

Original Article

STRUCTURAL, POTENTIOMETRIC AND THERMODYNAMIC STUDIES OF RHODANINE AZODYES AND THEIR METAL COMPLEXES

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ABSTRACT

A Rhodanine azodyes (HLI and HLI_i) have been prepared and characterized by elemental analyses, ¹H NMR and IR spectra. The IR spectral data indicate that, the compounds can exist in two resonance structures. The molecular structures of the investigated compounds (HLI and HLI_i) are optimized. Moreover, energy of HOMO & LUMO, HOMO-LUMO energy gap and electronic charge were calculated. In addition, absolute electronegativities, chemical potentials, and absolute hardness have been calculated. The influence of substituents on the dissociation and stability constants was examined on the basis of the electron repelling property. Proton-ligand dissociation constants of rhodanine azodyes and metal-ligand stability constant of their complexes with bivalent (Mn⁺², Co²⁺, Ni²⁺ and Cu²⁺) metal ions have been determined potentiometrically in 0.1 M KC1 and 30% (v/v) CH₃OH-water mixture. The stabilities of the complexes were found as follow: Mn⁺² > Co⁺² > Ni²⁺ > Cu²⁺. The effect of temperature was studied and the corresponding thermodynamic parameters (ΔG, ΔH and ΔS) were derived and discussed.

Keywords: Rhodanine azodyes, Potentiometry, Complexation and Thermodynamics.

INTRODUCTION

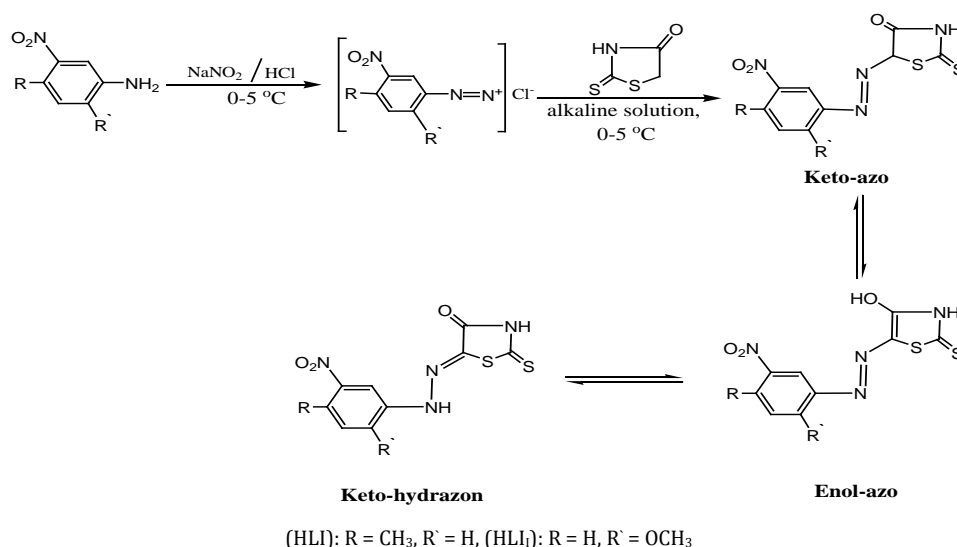
Efforts have been made to carry out detailed studies to synthesize and elucidate the structural and electronic properties of complexes with rhodanine derivatives. Rhodanine derivatives are a good series of ligands capable of binding metal ions leading to metal complexes with increasing properties. The high stable potential of rhodanine derivative complexes in different oxidation states increased the application of these compounds in a wide range. Ligands with potential sulfur, oxygen and nitrogen donors, such as rhodanine and its derivatives are quite interesting which have gained special attention, not only because of the structural chemistry and their importance in medical chemistry, but also because these materials are used as drugs and they are reported to possess a wide variety of biological activities against bacteria and fungi [1,2]. They also have become a useful model for bioinorganic processes, which have many biochemical and pharmacological activities [3-5]. In continuation of our earlier work [6-9], we report herein the preparation and characterization of some rhodanine azodyes. The geometrical structure of the ligands by HF method with 3-21G basis set was studied.

