Journal of Solution Chemistry (2023) 52:570–587
https://doi.org/10.1007/s10953-023-01248-5

Solvatochromism and Optoelectronic Properties of Thiosemicarbazone Derivatives Having π-Conjugated Systems

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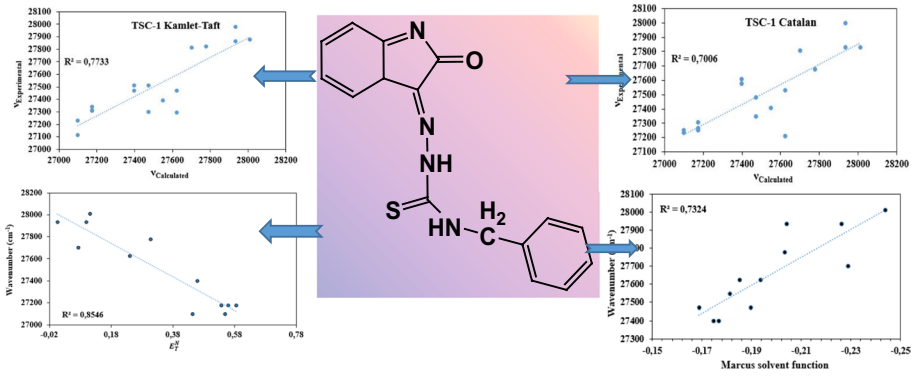
Received: 26 April 2022 / Accepted: 9 January 2023 / Published online: 13 February 2023

Abstract

The electronic structures, solvatochromism, and LSER (Linear Solvation Energy Relationship) properties of thiosemicarbazone derivatives having five different π-conjuged systems have been investigated. UV–Vis absorption spectra of TSC (Thiosemicarbazone) derivatives have been measured in 18 solvent media with different polarities. The global electronic transition in these compounds is described as $\pi-\pi^*$ electronic transition resulting from the resonance in the thiosemicarbazone group. The other lower wavelength maxima are denoted to the $\pi-\pi^*$ electronic transition in the indole ring and the $n-\pi^*$ electronic transition in the carboxyl group. To determine as analytical solvent–solute interactions of global electronic transitions has been studied with using LSERs with using Kamlet–Taft and Catalán parameters. The solvatochromic models between electronic transition wavenumbers with Reichardt parameter, and Marcus solvent function have been generated. Optoelectronic properties have been investigated using the Moss, Ravindra, Herve-Vándamme, Kumar, Singh, and Reddy relationships. According to E_g (molecular energy gap) values, the investigated compounds can be considered organic semiconductor materials.

Graphical Abstract



Keywords Thiosemicarbazone · Solvatochromism · LSER · Electronic transitions · Electronic structure · Optoelectronic · Bandgap · Kamlet–Taft · Catalán

Extended author information available on the last page of the article

1 Introduction

Over the past quarter century, TSCs have become remarkable molecules with the benefits that they provide in the pharmaceutical field. These molecules have shown strong agents such as antiviral, antibacterial, antioxidant, and anticancer [1, 2]. TSCs, which constitute an important part of the thiourea group, can combine with the transition metals or most of the rare-earth metal ions. The changes in molecular structure of TSCs have also been observed to eliminate their therapeutic properties [3, 4]. The conjugated *N*–*N* = *S* in the main structures of TSCs have an important effect on the interaction of the structure with biomolecules. However, TSCs have high biological activity forming hydrogen bonds in the O–HN *trans*-isomers. Due to its inductive effect, it develops a hydrogen bond acceptor with the ability of neighboring NH protons [1].

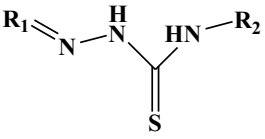
The solvatochromism occurs when there is a noticeable change in the absorption or other spectroscopic signals depending on solvent properties like particular polarity, density, and shape of the solutes in solvents by changing their polarity. The polarity and polarizability of a solvent are its overall dissolving capacity that has the global effect of solvent–solute interactions. While solvatochromic shifts are used to classify the solvent–solute media, they reflect different states involving many different intermolecular attraction forces [2, 4]. Solvatochromism can also be defined as the shifts in the investigated spectra of a compound in different solvents, and the source of these shifts depends on solvent polarity, polarizability, whether or not to make H-bonds both intramolecular and between the solvent and the solute molecules. In some case, observed change in the electronic spectra has been highly dependent on the presence on steric effect, inductive, mesomeric effects and conjugated structures in molecule. While some of these factors can be defined numerically with LSERs (Linear Solvation Energy Relationships), which is a quantitative method, the other only, the spectral shifts as a result of the orbital distributions that change with the effect occurring in one part of the compound can be interpreted by looking at the molecular geometry of the compound. In this case, while solvatochromic materials vary in their molecular orbitals depending on the environment, their electronic structure and interaction types may change according to the environment [5–12].

According to the literature, there are studies on the biological activity and complex structures of TSCs compounds. Since TSC compounds have π-conjugated system and there is no solvatochromic and optoelectronic study on TSCs before, our main motivation was to examine their electronic, solvatochromic, and optoelectronic properties in this study. So, we have investigated and interpreted the electronic, solvatochromic, and some optoelectronic properties of five different thiosemicarbazone derivatives including indoline group. Their electronic properties and solvatochromic properties have been investigated in detail. Absorbance spectra were recorded in variety solvent media with eighteen different properties. The LSERs models have been derived with multiple-linear regression analysis using both Kamlet–Taft and Catalán parameters to determine solvent–solute relationships. In addition, using the Reichardt parameters and Marcus solvent functions, the global transitions occurring in molecules have been analyzed by using linear relationships. Forbidden energy bandgap has been calculated by using Tauc method, and optoelectronic parameters like semi-empirical refractive index have been studied with Moss, Ravindra, Herve-Vándamme, Kumar, Singh, and Reddy relationships by using electronic absorption spectra.

2 Materials and Methods

2.1 Materials, Synthesis, Characterization, and Purification of the Investigated TSCs

It can been seen from Fig. 1 that to molecular structure, IUPAC nomenclature and abbreviation names of TSCs derivatives can also be named as ligand. The 3.5 mmol of isatin was stirred on a magnetic stirrer until dissolved in 25 mL of ethanol. A solution of 3.5 mmol 3-thiosemicarbazide derivative in 25 mL ethanol was added to the mixed solution and mixing was done. 2–3 drops of fuming sulfuric acid were added to the medium and reflux was made for 2–3 h. The product was filtered, purified, and dried. The solid product was obtained and synthesized ligands were first characterized, and spectroscopic methods such as ^{1}H-NMR, ^{13}C-NMR, elemental analysis were used for this characterization, and the results of the analysis showed that these ligands were obtained in pure form and the correctness of their structures, so characterization with IR, NMR, and elementel analysis were performed as given in. The (*E*)-4-benzyl-1-(2-oxoindolin-3-ylidene) thiosemicarbazide (TSC-1), (*E*)-4-cyclohexyl-1-(2-oxoindolin-3-ylidene) thiosemicarbazide (TSC-2), (*E*)-4-benzyl-1-(5-methoxy-2-oxoindolin-3-ylidene) thiosemicarbazide (TSC-3), (*E*)-4-(2-fluorobenzyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazide (TSC-4),



