55 (4.47)	21.21 (21.10)
Ie	Yellow	C ₉ H ₇ N ₃ S ₂ O	249	45.57 (45.40)	2.95 (2.87)	17.72 (17.56)
II	Orange	C ₁₃ H ₉ N ₃ S ₂ O	272	54.36 (54.17)	3.14 (3.10)	14.63 (14.59)

(a) Calc. (found).

Results and Discussion

Electronic absorption spectra

The spectrum of an organic compound is affected in most cases by the nature of the solvent used; changes in the intensity and displacement of absorption band take place. This displacement includes either a red shift or a blue shift on going from a nonpolar to a polar solvent. This effect is actually due to several factors e.g. physical properties of the solvent like dipole moment, dielectric constant, refractive index or its ability to interact through hydrogen bonding, the difference in solvation energy from one solvent to another as well as the polarities and dipole moments of the solute. Accordingly, the solvent effect is the sum of several individual factors which reinforce and sometimes cancel out one another such that an accurate method to measure this effect is so difficult.

The electronic absorption spectra of the Schiff bases under investigation were measured in ethanol while for compound (Id) the electronic spectra were measured in organic solvents of different polarity, namely methanol, isopropanol, chloroform, carbon tetrachloride, dichloromethane, dichloroethane and toluene. The electronic absorption spectra of the Schiff bases in ethanol are characterized by four mainly bands (Table 2). The first band at $\lambda_{\max} = 208-238$ nm can be assigned to the medium energy $\pi-\pi^*$ transition of the aromatic ring, while the second band at $\lambda_{\max} = 251-297$ nm

is due to the low energy π - π^* transition. The third band within the range $\lambda_{\max} = 303$ - 334 nm is due to the excitation of the electrons of the azomethine group. The last band in the range ($\lambda_{\max} = 401$ - 425 nm) which is not present in the spectrum of the free amine, is assigned to an intermolecular charge transfer absorption involving the whole molecule. For Schiff bases (*Ie and II*) another band is observed at 440 nm corresponding to the intermolecular hydrogen bond between *o*-OH and CH=N groups.

The application of the dielectric relations given by Gati and Szalay (1959) and Suppan (1968) to the electronic absorption data of solvent shift does not give any linear relationships, indicating that the dielectric constant of the medium is not the main controlling factor influencing the band shift. However, the specific solute solvent interaction plays an important role in determining the band position. This involves changes in the solution energies of the ground and excited states as well as solute solvent hydrogen bonding. Furthermore, the plots of λ_{\max} versus the various molecular microscopic solvent parameters α (acidity), β (basicity) and π^* (dipolarity), Z . (Kosower 1956) and E_T values (Brame 1974) show non-linear relations indicating that these solvent parameters are not the main factors causing CT band shift. The change in the position of CT band is to be considered as being the resultant of the different factors governed by the various parameters. This leads to the conclusion that several superimposed individual effects contribute to the observed change confirming that there is a difficulty in obtaining a single solvent parameter. These may be additive, counter-acting or may even cancel out each other.

IR spectra

The important diagnostic bands in the IR spectra were assigned and the band positions are compiled in Table 2.

All compounds give a sharp $\nu_{C=N}$ band in the range 1589 - 1639 cm^{-1} , the low frequency values of the compounds (*Ie and II*) indicate that the azomethine group is involved in hydrogen bonds of the intramolecular type with the OH group in *ortho* position to it. This is further supported by the appearance of a broad band ν_{OH} at 3425 and 3429 cm^{-1} for compounds *Ie* and *II*, respectively. The Schiff bases under investigation exist in both thiol and thione forms. A medium band occurs within the range 3042 - 3124 cm^{-1} is due to ν_{NH} (thione form) whereas medium intensity broad band in the region 2350 - 2366 cm^{-1} is due to ν_{SH} (thiol form) (Kornis 1984). These

observations confirm the thiol-thione tautomerism [11]. Bands were also observed at 600-632 and 680-756 cm^{-1} corresponds to (-C-S-H stretching of the mercapto group) while the bands at 1370-1400 cm^{-1} assign to -S-C stretching. The IR spectra of the Schiff bases Ib and Ic showed the following characteristic bands: 1330 cm^{-1} (symmetric stretching) due to NO_2 group, and 679 cm^{-1} attributed to (C-Cl group).

The position of the $\nu_{\text{C=N}}$ varies with the of changes in the molecular structure of the Schiff bases. The position of this band varies according to the type of substitution in the aromatic ring. Figure 1 shows the $\nu_{\text{C=N}}$ values plotted against Hammett substituent constant values. There is an almost linear relationship between these values apart from a small deviation in the case of NO_2 derivative. Generally, the electron donating substituents show a blue shift for the $\nu_{\text{C=N}}$ values while the electron withdrawing ones cause a red shift.