The dissociation constant of the ligands (HLI and HLI_i) and the stability constants of their complexes with Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺ at different temperatures were determined potentiometrically. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

MATERIALS AND METHODS

Synthesis of rhodanine azodyes (HLI and HLI_i)

Rhodanine azodyes (HLI and HLI_i) were prepared from substituted derivatives of aniline (10 mmol) was dissolved in hydrochloric acid (20 mmol/25 ml distilled H₂O). The hydrochloric compound was diazotized below -5 °C with a solution of sodium nitrite (0.8 g, 10 mmol, 30 ml distilled H₂O). The diazonium chloride was coupled with an alkaline solution of 2-thioxo-4-thiazolidinone (1.33 g, 10 mmol) in 20 ml of ethanol as shown in Scheme 1. The resulting formed ligands are: (E)-5-((4-methyl-3-nitrophenyl)diazonyl)-2-thioxothiazolidin-4-one (HLI) and (E)-5-(2-(2-methoxy-5-nitrophenyl)diazonyl)-2-thioxothiazolidin-4-one (HLI_i). The ligands were also characterized by elemental analysis (Table 1), ¹H NMR and IR spectroscopy.



Scheme 1: The formation mechanism of rhodanine azodye derivatives.

Table 1: Analytical data of rhodanine azodyes

Compound ^a	Empirical formula	Color	M.P (°C)	Formula Weight (g/mol)	Calc. (Exp.) %		
					C	H	N
HLI	C ₁₀ H ₈ N ₄ O ₃ S ₂	Yellow	220	296	40.54 (41.05)	2.02 (1.97)	18.92 (19.05)
HLI ₁	C ₁₀ H ₈ N ₄ O ₄ S ₂	Orange	230	312	38.46 (39.01)	2.56 (2.49)	17.95 (17.69)

^a Further studies with title ligands, using different metal, are in progress and will be published in due course

Measurements

All the compounds and solvents used were purchased from Alderich and Sigma. Elemental microanalyses of the separated ligands for C, H, and N were determined on Automatic Analyzer CHNS Vario ELIII, Germany. The ¹H NMR spectrum was obtained by Bruker WP 300 MHz using DMSO-d₆ as the solvent and TMS as an internal reference. FT-IR spectra (KBr disks, 4000-400 cm⁻¹) by Jasco-4100 spectrophotometer. The molecular structures of the investigated compounds were optimized by HF method with 3-21G basis set.

The pH measurements were performed with a Metrohm 836 Titrando (KF & Potentiometric Titrator) equipped with a combined porolyte electrode. The pH-meter readings in the non-aqueous medium were corrected [10]. The electrode system was calibrated according to the method of Irving et al. [11]. All titrations have been carried out between pH 4.0 – 11.0 and under nitrogen atmosphere. The molecules were built with the Perkin Elmer Chem Bio Draw and optimized using Perkin Elmer ChemBio3D software [12]. Quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}) and HOMO-LUMO energy gap (ΔE) for the investigated molecules are calculated.

Potentiometry

A ligand solution (0.001 M) was prepared by dissolving an accurately weighted amount of the solid in CH₃OH (Analar). Metal ion solutions (0.0001 M) were prepared from Analar metal chlorides in bidistilled water. Solutions of 0.001 M HCl and 1 M KCl were also prepared in bidistilled water. A carbonate-free NaOH solution in 30 % (by volume) methanol-water mixture was used as titrant and standardized oxalic acid (Analar). The apparatus, general conditions and methods of calculation were the same as in previous work [6-9]. The following mixtures (i) - (iii) were prepared and titrated potentiometrically at 298 K against standard 0.001 mol.dm⁻³ KOH in a 30 % (v/v) methanol-water mixture:

(i) 5 ml 0.001 M HC1 + 5 ml 1 M KC1 + 15 ml CH₃OH

(ii) 5 ml 0.001 M HC1 + 5 ml 1 M KC1 + 10 ml CH₃OH + 5 ml 0.001 M ligand

(iii) 5 ml 0.001 M HC1 + 5 ml 1 M KC1 + 10 ml CH₃OH + 5 ml 0.001 M ligand + 10 ml 0.0001 M metal chloride.