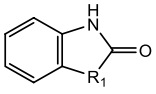
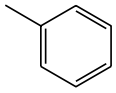
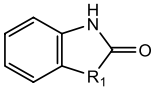
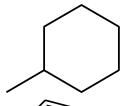
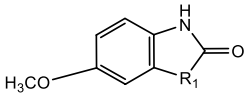
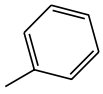
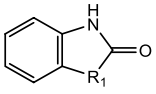
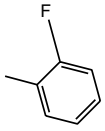
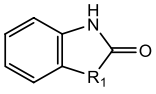
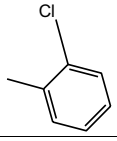
IUPAC Name	R_1	R_2	(Abbreviated)
(E)-4-benzyl-1-(2-oxoindolin-3-ylidene)thiosemicarbazide			TSC-1
(E)-4-cyclohexyl-1-(2-oxoindolin-3-ylidene)thiosemicarbazide			TSC-2
(E)-4-benzyl-1-(5-methoxy-2-oxoindolin-3-ylidene)thiosemicarbazide			TSC-3
(E)-4-(2-fluorobenzyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazide			TSC-4
(E)-4-(2-chlorobenzyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazide			TSC-5

Fig. 1 The molecular structure of the investigated thiosemicarbazone derivatives

and (*E*)-4-(2-chlorobenzyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazide (TSC-5) compounds have been previously reported by Kandemirli et al. [13–16]. All of the solvents were purchased from Sigma-Aldrich, and these have used without further purification due to spectroscopic grade properties. These solvents are *n*-pentane, cyclohexane, benzene, toluene, xylene, diethyl ether, n-butyl acetate, DCM (dichloromethane), 1-octanol, 1-heptanol, 1-hexanol, 1-butanol, iso-butanol, 1-propanol, ethanol, methanol, 1-acetonitrile, and DMSO (dimethyl sulfoxide), respectively.

2.2 Spectroscopy Measurements

All the solutions were prepared approximately 2×10^{-5} M. In this study, UV–Vis absorption spectra of TSC derivatives were measured using Perkin Elmer Lambda-35 UV–Vis spectrophotometer (200–700 nm) in a standard quartz cuvette at room temperature and in eighteen solvents having different polarities.

2.3 LSERs Calculations (Linear Solvation Energy Relationships)

Solvatochromism is defined as the change of properties such as the position and intensity of any spectrum depending on the particular polarity of the medium. These spectra, which are electronic absorbance and emission spectra, can sometimes be measured differently in terms of sometimes both the position and the intensity of electronic transition bands with change of solvent properties such as hydrogen bond donor ability, hydrogen bond acceptor ability, the dipolarity, polarizability, solvent of acidity, and solvent of basicity.

Eq. 1 is the first to develop a multiparameter correlation equation based on solvatochromic measurements. The Kamlet–Abboud–Taft (KAT) solvent parameters, one of the most solvatochromism basic equations, are the hydrogen bond donation ability (α), the hydrogen bond acceptor ability(β), the dipolarity–polarizability (π^*), and a correction term, δ, to the dipolarity–polarizability to account for variations in solvent polarizability, respectively. The C_0, C_1, C_2, and C_3 coefficients, and the changes in the spectrum of the molecule used in Eq. 1 show the inert and gasous phase wavenumber and contribution of these properties of the solvent, respectively [17–21].

$$\nu_{\max} = C_0 + C_1\pi^* + C_2\beta + C_3\alpha \tag{1}$$

According to the Koppel–Palm approach, the above π^* dipolarity/polarizability parameter can be separately writable the $f(n)$ and $f(\varepsilon)$ functions, in here [20–23], the Kirkwood function $f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 2)$, which expresses the molar polarization, will be replaced by $f(n) = (n^2 - 1)/(n^2 + 2)$, which is defined as a quantum mechanical polarizability parameter, respectively. As a result, the KAT equation will be as follows:

$$\nu_{\max} = C_0 + C_1 f(n) + C_2 f(\varepsilon) + C_3\beta + C_4\alpha. \tag{2}$$

In here, the coefficient C_1 (polarizability or dispersion-polarization) and C_2 (polarity or orientation-induction) show specific interactions, while C_3 (Hydrogen bonding acceptor) and C_4 (Hydrogen bonding donor) show non-specific interactions.

Catalán has improved a general and multi-parameters, a model for two non-global interactions (*SA* and *SB* parameters) and for two global (*SP* and *SdP* parameters) interactions

of 163 solvents to determine solute–solvent interactions. In this study, it was formulated mathematically as follows [24]:

$$\nu_{max} = C_5 + C_6SP + C_7SdP + C_8SA + C_9SB, \quad (3)$$

C_5 corresponds to the value of the property in the gas phase; *SA*, *SB*, *SP*, and *SdP* represent solvent parameters done independent variable describing various types of solute–solvent interactions; and C_6, C_7, C_8, and C_9 are regression coefficients describing the sensitivity of property ν_{max} to different solute–solvent interaction mechanisms.

The correlation of the Marcus optical dielectric solvent function $(1-D_{opt})/(2D_{opt}+1)$ versus maximum electronic absorption wavenumbers clarifies the direction of ground and excited-state dipole moments [25, 26]. The linear correlations of maximum absorption energy versus Reichardt solvent E_T^N parameter provide information about the solvatochromic behaviors of the studied compounds [18, 27]. The parameters used in LSER studies have been listed in Table S1 in Supplementary materials. All statistical calculations have been performed in SPSS15 packet program.

2.4 Optoelectronic Calculations

The main factors that determine the optical and electronic properties of semiconductors are the refractive index (n) and the energy gap (E_g). The specific behavior of semiconductor materials is determined by the size of the energy gap and refractive index [28, 29]. The reason why the refractive index is in the main elements of the materials is related to the electronic polarizability of the ions and the local fields in the materials. The relations between the high-frequency refractive index and the energy gap have been proposed empirically [30]. The E_g value of TSCs has been calculated with the Tauc method [28–30]. The $E=h\nu$ versus $(\alpha h\nu)^2$ graphs for the E_g values of the TSCs compounds by the Tauc method are given in Fig. 5. The forbidden band-gap values of the investigated compounds were calculated for Benzene, diethyl ether, DCM, DMSO, and methanol solvents. The E_g values of the investigated compounds are listed in Table 3. Since TSCs have a conjugated structure, and E_g values are around 2.5 eV, they have semiconductor organic compounds [30].

The refractive index of TSCs can be calculated using the Moss [31, 32], Ravindra [33], Hervè–Vandamme [34], Kumar–Singh [35], and Reddy [36] approaches. Moss, Ravindra, Hervè–Vandamme, Kumar–Singh, and Reddy approaches can be shown as follows, respectively.

$$n^4 = 95eV/E_g \text{(Moss relation)}$$

$$n = 4.084 - 0.62E_g \text{(Ravindra relation)}$$

$$n^2 = 1 + \left(\frac{A}{E_g + B}\right)^2 \text{(Herve} - \text{Vandammerelation;} A = 13.6 \text{ eV and } B = 3.47 \text{ eV)}$$

$$n = \frac{3.3668}{(E_g)^{0.32234}} \text{(Kumar} - \text{Singh relation)}$$

$$n = \left(\frac{154}{E_g - 0.365}\right)^{\frac{1}{4}} \text{(Reddy relation)}$$