Table (2)
IR and Electronic spectra of Schiff bases

No.	IR bands (cm^{-1})				Electronic spectra $\lambda(\text{nm})$ / Ethanol
	NH	SH	C=N	C=S	
Ia	3042	2366	1608	770	238, 297, 316, 401
Ib	3095	2350	1639	750	213, 265, 303, 410
Ic	3124	2350	1610	756	220, 251, 316, 403
Id	3094	2355	1589	779	208, 251, 306, 425
Ie	3061	2365	1604	753	239, 260, 334, 416, 440
II	3071	2364	1605	750	218, 257, 316, 440*

*Hydrogen bond and CT band.

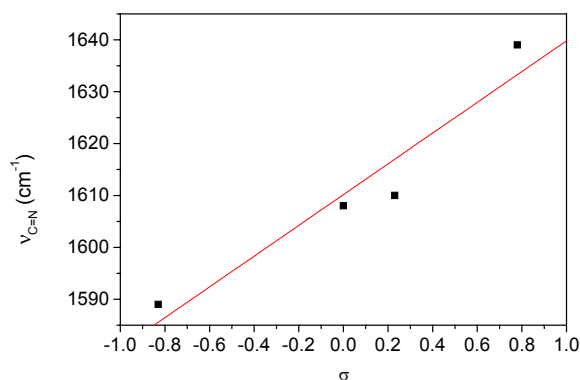


Fig. 1 The relation between $\nu_{\text{C=N}}$ and σ -Hammett

¹H- and ¹³C-NMR spectra

The structures of Schiff bases under investigation were further supported by the ¹H- and ¹³C-NMR spectral measurements. The ¹H- and ¹³C-NMR spectra of some Schiff bases are recorded and assigned in Table 3.

Table 3

No.	¹ H- and ¹³ C-NMR spectral data
Ia	¹ H-NMR (400 MHz, CDCl ₃): δ 7.21-7.61 (5H, m, Ph-H), 9.74 (1H, s, -N=CH), 12.65 (1H, br s, -SH, exchangeable with D ₂ O).
Ib	¹ H-NMR (400 MHz, CDCl ₃): δ 7.12 [2H, d, <i>J</i> = 8.0 Hz, (H-3 and H-5) <i>p</i> -NO ₂ -ph], 7.30 [2H, d, <i>J</i> = 8.0 Hz, (H-2 and H-6) <i>p</i> -NO ₂ -ph], 6.58 (1H, s, -N=CH-), 12.56 (1H, br s, -SH, exchangeable with D ₂ O).
Ic	¹ H-NMR (400 MHz, CDCl ₃): δ 7.18 [2H, d, <i>J</i> = 8.0 Hz, (H-3 and H-5) <i>p</i> -Cl-Ph], 7.50 [2H, d, <i>J</i> = 8.0 Hz, (H-2 and H-6) <i>p</i> -Cl-Ph], 6.69 (1H, s, -N=CH-), 12.67 (1H, br s, -SH, exchangeable with D ₂ O).
Id	¹ H-NMR (400 MHz, DMSO- <i>d</i> ₆): δ 3.07 [6H, s, -N(CH ₃) ₂], 6.80 [2H, d, <i>J</i> = 8.2 Hz, (H-3 and H-5) <i>p</i> -N(CH ₃) ₂ -Ph], 7.79 [(2H, d, <i>J</i> = 8.2 Hz, (H-2 and H-6) <i>p</i> -N(CH ₃) ₂ -Ph], 8.41 (1H, s, -N=CH-), 14.25 (1H, br s, -SH).
Ie	¹ H-NMR (400 MHz, DMSO- <i>d</i> ₆): δ 7.25 [1H, d, <i>J</i> = 8.0 Hz, H-3 <i>o</i> -OH-ph], 7.95 [1H, d, <i>J</i> = 8.0 Hz, H-4 <i>o</i> -OH-ph], 7.48-7.62 [2H, d, <i>J</i> = 8.0 Hz, (H-5 and H-6) <i>o</i> -OH-ph], 9.32 (1H, s, -N=CH-), 13.15 (1H, br s, -OH), 14.40 (1H, br s, -SH).
II	¹ H-NMR (400 MHz, DMSO- <i>d</i> ₆): δ 7.24 (1H, d, <i>J</i> = 8.0 Hz, H-3 napht.), 7.45 (1H, t, <i>J</i> = 8.0 Hz, H-6 napht.), 7.64 (1H, t, <i>J</i> = 8.0 Hz, H-7 napht.), 7.90 (1H, d, <i>J</i> = 8.0 Hz, H-5 napht.), 8.11 (1H, d, <i>J</i> = 8.0 Hz, H-4 napht.), 8.82 (1H, d, <i>J</i> = 8.0 Hz, H-8 Napht.), 9.41 (1H, s, -N=CH-), 13.20 (1H, br s, -OH), 14.50 (1H, br s, -SH). ¹³ C-NMR (100 MHz, DMSO- <i>d</i> ₆): δ 110.4, 165.6, 124.9, 138.5, 129.7, 123.1, 129.4, 119.2, 132.5, 128.3 [(C-1 - C-10) napht.], 163.9 (-N=CH-), 164.2 (-N=CNS), 186.9 (C=S).