For each mixture, the volume was made up to 50 ml with bidistilled water before the titration. These titrations were repeated for temperatures of 313 K and 323 K. The temperature was controlled

to within ± 0.05 K by circulating thermostated water (Neslab 2 RTE 220) through the outer jacket of the vessel.

RESULTS AND DISCUSSION

Structural of the ligands

The analytical data agrees satisfactory with the expected formulae represented as given in Scheme 1 (see experimental). HLI and HLI₁ ligands are air-stable, high melting temperature, colored, insoluble in water, but soluble in most common organic solvents. The molecular structures of these ligands can exist in threetautomeric forms (Scheme 1). IR spectra exhibit a medium to strong band in the region 1520-1570 cm⁻¹ which could be assigned to νN=N stretching vibration [13-17]. The broad absorption of a band located at ~3400 cm⁻¹ is assigned to νOH. The low frequency bands indicate that the hydroxy hydrogen atom is involved in keto ⇌ enol tautomerism through hydrogen bonding (Scheme 1). The higher value of the δ_{OH} may account for the existence of hydrogen bonding. El-Sonbati et al. [18-24] found three kinds of bonded -OH structures on the basis of the frequencies: i) only the oxygen is in the bridge while the hydrogen is free, ii) a polymer chain is formed in which both hydrogen and oxygen atoms participate in the hydrogen bond, iii) dimmer associates are formed.

The IR spectral data exhibits a very strong band at 1585 ± 10 cm⁻¹ is apparent and assignable to νC=C of the phenyl ring. The very interesting region is that in the frequency range 2800-3550 cm⁻¹. This is a characteristic region to the vibrational frequency of the -OH group where vibrational bands at 2900 cm⁻¹ of medium appearance and a broad at 3400 - 3550 cm⁻¹ are apparent. The ¹H NMR spectra of HLI showed that, signal for CH (~ 3.37 ppm). The broad signal assigned to the OH proton at ~11.11 ppm is not affected by dilution. The previous two protons disappear in the presence of D₂O. Absence of -CH proton signal of the ligand moiety indicated the existence of the ligand in the enol-azo form. A signal at 2.48 ppm region assigned to hydrogen of CH₃ group. The aromatic protons have resonance at 7.55-7.83 ppm for the ligand.

Molecular structure

The selected geometrical structures of the investigated ligands are calculated by optimizing their bond lengths and bond angles. The calculated molecular structures for HLI and HLI₁ are shown in Fig. 1. The selected geometric parameters are listed in Tables 2 and 3. The N8-N9 bond with length 1.3 and 1.251 Å for HLI and HLI₁, respectively. The surfaces of frontier molecular orbital theory (FMOs) are shown in Fig. 2.

Table 2: The selected geometric parameters for HLI

Bond lengths (Å)		Bond angles (°)	
C(16)-H(27)	1.114	H(27)-C(16)-H(26)	105.658
C(16)-H(26)	1.113	H(27)-C(16)-H(25)	110.282
C(16)-H(25)	1.114	H(27)-C(16)-C(12)	111.016
C(14)-H(24)	1.104	H(26)-C(16)-H(25)	105.66
C(13)-H(23)	1.103	H(26)-C(16)-C(12)	112.949
C(10)-H(22)	1.101	H(25)-C(16)-C(12)	111.024
O(7)-H(21)	0.972	H(23)-C(13)-C(14)	117.681
N(1)-H(20)	1.046	H(23)-C(13)-C(12)	120.071
C(10)-C(15)	1.347	C(14)-C(13)-C(12)	122.248
C(14)-C(15)	1.343	C(11)-N(17)-O(19)	122.784
C(13)-C(14)	1.34	C(11)-N(17)-O(18)	125.826