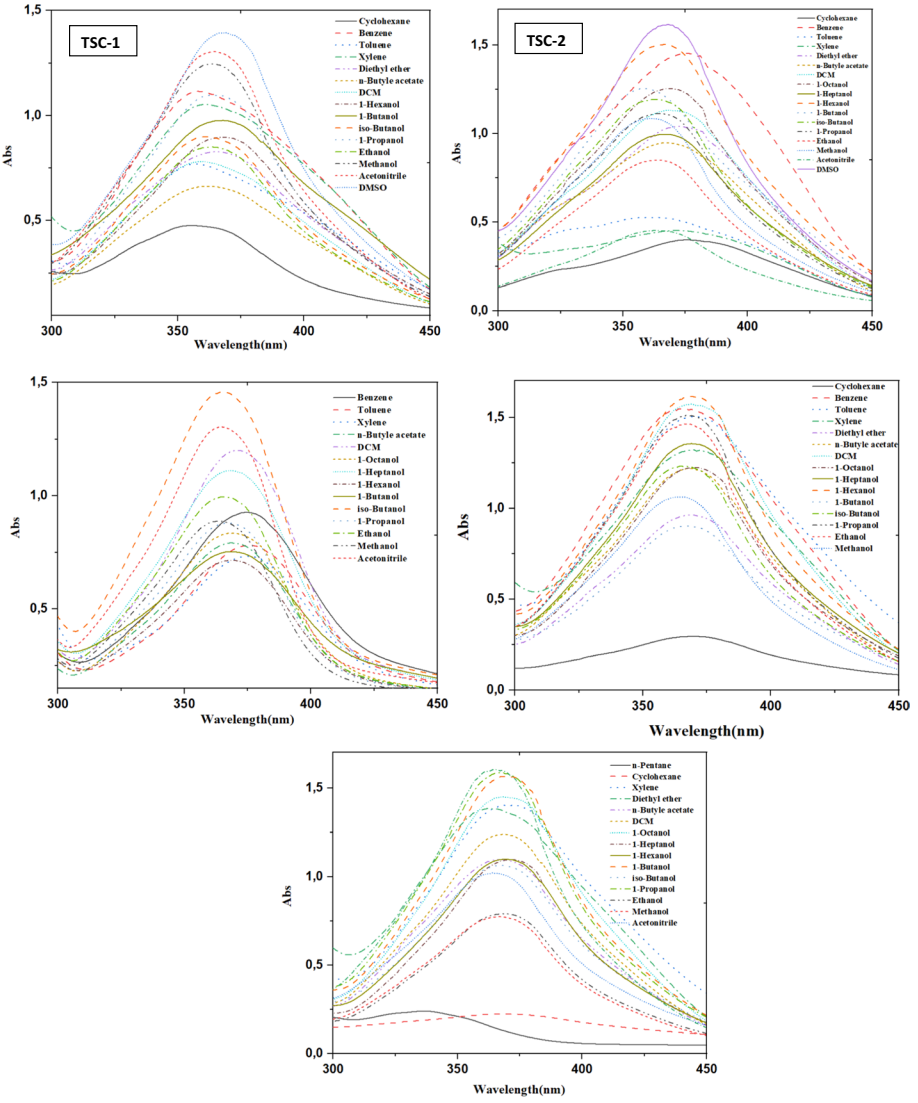


Fig. 2 The absorbance spectra in different solvent medium of thiosemicarbazone derivatives

3 Results and Discussion

3.1 Electronic Transitions and UV–Vis Spectra

UV–Vis spectra of the investigated compounds are shown in Fig. 2. The absorbance spectral data of investigated TSCs are listed in Table 1. These plots indicate the absorbance spectra of TSC derivatives in eighteen different solvents having different polarity and properties from eighteen different solvents having different polarity and properties,

Table 1 The absorbance spectra data of investigated TSCs

Solvents	TSC-1			TSC-2			TSC-3		
	$\lambda_{abs1\ (nm)}$	$\lambda_{abs2\ (nm)}$	$\nu\ (cm^{-1})$	$\lambda_{abs1\ (nm)}$	$\lambda_{abs2\ (nm)}$	$\nu\ (cm^{-1})$	$\lambda_{abs1\ (nm)}$	$\lambda_{abs2\ (nm)}$	$\nu\ (cm^{-1})$
n-Pentane	–	–	–	–	379	26,385	228, 273	–	–
Cyclo-hexane	–	358	27,932	278	376	26,595	–	–	–
Benzene	–	357	28,011	–	376	26,595	–	374	26,737
Toluene	–	358	27,932	–	362	27,624	–	375	26,666
Xylene	–	361	27,700	–	371	26,954	–	376	26,595
Diethyl-ether	260	365	27,397	246, 256, 272	375	26,666	257, 265, 286	371	26,954
n-Butyl-acetate	–	362	27,624	277	368	27,173	267, 287	370	27,027
DCM	250	360	27,777	279	370	27,027	261, 286	370	27,027
1-Octanol	253, 258	368	27,173	245, 279	369	27,100	256, 267, 287	369	27,100
1-Heptanol	259, 272	369	27,100	257, 273	367	27,247	267, 279	368	27,173
1-Hexanol	248, 255	368	27,173	248, 278	367	27,247	256, 265, 285	369	27,100
1-Butanol	250	368	27,173	250, 256, 271, 277	359	27,855	257, 264, 281	370	27,027
iso-Butanol	–	362	27,624	278	364	27,472	261, 268, 287	366	27,322
1-Propanol	257	364	27,472	278	365	27,397	258, 266, 288	368	27,173
Ethanol	251, 256	363	27,548	278	364	27,472	257, 264, 285	366	27,322
Methanol	250, 257	364	27,472	246, 278	362	27,624	256, 264, 286	363	27,548
Acetonitrile	257	365	27,397	248, 254, 277	364	27,472	257, 264, 285	365	27,397
DMSO	–	369	27,100	276	368	27,173	283	369	27,100

TSC-4			TSC-5		
$\lambda_{abs1\ (nm)}$	$\lambda_{abs2\ (nm)}$	$\nu\ (cm^{-1})$	$\lambda_{abs1\ (nm)}$	$\lambda_{abs2\ (nm)}$	$\nu\ (cm^{-1})$
270, 276	–	–	268, 336	–	–
260	370	27,027	251	372	26,881
–	366	27,322	–	366	27,322
–	371	26,954	–	372	26,881
–	371	26,954	–	363	27,548
250, 260	370	27,027	251, 260, 273	367	27,247
–	368	27,173	273	369	27,100
250, 256	370	27,027	252, 259	370	27,027
251, 260	370	27,027	252, 259	372	26,881
259, 273	369	27,100	261–272	371	26,954
252, 259	369	27,100	251, 258	370	27,027
252	368	27,173	250, 257	368	27,173
255	366	27,322	257	367	27,247

Table 1 (continued)

TSC-4			TSC-5		
$\lambda_{abs1\ (nm)}$	$\lambda_{abs2\ (nm)}$	$\nu^{-1}_{(cm)}$	$\lambda_{abs1\ (nm)}$	$\lambda_{abs2\ (nm)}$	$\nu^{-1}_{(cm)}$
257	368	27,173	258,270, 277	369	27,100
250, 257, 274	368	27,173	253, 272	366	27,322
248, 256, 272	365	27,397	250,257, 272	365	27,397
249, 257, 272	365	27,397	257, 272	366	27,322
–	369	27,100	275	369	27,100

from *n*-pentane with dielectric constant $\varepsilon = 1.84$ to DMSO with $\varepsilon = 46.45$. All values of dielectric constants (or dipole moments D) of 18 solvents are seen in Table S1.