References

1. Ahmed, M., Jahan, J. I. and Banoo, S. (2002), A simple spectrophotometric methods for the determination of Cu in industrial, environmental, Biological and soil, samples using 2,5-dimercapto-1,3,4-thiadiazole, *Anal. Sci.*, 18, 805-810.
2. Brame, E. G. (1974), "Applied spectroscopy review", 8 (13) Marcel Dekker, New York, pp. 194-196.
3. Dziembowska, T., Jagodzinska, E., Rozwadowski, Z. and Kotfica, M. (2001), Solvent effect on intramolecular proton transfer equilibrium in some N-(R-Salicylidene)-alkyl amines, *J. Mol. Struct.*, 598, 229-234.
4. Gaber, M., Mabrouk, H. and Al-Shihry, S.S. (2001), Complexing behaviour of naphthylidene sulfamethazine Schiff base ligand towards some metal ions, *Egypt J. Chem.*, 44, 191-200.
5. Gati, L. and Szalay, L. (1959), bemerkung zur verschiebung der absorptions maxima von verschiedenen wassrig-glyzerinischen fluoreszenzlosungen, *Acta. Phys. Chem.*, Eine 5, 87-89.
6. Guha, D., Mandal, A., Koll, A., Filarowski, A. and Mukherjee, S. (2000). Proton transfer reaction of a new orth-hydroxy Schiff base in protic solvents at room temperature, *Spectrochimica Acta A*, 56, 2669-2677.
7. Hossain, M. E., Alam, M. N., Ali, M. A., Nazimuddin, M., Smith, F. E. and Hynes, R. C. (1996), The synthesis, characterization and bioactivities of some copper (II) complexes of the 2-acetylpyridine Schiff base of 5-methyl and 5-benzylidithiocarbamate and the x-ray crystal Structure of the nitrate(5-benzyl-B-n-(2-acetylpyridyl)methylenedithiocarbamate) copper (II) complex, *Polyhedron*, 15, 973-980.
8. Issa, R. M., El-Daly, S. A. and El-Wakiel, N. A. (2003), IR and ¹H-NMR spectroscopic studies of bisazo-dianil compounds based on 5-(2-carboxy phenylazo)-salicylaldehyde and primary diamines. *Spectrochimica Acta A*, 59, 723-728.
9. Jeewoth, T., Bhowon, M. G. and Wah, H. L. K. (1999), Synthesis, characterization and antibacterial properties of Schiff bases and Schiff base metal complexes derived from 2,3-diaminopyridine. *Transition Met. Chem.*, 24, 445-448.
10. Kornis, G. (1984), "Comprehensive Heterocyclic Chemistry", Vol. 6, part 4B, pp 575-577 (Edit by A. Katritzky, C. W. Rees and K. T. Potts) press, Oxford.
11. Kosower E. M. (1956), The effect of solvent on charge-transfer complex spectra, *J. Am. Chem. Soc.*, 78, 5700-5701.

-
12. Papie, S., Kaprivanae, N., Grabarie, Z. and Paracosterman, D. (1994), Metal complex dyes of Ni with Schiff bases, *Dyes and Pigments*, 25, 229-240.
 13. Schiff, W., Szady-Chelmieniecka, A., Grech, E., Przybylski, P. and Brzezinski, B. (2002), Spectroscopic studies of new Schiff and Schiff-Mannich bases of *ortho*-derivatives of 4-bromophenol, *J. Mol. Struct.*, 643, 115-121.
 14. Suppan, P. (1968), Solvent effects on the energy of electronic transitions: experimental observations and applications to structural problems of excited molecules. *J. Chem. Soc. A*: 1, 3125-3127.
 15. Zhao, J., Zhao, B., Liu, J., Xu, W. and Wang, Z. (2001), Spectroscopy study on the photochromism of Schiff bases N,N-bis (salicylidene)-1,2-diamino ethane and N,N'-bis(salicylidene)-1,6-hexanediamine, *Spectrochimica Acta A*, 57, 149-154.

شار بن سعد الشهري

قسم الكيمياء - كلية العلوم - جامعة الملك فيصل
الأحساء - المملكة العربية السعودية

الملخص :

يتضمن البحث تحضير ودراسة الأطياف لبعض قواعد شيف المشتقة من ٢- أمينو - ٥- ميركبتو، ٤,٣,١- ثياديازول. وتم دراسة تركيب قواعد شيف من خلال تحليل العناصر، أطياف الأشعة تحت الحمراء والرنين النووي المغناطيسي. واشتملت الدراسة أيضاً قياس أطياف الأشعة فوق البنفسجية والمرئية في عدد من المذيبات مختلفة القطبية. يعتمد الطول الموجي على نوع ومكان المستبدل في هذه المركبات.