C(12)-C(13)	1.347	O(19)-N(17)-O(18)	111.39
C(11)-C(12)	1.353	C(13)-C(12)-C(11)	118.775
C(10)-C(11)	1.351	C(13)-C(12)-C(16)	117.553
C(4)-S(5)	1.789	C(11)-C(12)-C(16)	123.672
C(3)-S(5)	1.483	C(12)-C(11)-C(10)	117.655
C(2)-C(3)	1.355	C(12)-C(11)-N(17)	124.569
N(1)-C(2)	1.272	C(10)-C(11)-N(17)	117.776
C(4)-N(1)	1.263	H(24)-C(14)-C(15)	120.622
C(15)-N(9)	1.269	H(24)-C(14)-C(13)	119.1
C(11)-N(17)	1.26	C(15)-C(14)-C(13)	120.277
C(12)-C(16)	1.516	H(22)-C(10)-C(15)	117.684
C(3)-N(8)	1.265	H(22)-C(10)-C(11)	118.196
N(8)-N(9)	1.252	C(15)-C(10)-C(11)	124.119
C(2)-O(7)	1.363	C(10)-C(15)-C(14)	116.925
C(4)-S(6)	1.571	C(10)-C(15)-N(9)	125.353
N(17)-O(19)	1.317	C(14)-C(15)-N(9)	117.721
N(17)-O(18)	1.311	C(15)-N(9)-N(8)	118.18
		S(5)-C(4)-N(1)	106.262
		S(5)-C(4)-S(6)	126.891
		N(1)-C(4)-S(6)	126.847
		C(3)-N(8)-N(9)	120.724
		C(4)-S(5)-C(3)	92.812
		H(21)-O(7)-C(2)	111.048
		H(20)-N(1)-C(2)	122.425
		H(20)-N(1)-C(4)	123.92
		C(2)-N(1)-C(4)	113.655
		S(5)-C(3)-C(2)	111.027
		S(5)-C(3)-N(8)	132.31
		C(2)-C(3)-N(8)	116.662
		C(3)-C(2)-N(1)	116.243
		C(3)-C(2)-O(7)	124.679
		N(1)-C(2)-O(7)	119.067

Table 3: The selected geometric parameters for HLI₁

Bond lengths (Å)		Bond angles (°)	
C(20)-H(28)	1.113	H(28)-C(20)-H(27)	112.991
C(20)-H(27)	1.112	H(28)-C(20)-H(26)	107.942
C(20)-H(26)	1.113	H(28)-C(20)-O(19)	110.65
C(13)-H(25)	1.105	H(27)-C(20)-H(26)	106.742
C(12)-H(24)	1.103	H(27)-C(20)-O(19)	110.683
C(10)-H(23)	1.101	H(26)-C(20)-O(19)	107.572
O(7)-H(22)	0.972	C(14)-O(19)-C(20)	121.454
N(1)-H(21)	1.046	H(25)-C(13)-C(14)	118.361
C(10)-C(15)	1.351	H(25)-C(13)-C(12)	117.59
C(14)-C(15)	1.356	C(14)-C(13)-C(12)	124.049
C(13)-C(14)	1.349	C(11)-N(16)-O(18)	122.015
C(12)-C(13)	1.34	C(11)-N(16)-O(17)	123.043
C(11)-C(12)	1.342	O(18)-N(16)-O(17)	114.941
C(10)-C(11)	1.345	H(24)-C(12)-C(13)	118.369
C(4)-S(5)	1.789	H(24)-C(12)-C(11)	121.506
C(3)-S(5)	1.482	C(13)-C(12)-C(11)	120.123
C(2)-C(3)	1.356	C(12)-C(11)-C(10)	116.144
N(1)-C(2)	1.272	C(12)-C(11)-N(16)	122.985
C(4)-N(1)	1.263	C(10)-C(11)-N(16)	120.871
C(15)-N(9)	1.27	C(15)-C(14)-C(13)	116.244
C(14)-O(19)	1.38	C(15)-C(14)-O(19)	127.737
C(11)-N(16)	1.258	C(13)-C(14)-O(19)	115.908
C(3)-N(8)	1.264	H(23)-C(10)-C(15)	119.764
N(8)-N(9)	1.251	H(23)-C(10)-C(11)	115.798
C(2)-O(7)	1.362	C(15)-C(10)-C(11)	124.437
C(4)-S(6)	1.571	C(10)-C(15)-C(14)	118.981
O(19)-C(20)	1.408	C(10)-C(15)-N(9)	121.013
N(16)-O(18)	1.316	C(14)-C(15)-N(9)	119.984
N(16)-O(17)	1.313	C(15)-N(9)-N(8)	119.777
		S(5)-C(4)-N(1)	106.259
		S(5)-C(4)-S(6)	126.861
		N(1)-C(4)-S(6)	126.881
		C(3)-N(8)-N(9)	121.199
		C(4)-S(5)-C(3)	92.796
		H(22)-O(7)-C(2)	111.016
		H(21)-N(1)-C(2)	122.417
		H(21)-N(1)-C(4)	123.898