The n–π^* electronic transitions in C=N group for isatin-3-thiosemicarbazones have assigned as 2070 cm^{-1} (483 nm) [37]. These bands were found to be 372, 373, 370, and 370 nm for different TSC compounds, respectively. In this study, the π–π^* electronic transition bands of semicarbazone group for isatin-3-thiosemicarbazone have been observed as between the range of 400–286 nm [37]. We can say form Fig. 2 and Table 1 that the main band belongs to TSC molecules are observed in the range of 358–379 nm (3.46–3.27 eV). This wide band is seen, which includes the π–π^* electronic transition caused by π-delocakization in isatin-3-thiosemicarbazone group. This transition is a global transition. In addition, we have observed as two bands in some solvent between 248 and 272 nm (5–4.55 eV) for the TSC-1 molecule. If there are electron-withdrawing substituents in the indole ring, the bathochromic shift of Hammett substituent constant is $\sigma > 0$. On the other hand, if there is an electron donor substituent, there is hypsochromic shift because the Hammett substituent constant is $\sigma < 0$ [38, 39].

The *ortho*, *para,* and *meta* Hammett constants have changed depending on the position and the type of the respective substituents. It is worth noting that the electron density on the nitrogen atom of the indole ring shows a slight decrease when going from the ground state to the first excited singlet state (qN, 1.629 Coulomb and 1.610 Coulomb for S_0 and S_1, respectively), thus, indicating a decrease of the basicity of the indole system in the first excited singlet state. In substituted indoles, this decrease is observed to regardless of the nature of the substituent (electron donating or electron withdrawing) and its position [40]. A band at 272 nm has been observed in the TSC-1 molecule only in 1-heptanol solution. The global absorbance band of TSC-1 has shifted to high wavelength which is bathochromic effect. This band is the n–π^* electronic transition that originates from lone pairs of the carboxyl group in the indole ring. The global absorbance band of TSC-1 has shifted to high wavelength which is bathochromic effect. A bathochromic shift is observed as the wavelength of the TSC-1 compound increases with increasing solvent polarity. As the molecular orbitals, in which this transition belongs to polarized with the solvent polarity, their transition energies decrease. Absorbance bands around 225, 272, and 288 nm give rise to indole ring, when the indole is included in TSC group.

We can see that TSC-2 compound for electronic absorbance transitions is in the range of 379–362 nm (3.27–3.42 eV), 245–256 nm (5.06–4.84 eV) 2 bands or 3 or more bands in some solvent. It can be seen from Table 2 that the long wavelength band is the π–π^* electronic transition that takes place in the thiosemicarbazone group. The first bands are the π–π^* and n–π^* electronic transitions originating from the indole ring and carboxyl group. For this compound, the second wavelength indicates the presence of

Table 2 Derived LSER Models' coefficients and statistical parameters with using Kamlet–Taft and Catalan solvatochromism for the absorption spectra data of TSC molecules

Kamlet–Taft Solvatochromism										
Molecules	C_0	C_1	C_2	C_3	C_4	R	R^2	F	P	N
TSC-1	28011.39	81.17	− 211.14	− 951.29	308.616	0.88	0.774	10.259	0.001	17
TSC-2	26135.11	480.63	1266.55	− 233.50	375.347	0.907	0.823	13.985	0.000	17
TSC-3	27135.40	− 2350.77	814.65	− 208.720	165.189	0.940	0.884	20.887	0.000	16
TSC-4	27479.86	− 2284.03	386.93	− 143.229	51.151	0.846	0.716	6.948	0.005	16
TSC-5	28091.20	− 4869.72	353.32	− 28.483	− 81.846	0.899	0.808	10.515	0.001	15
Catalan solvatochromism										
Molecules	C_5	C_6	C_7	C_8	C_9	R	R^2	F	P	N
TSC-1	28443.73	− 570.32	− 263.994	36.824	− 735.340	0.837	0.701	7.020	0.004	17
TSC-2	26705.98	− 317.76	746.483	633.105	250.806	0.889	0.790	11.300	0.000	17
TSC-3	27573.86	− 1396.17	634.046	189.256	115.860	0.950	0.903	25.687	0.000	16
TSC-4	27973.94	− 1559.03	377.535	− 78.023	33.161	0.857	0.734	8.299	0.002	17
TSC-5	28212.84	− 1931.76	458.747	− 140.888	− 42.507	0.934	0.872	17.039	0.000	15

hypsochromic effect. The piperazine substituent effect can be said to be the effect of an electron donor substituent to piperazine.

As seen in Fig. 2, there are two bands for TSC-3 compound. The second bands occur between 363 and 376 nm (3.41–3.29 eV), which are the π–π* electronic transition that takes place in the TSC group. In the first band, different peaks have been observed. These are 256–268 nm (4.84–4.62 eV) which are the π–π* electronic transition in the indole ring and the n–π* electronic transition due to the carboxyl group at 281–288 nm (4.41–4.30 eV), respectively. Since the second band has shifted towards lower wavelengths as solvent increasing polarity, in that there is a hypsochromic effect. The Hammett constant at the methoxy para position is − 0.268, while the Hammett constant at the meta position is + 0.115. The Hammett constants of the flourine substituent are $\sigma_m = 0.34$ and $\sigma_p = 0.06$. Thus, in the second band, there was a hypsochromic effect depending on the polarity [38, 39].

The absorbance spectra and data for the TSC-4 compound in different solvents are given in Fig. 2 and Table 1. We can see that there are two main bands, where the second band can be defined as the π–π* electronic transition in the thiosemicarbazone group, which are around 365–370 nm (3.39–3.35 eV). We can say that there are no obvious changes to wavelength band position of this transition increasing in polarity of used solvents. The first band is observed to a lot of peaks 248–260 nm (5–4.79 eV), and the second peak is the electronic transition peak around 272 nm (4.55 eV) observed only in *n*-pentane, ethanol, methanol, and acetonitrile solvents. We have observed to different wavelengths 273 nm in diethyl ether, 277 nm in 1-propanol, and 275 nm in DMSO. This transition can be ascribed as n–π* electronic transitions arising from oxo-indole group.

It can be seen in Fig. 2 that two or more bands for the TSC-5 molecule have been observed between 251 and 272 (nm) (4.94–4.55) eV. The main transition band of the TSC-5 molecule was observed in the range of 366–372 nm (3.66–3.60) eV. This main electronic transition band is the π–π * electronic transition that takes place in the

thiosemicarbazone group. There was no significant shift in this band due to the solvent effect. The first band is due to the indole ring.

3.2 The Substituent Effect on Electronic Absorbance Transitions

The TSC-1 has the benzyl ring, while TSC-2 has a cyclohexyl substituent. As seen from Table 1, TSC-1 has higher electronic absorbance band energies than TSC-2. In this case, the conjugation in TSC-2 has above the TSC group, and as the conjugation increased, the excitation energy decreased. Here, it can be said that its contribution to the conjugation is more than that of the benzene ring. This was observed in non-polar and polar aprotic solvents. It can be seen from Table 1 and Fig. 2 that the conjugation of TSC-1 compound is higher than other compounds.

When we look at the electronic absorbance transitions of the TSC-3 compound and the electronic transitions of the TSC-1 compound, the electronic absorbance wavelength properties of TSC-3 compared to TSC-1 are shifted to larger wavelengths including non-polar and polar aprotic solvents. The difference between TSC-1 and TSC-3 compounds is the methoxy substituent in the oxoindolin-3-ylidene group. It can be said that both the π bonds in the C=O bond in the methoxy group and the lonepairs in the oxygen atom directly affect the electronic transitions. Methoxy group directly has affected the conjugation of TSC-3 compound. Oxygen has inductive electron-withdrawing and mesmeric electron-repelling property.