C(2)-N(1)-C(4)	113.685
S(5)-C(3)-C(2)	111.098
S(5)-C(3)-N(8)	132.233
C(2)-C(3)-N(8)	116.669
C(3)-C(2)-N(1)	116.163
C(3)-C(2)-O(7)	124.701
N(1)-C(2)-O(7)	119.135

The HOMO–LUMO energy gap, ΔE , which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems. The smaller is the value of ΔE , the more is the reactivity of the compound has [17].

The calculated quantum chemical parameters are given in Table 4. Additional parameters such as ΔE , absolute Electro -negativities, χ , chemical potentials, P_i , absolute hardness, η , absolute softness, σ , global electrophilicity, ω [9,12,15], global softness, S , and additional electronic charge ΔN_{\max} , have been calculated according to the following equations [9,12,15]:

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (1)$$

$$\chi = \frac{-(E_{HOMO} + E_{LUMO})}{2} \quad (2)$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (3)$$

$$\sigma = 1/\eta \quad (4)$$

$$P_i = -\chi \quad (5)$$

$$S = \frac{1}{2\eta} \quad (6)$$

$$\omega = P_i^2 / 2\eta \quad (7)$$

$$\Delta N_{\max} = -P_i / \eta \quad (8)$$

The values of the HOMO-LUMO energy gap, ΔE , for HLI and HLI_i are calculated and found to be 0.1121 and 0.0961 a.u., respectively, dependent on the nature of the substituent.

Table 4: The calculated quantum chemical parameters of the investigated Compounds (HLI and HLI_i)

Compound	HOMO (a.u)	LUMO (a.u)	ΔE (a.u)	χ (a.u)	η (a.u)	σ (a.u) ⁻¹	P_i (a.u)	S (a.u) ⁻¹	ω (a.u)	ΔN_{\max}
HLI	-0.1927	-0.0807	0.1121	0.1367	0.0560	17.849	-0.1367	8.925	0.1668	2.440
HLI _i	-0.1772	-0.0811	0.0961	0.1292	0.0480	20.820	-0.1292	10.410	0.1737	2.689

Potentiometric studies

The average number of the protons associated with ligands (HLI and HLI_i) at different pH values, \bar{n}_A , was calculated from the titration curves of the acid in the absence and presence of ligands by applying the following equation:

$$\bar{n}_A = Y \pm \frac{(V_1 - V_2)(N^o + E^o)}{(V^o - V_1)TC_L^o} \quad (9)$$

Where Y is the number of available protons in ligands (HLI and HLI_i) ($Y=1$) and V_1 and V_2 are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and reagent, respectively, V^o is the initial volume (50 cm³) of the mixture, TC_L^o is

the total concentration of the reagent, N^o is the normality of sodium hydroxide solution and E^o is the initial concentration of the free acid. Thus, the formation curves (\bar{n}_A vs. pH) for the proton-ligand systems were constructed and found to extend between 0 and 1 in the \bar{n}_A scale. This means that rhodanine has one ionizable proton (the enolized hydrogen ion of the carbonyl oxygen in the rhodanine moiety, pK^H). Different computational methods were applied to evaluate the dissociation constant [25]. Three replicate titrations were performed; the average values obtained are listed in Table 5. The completely protonated form of ligands (HLI and HLI_i) has one dissociable proton, that dissociates in the measurable pH range. The deprotonation of the hydroxy group most probably results in the formation of stable intramolecular H-bonding with nitrogen of the azo group. Such an interaction decreases the dissociation process of rhodanine, *i.e.* increases the pK^H value [26].