It can be said that the substituents to electronic absorbance transitions in TSC-2, TSC-3, TSC-4, and TSC-5 compounds do not cause dominant molecular behavior.

3.3 Solvatochromism

The Kamlet–Taft solvatochromism results of multiple-linear regression analysis (MLRA) in LSER (Linear Solvation Energy Relationship) studies for absorption spectra are shown in Table 2. The solvatochromic models for TSC-1, TSC-2, TSC-3, TSC-4, and TSC-5 have been derived using 17, 17, 16, 16, and 15 solvents. The correlation graphs between experimental and calculated LSERs model for Kamlet–Taft and Catalan solvatochromism of investigated Thiosemicarbazone derivatives have been shown in Figs. S1–2S.

As seen from Table 2, hydrogen bonding acceptor capacities for TSC-1, TSC-3, and TSC-4 molecules are greater than hydrogen bonding donor capacities, while for TSC-2 and TSC-5 molecules, hydrogen bonding donor capacities are greater than hydrogen bonding acceptor capacities. It was observed that the polarity coefficient for TSC-1 and TSC-2 molecules was greater than the polarizability coefficient, while for TSC-3, TSC-4, and TSC-5 molecules, the polarizability coefficient was observed to be greater than the polarity coefficient.

Results of Catalán solvatochromic model derived for absorption spectra are shown in Table 2. Here, for TSC-2, TSC-3, TSC-4, and TSC-5 molecules, the solvent acidity was greater than the solvent basicity, while the TSC-1 molecule had a higher solvent basicity than the solvent acidity. For TSC-1, TSC-3, TSC-4, and TSC-5 molecules, the polarizability of the solvent was seen to be more effective than the solvent dipolarity, while the solvent dipolarity of the solvent was more effective for the TSC-2 molecule.

The correlation of the Marcus optical dielectric solvent function $(1-Dopt)/(2Dopt+1)$ [25, 26] versus maximum electronic absorption wavenumbers clarifies the direction of ground- and excited-state dipole moments. The correlation graphs between experimental

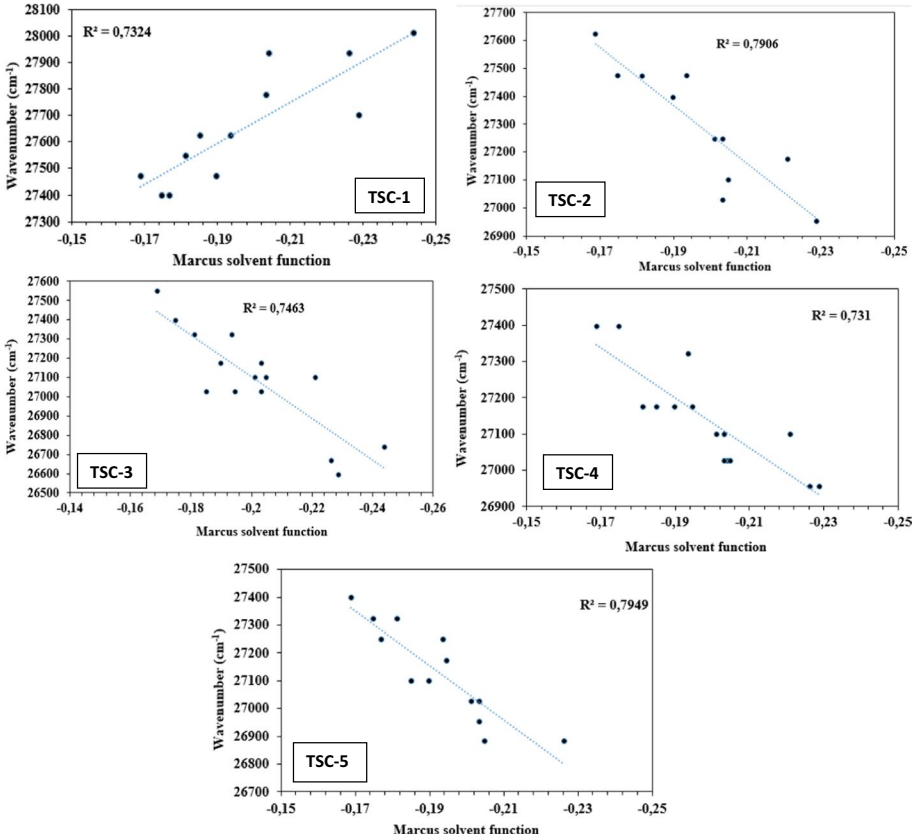


Fig. 3 The correlation graphs between experimental with the Marcus solvent function of investigated Thiosemicarbazone derivatives

wavenumbers and Marcus parameters of investigated thiosemicarbazone derivatives are depicted in Figs. 3 and 4. The linear correlations between maximum absorption wavenumbers and Marcus optical dielectric solvent function of thiosemicarbazone derivatives indicate that transition dipole moments of TSCs molecules are associated with absorption spectra and directions of the ground-state and excited-state dipole moments are parallel and makes an angle. The correlation values between absorption wavenumbers and Marcus solvent function for thiosemicarbazone derivatives have been found as $R^2 = 0.7324$ for TSC-1, $R^2 = 0.7906$ for TSC-2, $R^2 = 0.7463$ for TSC-3, $R^2 = 0.731$ for TSC-4, and $R^2 = 0.7949$ for TSC-5.

Solvent polarity is important data being used in solvent selections for preliminary engineering design of chemical processes. In this work, a predictive model is proposed for estimating the solvatochromic polarity of electronic transition energy (E_T^N) of Reichardt indicator for aqueous mixtures. Figure 5 shows the correlation graphs between experimental wavenumbers and Reichardt parameters of investigated thiosemicarbazone derivatives. The correlation coefficients between Reichardt solvent parameter and wavenumber of maximum absorbance bands of investigated compounds have been found to be 0.8546, 0.784, 0.7363, 0.7358, and 0.7337, respectively. This relation is indicative for positive solvatochromism

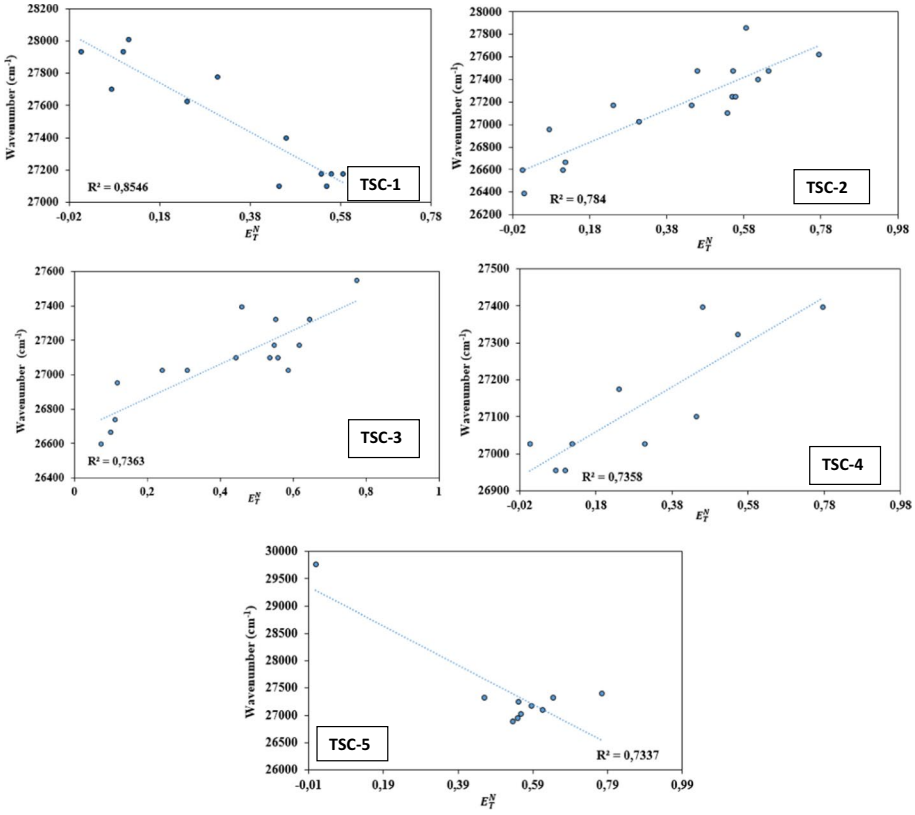


Fig. 4 The correlation graphs between experimental with the Reichardt parameters of investigated Thiosemicarbazone derivatives