Table 5: Thermodynamic function of rhodanine azodyes in 30% (v/v) CH₃OH-water mixture and 0.1 M KCl at different temperatures

Compound	Temp. (K)	Dissociation constant (pK ^H)	GIBBS Enthalpy change (kJ.mol ⁻¹)	Enthalpy change (kJ.mol ⁻¹)	Entropy change (J.mol ⁻¹ .K ⁻¹)
	T	pK ^H	ΔG	ΔH	$-\Delta S$
HLI	298	9.25	52.77	30.63	74.30
	308	9.11	53.72		74.96
	318	8.95	54.49		75.02
HLI _i	298	9.40	53.63	26.80	90.03
	308	9.26	54.60		90.27
	318	9.10	55.40		89.94

An inspection of the results in Table 5 reveals that the pK^H values of HLI and HLI_i are influenced by the inductive or mesomeric effect of the substituents [27]. The p-CH₃ and o-OCH₃ derivatives will lower

acidic character (higher pK^H values) as well as m-NO₂ will be. This is quite reasonable because the presence of o-OCH₃ group (HLI_i) will enhance the electron density the rhodanine ring more than p-

CH₃ (HLI). The *ortho* and *para* substituents in the ligands moiety have a direct influence on the pK^H values of the investigated compounds, revealing the coplanarity of the molecule and thus affording a maximum resonance *via* delocalization of its π -system.

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion (\bar{n}_A) vs. the free ligands exponent (pL), according to Irving and Rossotti [28]. The average number of the reagent molecules attached per metal ion, \bar{n} , and free ligands exponent, pL, can be calculated using eqs. 10 and 11:

$$\bar{n} = Y \pm \frac{(V_3 - V_2)(N^o + E^o)}{(V^o - V_2).n_A.TC_M^o} \quad (10)$$

Table 6: Stepwise stability constants for the complexation of rhodanine azodyes in 30% (v/v) CH₃OH-water mixture and 0.1 M KCl at different temperatures

Comp.	M ⁿ⁺	298 K			308 K			318 K		
		log K ₁	log K ₂	log K _β	log K ₁	log K ₂	log K _β	log K ₁	log K ₂	log K _β
HLI	Cu ²⁺	8.50	6.61	15.11	8.74	6.88	15.62	8.95	7.15	16.10
	Ni ²⁺	7.05	5.74	12.79	7.26	6.03	13.29	7.55	6.28	13.83
	Co ²⁺	6.74	5.38	12.12	7.01	5.55	12.56	7.26	5.81	13.07
	Mn ²⁺	6.50	5.20	11.7	6.75	5.44	12.19	7.02	5.68	12.70
HLII	Cu ²⁺	9.01	7.05	16.06	9.26	7.28	16.54	9.50	7.53	17.03
	Ni ²⁺	7.62	6.30	13.92	7.85	6.58	14.43	8.11	6.84	14.95
	Co ²⁺	7.25	5.95	13.2	7.48	6.22	13.70	7.73	6.48	14.21
	Mn ²⁺	7.05	5.70	12.75	7.30	5.98	13.28	7.54	6.23	13.77

The following general remarks can be pointed out:

(i) The maximum value of \bar{n} was ≈ 2 indicating the formation of 1:1 and 1:2 (metal: ligand) complexes only.

(ii) The metal ion solution used in the present study was very dilute (2×10⁻⁵ M); hence there was no possibility of formation of poly nuclear complexes [31-33].

(iii) The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves point to the formation of strong metal complexes [34].

(iv) In most cases, the color of the solution after complex formation was observed to be different from the color of the ligand at the same pH.

(v) For the same ligand at constant temperature, the stability of the chelates increases in the order Cu²⁺ > Ni²⁺ > Co²⁺ > Mn²⁺ [35,36]. This order largely reflects the changes in the heat of complex formation across the series from a combination of the influence of both the polarizing ability of the metal ion [37] and the crystal field stabilization energies [38]. The greater stability of Cu²⁺ complexes is produced by the well-known Jahn-Teller effect [39,40]. An inspection of the results in Table 6 reveals that the stability constant values of the complexes of HLI and HLII are influenced by the inductive or mesomeric effect of the substituents. This behavior correlates with the effect of substitution on the phenyl ring as follows:

(i) The stability of HLII complexes can be attributed to the presence of the m-NO₂ and o-OCH₃ groups relative to the azo group.