occurring in maximum absorption bands. Solvents' dielectric function is responsible for this behavior. Solvent parameter E_T neglects the specific interactions in solute–solvent interactions.

4 Optoelectronic Properties

The results obtained from Moss, Ravindra, Hervè–Vandamme, Kumar–Singh, and Reddy equations in diethyl ether, benzene, DCM, DMSO, and methanol solvents are shown in the Table 3. The refractive indices of the investigated compounds were found in the range of 2.4 and 2.5 values, excluding the Reddy relationship. The refractive index in Reddy relationship was found to be about 2.9 value. The refractive indices obtained with using Moss, Ravindra, Hervè–Vandamme, and Kumar–Singh relations for TSC-1, TSC-2, TSC-3, TSC-4, and TSC-5 have lower values compared to Reddy's relation.

The shape of relationship between refractive index and solvents of TSCs compounds is seen in Fig. 6. The refractive index values calculated with the Reddy relation are higher than the other methods. The refractive index of the TSC-3 compound was found to be around 2.5, excluding the Reddy relationship, and was lower than the other TSCs

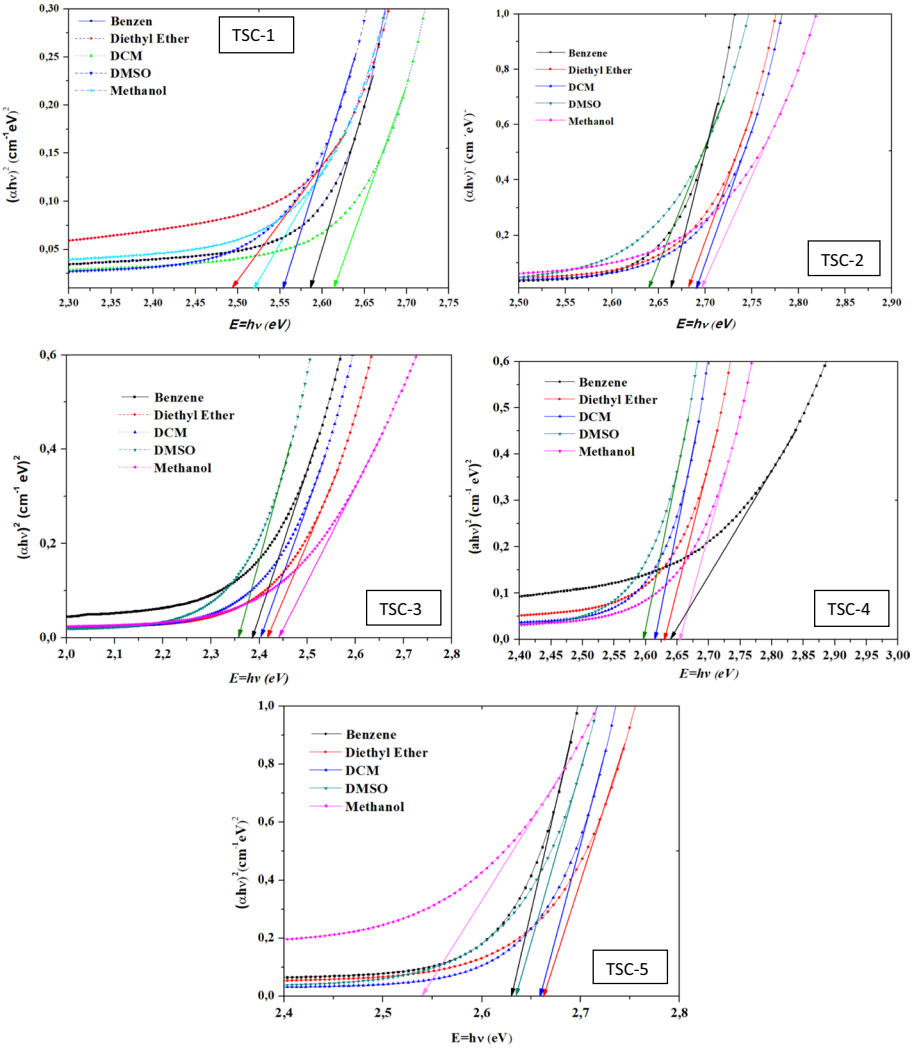


Fig. 5 The correlation graphs of E_g values of investigated Thiosemicarbazone derivatives

examined. There is methoxy substituent in the TSC-3 compound. It can be said that the E_g energy value in TSC-3 is low because of happened inductively transfers charge to indole group from methoxy.

5 Conclusions

The electronic structure, optoelectronic, and solvatochromic properties of five thiosemicarbazone derivatives were examined in detail by spectroscopic methods and in the solution phase. Electronic transitions were interpreted. Depending on the substituent, a global peak varying in the range of 350–370 nm was observed in the electronic transitions. This

Table 3 The Optoelectronic properties according to Moss, Ravindra, Herve–Vándamme, Kumar, Singh, and Reddy relationships of investigated compounds

Solvents	TSC-1 $E_{g\,(eV)}$	Moss	Ravindra	Hervè–Vandamme	Kumar–Singh	Reddy
Diethyl Ether	2.49	2.485	2.540	2.491	2.509	2.917
Benzene	2.586	2.461	2.480	2.458	2.478	2.885
DCM	2.615	2.455	2.462	2.448	2.469	2.876
DMSO	2.553	2.469	2.501	2.469	2.488	2.896
Methanol	2.52	2.477	2.521	2.480	2.499	2.907
Solvents	TSC-2 $E_{g(eV)}$	Moss	Ravindra	Hervè–Vandamme	Kumar–Singh	Reddy
Diethyl Ether	2.681	2.439	2.421	2.426	2.449	2.855
Benzene	2.662	2.444	2.433	2.432	2.455	2.861
DCM	2.69	2.437	2.416	2.423	2.447	2.852
DMSO	2.639	2.449	2.447	2.440	2.462	2.868
Methanol	2.696	2.436	2.412	2.421	2.445	2.850
Solvents	TSC-3 $E_{g(eV)}$	Moss	Ravindra	Hervè–Vandamme	Kumar–Singh	Reddy
Diethyl Ether	2.418	2.503	2.584	2.516	2.532	2.942
Benzene	2.386	2.511	2.604	2.528	2.543	2.954
DCM	2.404	2.507	2.593	2.522	2.537	2.947
DMSO	2.358	2.519	2.622	2.538	2.553	2.964
Methanol	2.44	2.497	2.571	2.509	2.525	2.935
Solvents	TSC-4 $E_{g\,(eV)}$	Moss	Ravindra	Hervè–Vandamme	Kumar–Singh	Reddy
Diethyl Ether	2.631	2.451	2.452	2.443	2.464	2.871
Benzene	2.641	2.449	2.446	2.439	2.461	2.868
DCM	2.614	2.455	2.463	2.448	2.470	2.876
DMSO	2.59	2.460	2.478	2.456	2.477	2.884
Methanol	2.655	2.445	2.437	2.435	2.457	2.863
Solvents	TSC-5 $E_{g\,(eV)}$	Moss	Ravindra	Hervè–Vandamme	Kumar–Singh	Reddy
Diethyl Ether	2.663	2.443	2.432	2.432	2.455	2.861
Benzene	2.629	2.451	2.454	2.443	2.465	2.871
DCM	2.658	2.445	2.436	2.434	2.456	2.862
DMSO	2.635	2.450	2.450	2.441	2.463	2.869
Methanol	2.539	2.473	2.509	2.474	2.493	2.901

electronic transitions have the π–π^* character due to the C=N substituent in the 3-isatin-thiosemicarbazone group. While the wavelength of electronic transitions in non-polar solvents changes remarkably for TSC compounds, the electronic transitions in polar solvents have the same wavelength in these compounds, for example, DMSO and acetonitrile.

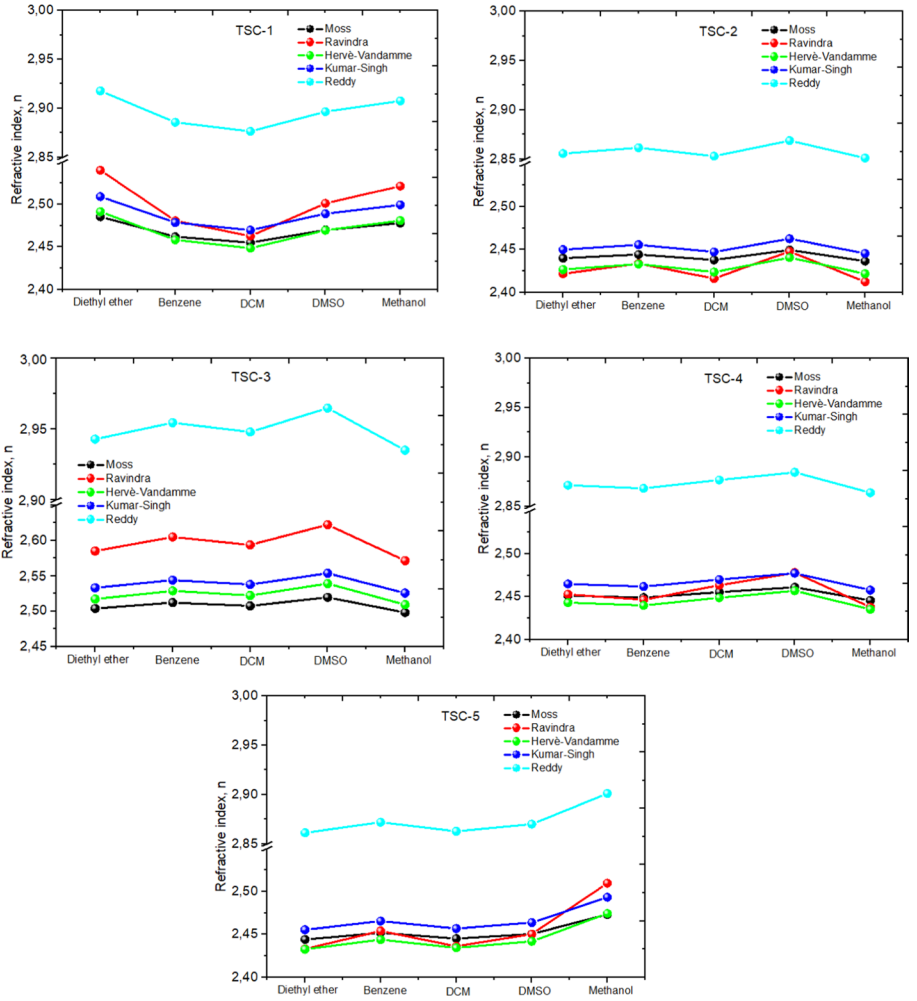


Fig. 6 The shape of relationship between refractive index and solvents of TSCs compounds

Solvatochromism models and energy bandgap indicate that investigated compounds have both solvatochromic and semiconductor material properties.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10953-023-01248-5.

Acknowledgements The authors thanks Bitlis Eren University for their support to the BEBAP2013.04 and BEBAP2014.05 projects.