(ii) For the ligands with the same metal ion at constant temperature, the stability of the chelates increases in the order: HLI > HLII. The dissociation constant (pK^H) for HLI and HLII, as well as the stability constants of its complexes with Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺ have been evaluated at (303, 313, 323) K, and are given in Table 7, respectively. The enthalpy (ΔH) for the dissociation and complexation process was calculated from the slope of the plot pK^H or log K vs. 1/T using the graphical representation of van't Hoff eqs. 12 and 13:

$$\Delta G = -2.303 RT \log K = \Delta H - T \Delta S \quad (12)$$

and

$$pL = \log_{10} \frac{\sum_{n=0}^n \beta_n^H \left(\frac{1}{[H^+]} \right)^n}{TC_L^o - n.TC_M^o} \cdot \frac{V^o + V_3}{V^o} \quad (11)$$

where TC_M^o is the total concentration of the metal ion present in the solution, β_n^H is the overall proton-reagent stability constant. V_1 , V_2 and V_3 are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand and complex, respectively. These curves were analyzed and the successive metal-ligand stability constants were determined using different computational methods [29,30]. The values of the stability constants (log K₁ and log K₂) are given in Table 6.

or

$$\log K = (-\Delta H / 2.303 R)(1/T) + (\Delta S / 2.303 R) \quad (13)$$

Where R gas constant = 8.314 J.mol⁻¹.K⁻¹, K dissociation constant for the ligand stability and T temperature (K)

From the ΔG and ΔH values one can deduce the entropy ΔS using the well known relationship:

$$\Delta S = (\Delta H - \Delta G) / T \quad (14)$$

All thermodynamic parameters of the dissociation process of HLI – HLII are recorded in Tables 5 and 7. From these results the following conclusions can be made:

(i) The pK^H values decrease with increasing temperature, i.e., the acidity of the ligands increases, independent of the nature of the substituent [6]. (ii) A positive value of ΔH indicates that the process is endothermic.

(iii) A large positive value of ΔG indicates that the dissociation process is not spontaneous.

(iv) The dissociation processes for the compounds have negative values of ΔS due to increased order as a result of the solvation processes. All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in table 7. It is known that the divalent metal ions exist in solution as octa hedrally hydrated species and the obtained values of ΔH and ΔS can then be considered as the sum of two contributions: (a) release of H₂O molecules, and

(b) metal-ligand bond formation. Examination of these values shows that:

(i) The stepwise stability constant (log K₁ and log K₂) for ligand complexes increases with increasing temperature, i.e., its stability constants increase with increasing the temperature.

(ii) The negative value of ΔG for the complexation process suggests the spontaneous nature of such process.

(iii) The ΔH values are positive, meaning that these processes are endothermic.

The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favorable.

Table 7: Thermodynamic functions for the complexation of HLI in 30% (v/v) CH₃OH-water mixture.

Comp.	M ⁿ⁺	Temp. (K)	Enthalpy change (kJ.mol ⁻¹)		Free energy change (kJ.mol ⁻¹)		Entropy change (J.mol ⁻¹ .K ⁻¹)	
			T	-ΔG ₁	-ΔG ₂	ΔH ₁	ΔH ₂	ΔS ₁
HLI	Cu ²⁺	298	48.49	37.71	45.95	51.69	316.95	300.04
		308	51.54	40.57			316.54	299.58
		318	54.49	43.53			315.87	299.47
	Ni ²⁺	298	40.22	32.75	40.20	55.52	269.91	296.23
		308	42.81	35.56			269.55	295.73
		318	45.97	38.23			271.00	294.85
	Co ²⁺	298	38.45	30.69	51.69	49.78	302.53	270.06
		308	41.34	32.73			302.06	267.89
		318	44.20	35.37			301.57	267.79
Mn ²⁺	298	37.08	29.67	47.86	45.95	285.08	253.77	
	308	39.80	32.08			284.65	253.35	
	318	42.74	34.58			284.94	253.26	
HLI ₁	Cu ²⁺	298	51.40	40.22	47.86	44.03	333.14	282.76
		308	54.60	42.93			332.71	282.37
		318	57.84	45.84			332.42	282.66
	Ni ²⁺	298	43.47	35.94	44.03	53.61	293.68	300.53
		308	46.29	38.80			293.28	300.05
		318	49.38	41.64			293.76	299.55
	Co ²⁺	298	41.36	33.94	44.03	51.69	286.59	287.40
		308	44.11	36.68			286.20	286.94
		318	47.06	39.45			286.49	286.64
	Mn ²⁺	298	40.22	32.52	47.86	53.61	295.61	289.04
		308	43.05	35.26			295.18	288.56
		318	45.90	37.93			294.89	287.87



Fig. 1: Molecular structure with atomic numbering for (a) HLI and (b) HLI₁.