References

1. Hussain, M., Jawaria, R., Shafiq, Z., Abbas, G., Naseer, M.M.: Ferrocene-based thiosemicarbazones: solvent effect on thiol-thione tautomerism and conformational polymorphism. J. Organomet. Chem. **846**, 121–128 (2017). https://doi.org/10.1016/j.jorganchem.2017.05.005
2. Bingül, M.: Synthesis of indole-3-carboxyaldehyde thiosemicarbazone derivatives and investigation of antioxidant and anticholinesterase properties. Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi **19**, 317–327 (2019). https://doi.org/10.35414/akufemubid.542712
3. Tom, L., Aiswarya, N., Sreejith, S.S., Kurup, M.P.: Self-organized three dimensional architectures based on non-covalent interactions in square planar Cu (II) thiosemicarbazone: solvent mediated crystallization and EPR based correlation study. Inorg. Chim. Acta **473**, 223–235 (2018). https://doi.org/10.1016/j.ica.2018.01.005
4. İlhan-Ceylan, B., Bolukbasi, O., Yilmaz, A., Kaya, K., Kurt, Y., Ülküseven, B.: Synthesis, spectroscopic characterization and quantum chemical studies of a dioxomolybdenum (VI) complex with an N S-substituted pyridoxal thiosemicarbazone. Polyhedron **193**, 114884 (2021). https://doi.org/10.1016/j.poly.2020.114884
5. Gülseven, Y., Taşal, E., Sıdır, İ, Güngör, T., Berber, H., Öğretir, C.: Solvatochromic effect studies on the absorption spectra of 4-((2-ethylphenyl)diazenyl)benzene-1,3-diol and 2-((2-ethylphenyl)diazenyl) benzene-1,3,5-triol molecules. Int. J. Hydrog. Energy **34**(12), 5255–5259 (2009). https://doi.org/10.1016/j.ijhydene.2008.10.070
6. Gülseven Sıdır, Y., Sıdır, İ, Taşal, E., Ermiş, E.: Studies on the electronic absorption spectra of some monoazo derivatives. Spectrochim. Acta Part A **78**, 640–647 (2011). https://doi.org/10.1016/j.saa.2010.11.040
7. Gülseven Sıdır, Y., Sıdır, İ, Berber, H., Taşal, E.: UV-spectral changes for some azo compounds in the presence of different solvents. J. Mol. Liq. **162**, 148–154 (2011). https://doi.org/10.1016/j.molliq.2011.07.002
8. Sıdır, İ, Gülseven Sıdır, Y., Berber, H., Taşal, E.: A study on solvatochromism of some monoazo dye derivatives. J. Mol. Liq. **178**, 127–136 (2013). https://doi.org/10.1016/j.molliq.2012.11.011
9. Gülseven Sıdır, Y., Sıdır, İ, Berber, H., Türkoğlu, G.: Solvatochromic behavior and electronic structure of some symmetric 2-aminophenol Schiff base derivatives. J. Mol. Liq. (2014). https://doi.org/10.1016/j.molliq.2014.08.018
10. Gülseven Sıdır, Y., Berber, H., Sıdır, İ: The solvatochromism, ground&excited state electric dipole moments and molecular electronic properties of ((4-phenoxybenzyliden)amino)phenol compounds. J. Solution Chem. **48**, 775–806 (2019). https://doi.org/10.1007/s10953-019-00885-z
11. Gülseven Sıdır, Y.: The solvatochromism, electronic structure, electric dipole moments and DFT calculations of benzoic acid liquid crystals. Liq. Crystals **47**(10), 1435–1451 (2020). https://doi.org/10.1080/02678292.2020.1733685
12. Sıdır, İ, Gülseven Sıdır, Y.: Investigation on the interactions of E-4 methoxycinnamic acid with solvent: Solvatochromism, electric dipole moment and pH effect. J. Mol. Liq. **249**, 1161–1171 (2018). https://doi.org/10.1016/j.molliq.2017.11.136
13. Kandemirli, F., Choudhary, M.I., Siddiq, S., Saracoglu, M., Sayiner, H., Arslan, T., Erbay, A., Köksoy, B.: Quantum chemical calculations for some ısatin thiosemicarbazones. Quantum Chem. Mol. Innovat. **3**, 25–58 (2012)
14. Ganim, M.A., Baloglu, M.C., Aygun, A., Altunoglu, Y.C., Sayiner, H.S., Kandemirli, F., Sen, F.: Analysis of DNA protection, interaction and antimicrobial activity of isatin derivatives. Int J. Biol. Macromol. **122**, 1271–1278 (2019). https://doi.org/10.1016/j.ijbiomac.2018.09.084
15. Kandemirli, F., Akkaya, Y., Vurdu, C.D.: Synthesis and quantum chemical calculations of 4-(2-fluorophenyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazone and its zinc(II) complex. Asian J. Chem. (2013). https://doi.org/10.14233/ajchem.2013.15221
16. Kandemirli, F., Arslan, T., Koksoy, B., Yilmaz, M.: Synthesis, characterization and theoretical calculations of 5-methoxyisatin-3-thiosemicarbazone derivatives. J. Chem. Soc. Pak. **31**(3), 498–504 (2009)
17. Kamlet, M.J., Abboud, J.L.M., Abraham, M.H., Taft, R.W.: Linear solvation energy relationships 23: A comprehensive collection of the solvatochromic parameters, π^*, α, and β, and some methods for simplifying the generalized solvatochromic equation. J. Org. Chem. (1983). https://doi.org/10.1021/jo00165a018
18. Reichardt, C.: Solvents and Solvent Effects in Organic Chemistry. VCH, New York (2008)
19. Reichardt, C., Welton, T.: Solvents and Solvent Effects in Organic Chemistry. Wiley, New York (2011)
20. Kamlet, M.J., Taft, R.W.: The solvatochromic comparison method 2: the alpha-scale of solvent hydrogen-bond donor (HBD) acidities. J. Am. Chem. Soc. **98**, 2886 (1976). https://doi.org/10.1021/ja00426a036

21. Abboud, J.L.M., Kamlet, M.J., Taft, R.W.: An examination of linear solvation energy relationships. Prog. Phy. Org. Chem. **13**, 485 (1981). https://doi.org/10.1002/9780470171929.ch6
22. Koppel, I.A., Palm, V.M.: The Influence of the solvent on organic reactivity. In: Chapman, N.B., Shorter, J.S. (eds.) Advances in Linear Free Energy Relationships. Plenum Press, London (1972)
23. Valeur, B.: Molecular Fluorescence-Principles and Applications. Wiley, Weinheim (2002)
24. Catalán, J.: Toward a generalized treatment of the solvent effect based on four empirical scales: dipolarity (SdP, a new scale), polarizability (SP), acidity (SA), and basicity (SB) of the medium. J. Phys. Chem. B **113**(17), 5951–5960 (2009). https://doi.org/10.1021/jp8095727
25. Marcus, R.A.: Free energy of nonequilibrium polarization systems. III. statistical mechanics of homogeneous and electrode systems. J. Chem. Phys. **39**, 1734 (1963). https://doi.org/10.1063/1.1734522
26. Marcus, R.A.: On the theory of shifts and broadening of electronic spectra of polar solutes in polar media. J. Chem. Phys. **43**, 1261 (1965). https://doi.org/10.1063/1.1696913
27. Reichardt, C.: Solvatochromic dyes as solvent polarity indicators. Chem. Rev. **24**, 2319–2358 (1994). https://doi.org/10.1021/cr00032a005
28. Tauc, J., Menth, A.: States in the gap. J. Non-Crystal. Solid. **8–10**, 569–585 (1972). https://doi.org/10.1016/0022-3093(72)90194-9
29. Tauc, J.: Amorphous and Liquid Semiconductors. Plenum Press, New York (2000)
30. El-Asmy, A.A., Shaibi, Y.M., Shedaiwa, I.M., Khattab, M.A.: Coordination compounds of some thiosemicarbazone derivatives: their preparation, characterization and electrical properties. Synth. React. Inorg. Met.-Org. Chem. (1990). https://doi.org/10.1080/00945719008048148
31. Moss, T.S.: Relations between the refractive index and energy gap of semiconductors. Phys. Stat. Sol. B **131**, 415 (1985). https://doi.org/10.1002/pssb.2221310202
32. Moss, T.S.: A Relationship between the refractive index and the infra-red threshold of sensitivity for photoconductors. Proc. Phys. Soc. B (1950). https://doi.org/10.1088/0370-1301/63/3/302
33. Ravindra, N.M., Auluck, S., Srivastava, V.K.: On the penn gap in semiconductors. Phys. Stat. Sol. B **93**(2), K155–K160 (1979). https://doi.org/10.1002/pssb.2220930257
34. Herve, P., Vandamme, L.K.J.: General relation between refractive index and energy gap in semiconductors. Infrared Phys. Technol. **35**(4), 609–615 (1994). https://doi.org/10.1016/1350-4495(94)90026-4
35. Kumar, V., Singh, J.K.: Model for calculating the refractive index of different materials. Indian J. Pure Appl. Phys. **48**(8), 571–574 (2010)
36. Reddy, R., Anjaneyulu, S.: Analysis of the Moss and Ravindra relations. Phys. Stat. Sol. B (1992). https://doi.org/10.1002/pssb.2221740238
37. Akinchan, N.T., Akinchan, R.: Synthesis and spectroscopic studies on platinum (II) complexes of thiosemicarbazone derivatives of p-anisaldehyde, p-tolualdehyde and p-vanilin. Indian J. Chem. **41A**, 1152–1156 (2002)
38. Hansch, C., Leo, A., Taft, R.W.: A survey of Hammett substituent constants and resonance and field parameters. Chem. Rev. **91**, 165–195 (1991). https://doi.org/10.1021/cr00002a004
39. Chapman, N.B., Shorter, J. (eds.): Correlation Analysis in Chemistry : Recent Advances. Plenum Press, New York (2012)
40. Aaron, J.J., Tive, A., Villiers, C., Parklanyi, C., Bouin, D.: Electronic absorption and fluorescence spectra of indole derivatives: quantatie treatment of the substituent effects and a theoretical study. Croatia Chem. Acta **56**(2), 157–168 (1983)

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