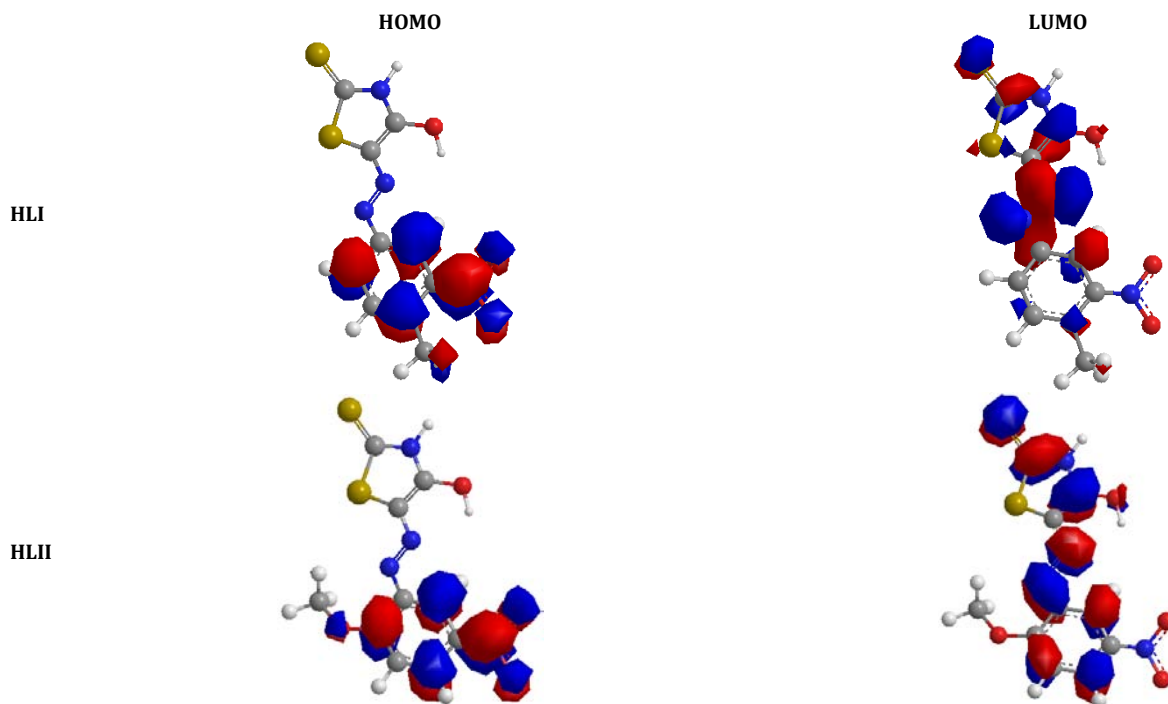


Fig. 2: Surface of FMOs for HLI and HLI₁.

CONCLUSION

The ligands of rhodanine azodyes have been synthesized and characterized using spectroscopic techniques. The molecular structures of the investigated compounds (HLI and HLI₁) are optimized. The values of the HOMO–LUMO energy gap, ΔE, for HLI and HLI₁ are calculated and found to be 0.1121 and 0.0961 a.u., respectively, dependent on the nature of the substituent. The proton-ligand dissociation constant of (HLI and HLI₁) and metal-ligand stability constants of their complexes with metal ions (Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺) were determined at different temperatures. The stability constants of the formed complexes increases in the order Mn²⁺ < Co²⁺ < Ni²⁺ < Cu²⁺. The dissociation process is non-spontaneous, endothermic and entropically unfavorable. The formation of the metal complexes has been found to be spontaneous, endothermic and entropically favorable.

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